# The Second Law of Thermodynamics

## So far…

- We have studied the second law by looking at its results
- We don't have a thermodynamic property that can describe it
- In this chapter we will develop a mathematical definition for entropy
  - Entropy is a quantitative measure of disorder

# How does the second law relate to disorder?

- Disorder naturally increases, just like water flows down hill and gases expand
- Natural processes proceed spontaneously toward disorder

# Disorder

- Cleaning your room takes a lot of effort
  - Messing it up is much easier
- Dissolving sugar in water increases disorder
  - Sugar dissolves spontaneously
  - Sugar and water don't separate spontaneously

# Energy

- It takes the same amount of energy to clean your room as to mess it up.
- It takes the same amount of energy to dissolve sugar as to separate it.
- We all know that these are not equivalent, reversible, processes.

- What is it?
  - It's a measure of disorder
- We can define entropy about as well as we can define energy
- Remember – we define energy as the ability to do work

# Clausius Inequality
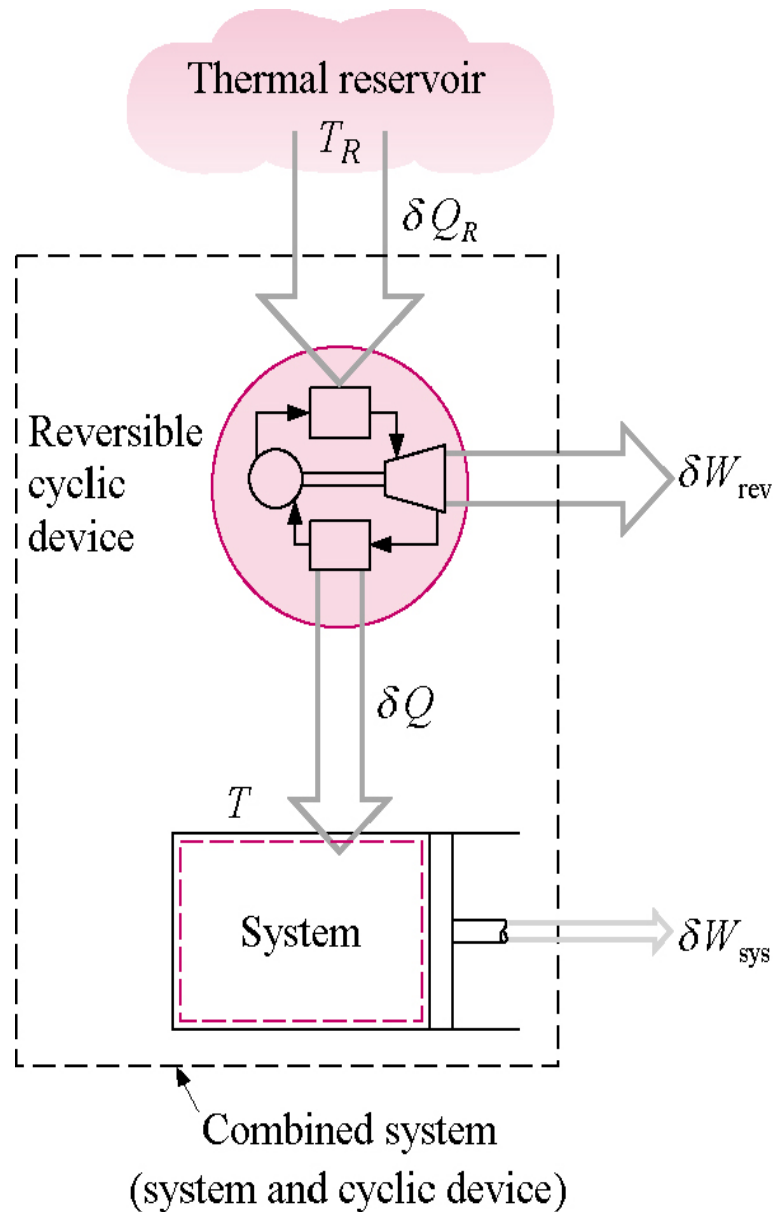


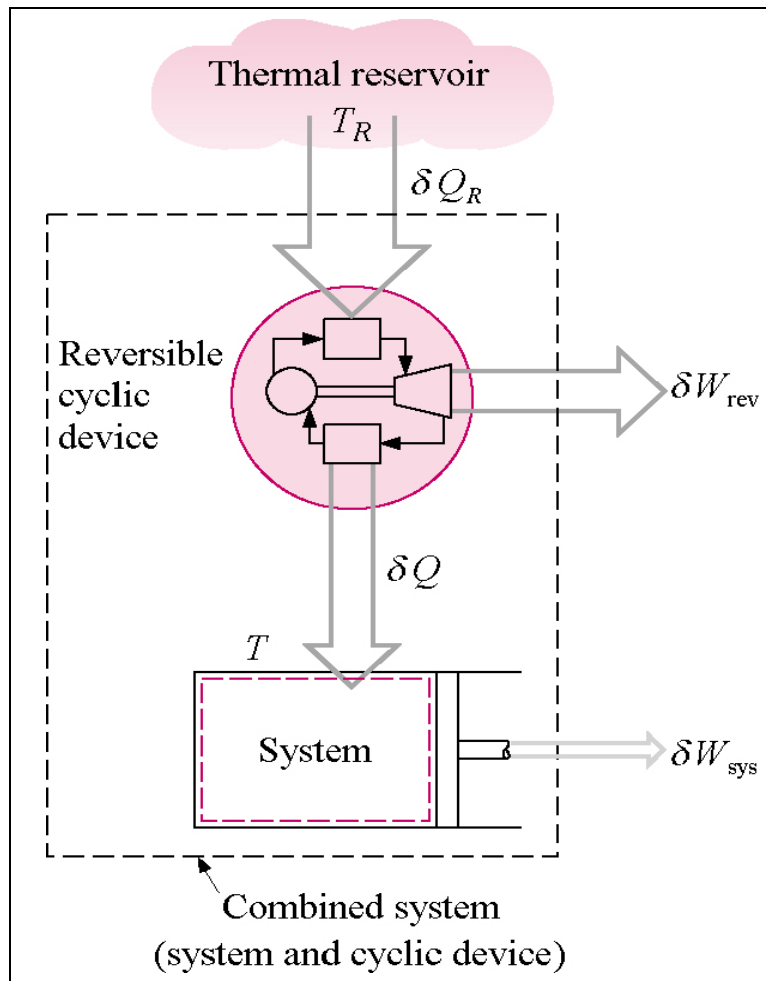Consider an energy balance for the entire system

$$E_{in} - E_{exit} = \Delta E_c$$

$$\delta Q_R - \left( \delta W_{rev} + \delta W_{sys} \right) = dE_c$$

$$\delta W_c = \delta W_{rev} + \delta W_{sys}$$

$$\delta Q_R - \delta W_c = dE_c$$

# Clausius Inequality

If the heat engine is completely reversible then…



Thermal reservoir
$T_R$

$\delta Q_R$

Reversible cyclic device

$\delta W_{rev}$

$\delta Q$

$T$

System

$\delta W_{sys}$

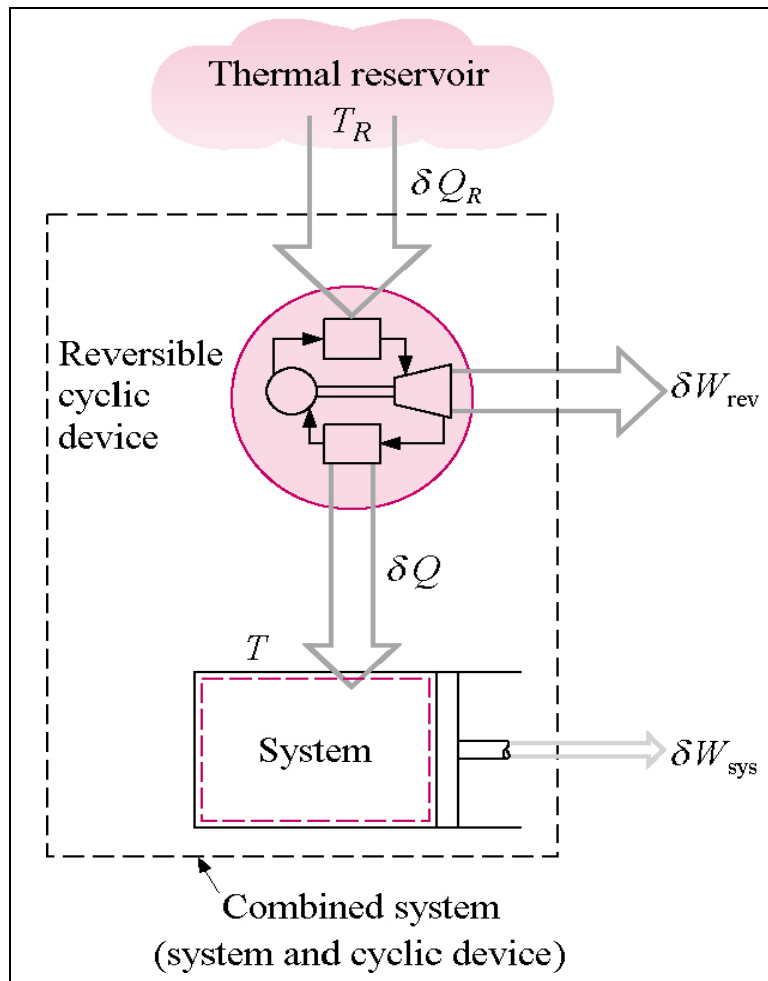Combined system
(system and cyclic device)

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

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

This is based on Chapter 5, where we said that heat transfer rate in a reversible system is proportional to the temperature

# Clausius Inequality

That means that we can rewrite the energy balance, and solve for the net work (the work of the combined system.



Thermal reservoir
$T_R$

$\delta Q_R$

Reversible cyclic device

$\delta W_{rev}$

$\delta Q$

$T$

System

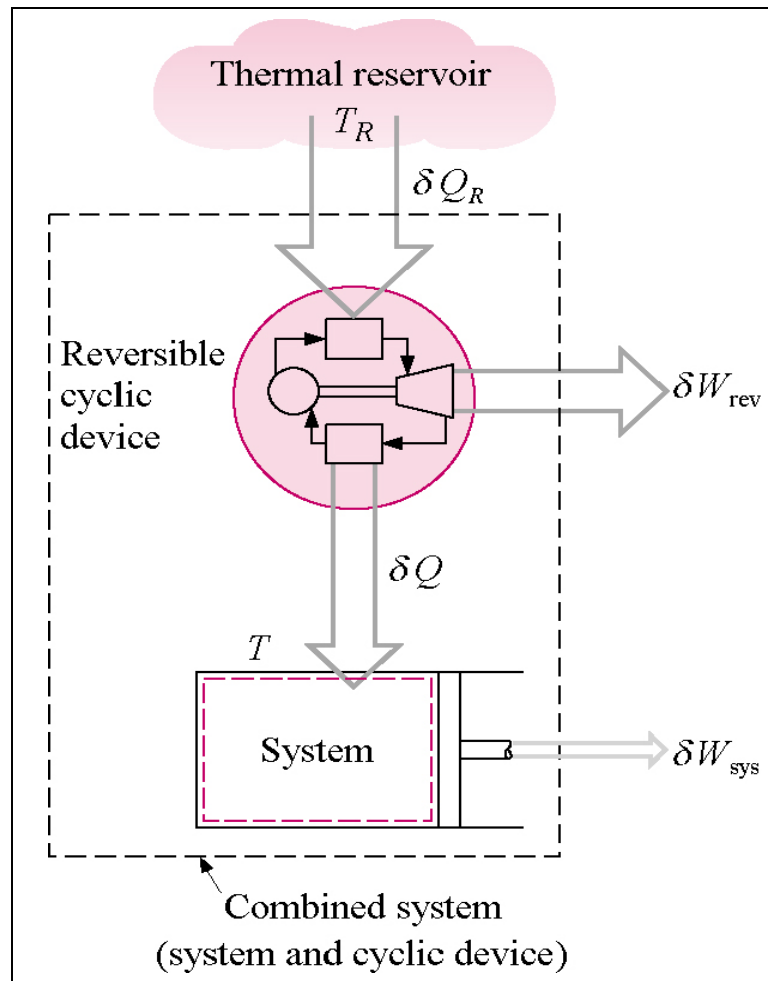$\delta W_{sys}$

Combined system
(system and cyclic device)

$$\delta W_c = T_R \frac{\delta Q}{T} - dE_c$$

To find the total net work we need to integrate over time

$$W_c = T_R \oint \frac{\delta Q}{T} - \cancel{\oint dE_c}^{\;0}$$

# Clausius Inequality

But we know that it is impossible for a system to exchange heat with only one reservoir, and produce work!!
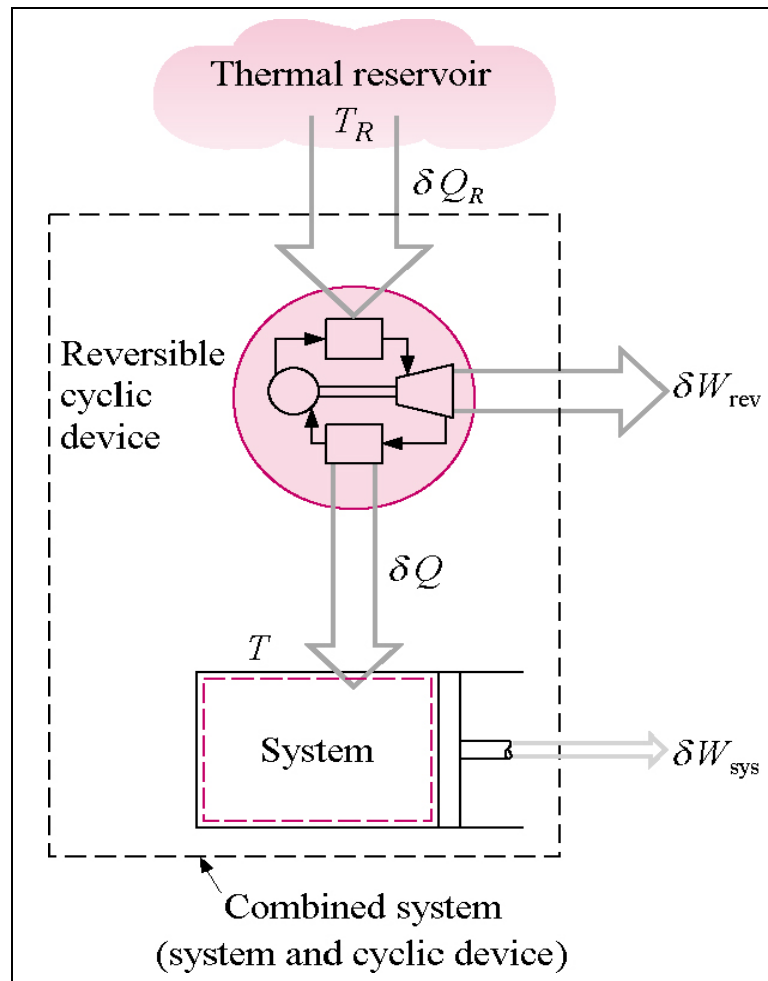


$$W_c = T_R \oint \frac{\delta Q}{T}$$

That means $W_c$ can't be positive, but it can be zero or negative!!

$$W_c = T_R \oint \frac{\delta Q}{T} \leq 0$$

# Clausius Inequality

Since $T_R$ is always positive…



Thermal reservoir $T_R$

$\delta Q_R$

Reversible cyclic device

$\delta W_{rev}$

$\delta Q$

$T$

System

$\delta W_{sys}$
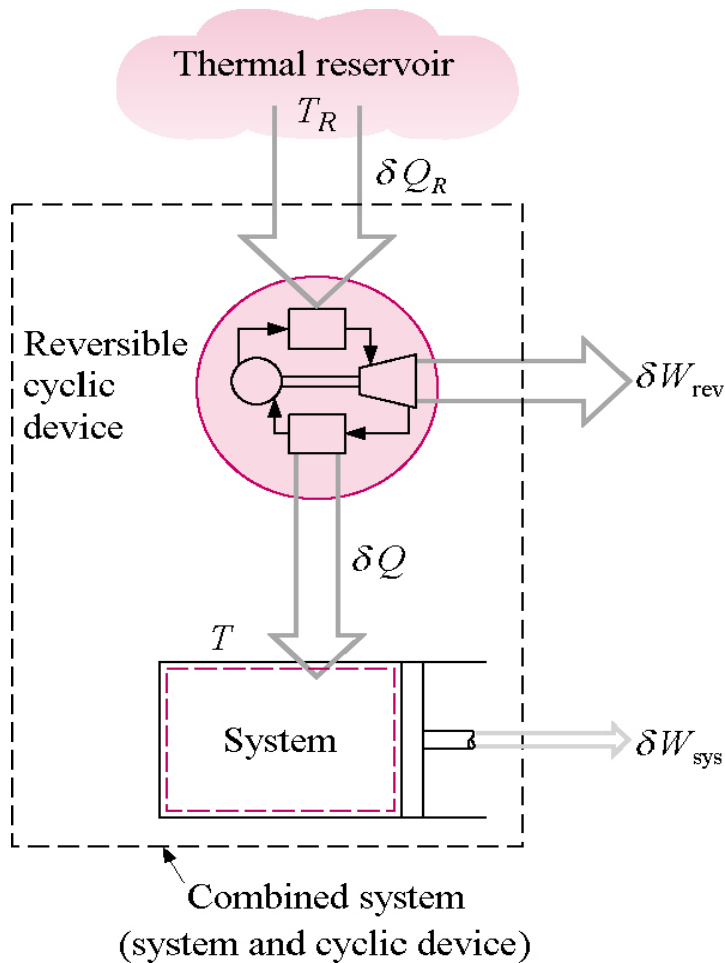
Combined system (system and cyclic device)

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

This is called the _Clausius inequality_

It is equal to 0 for the reversible case, and is less than 0 for the irreversible case

# Clausius Inequality

Can we prove that it is 0 for the reversible case?



Thermal reservoir $T_R$

$\delta Q_R$

Reversible cyclic device

$\delta W_{rev}$

$\delta Q$

$T$

System

$\delta W_{sys}$

Combined system (system and cyclic device)

If the the "system" is reversible, we can run it backwards.

If it produces negative work going one way, it will produce positive work going the other way

But we know you can't exchange heat with only one reservoir, and produce work!!

Therefore, for a reversible system, the cyclic integral must be 0!!!
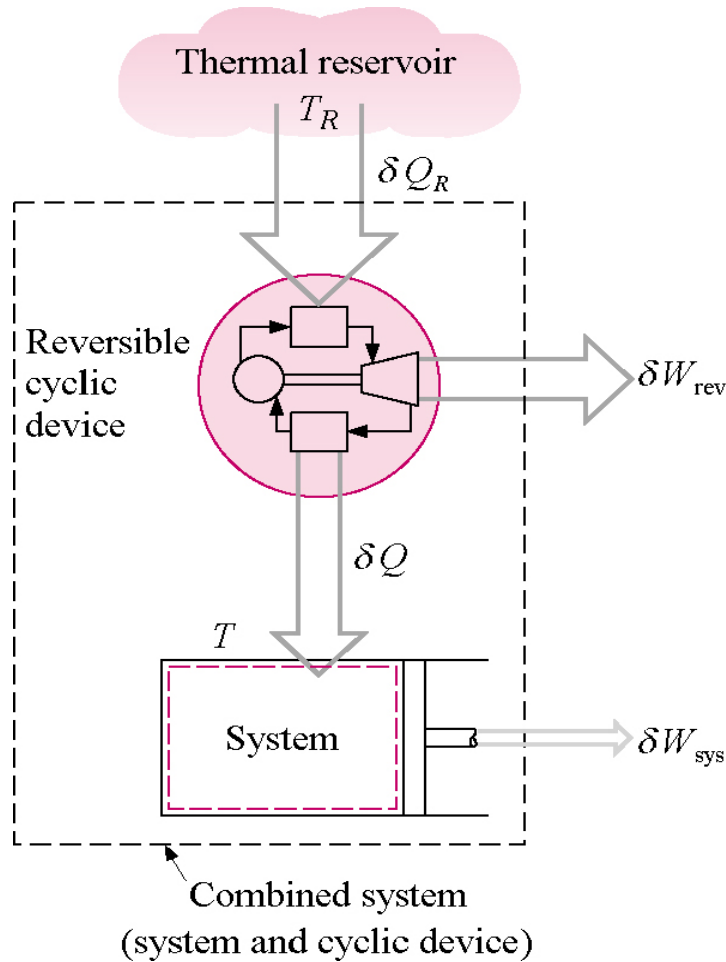


$$\oint \left( \frac{\delta Q}{T} \right)_{rev} = 0$$

# Entropy

Entropy *(S)* is a measure of the disorder or randomness in a system, and is a state variable (like *P,V,T*) that does not depend on the path taken.

$$dS = \frac{dQ}{T} \quad \text{(change in entropy S)}$$

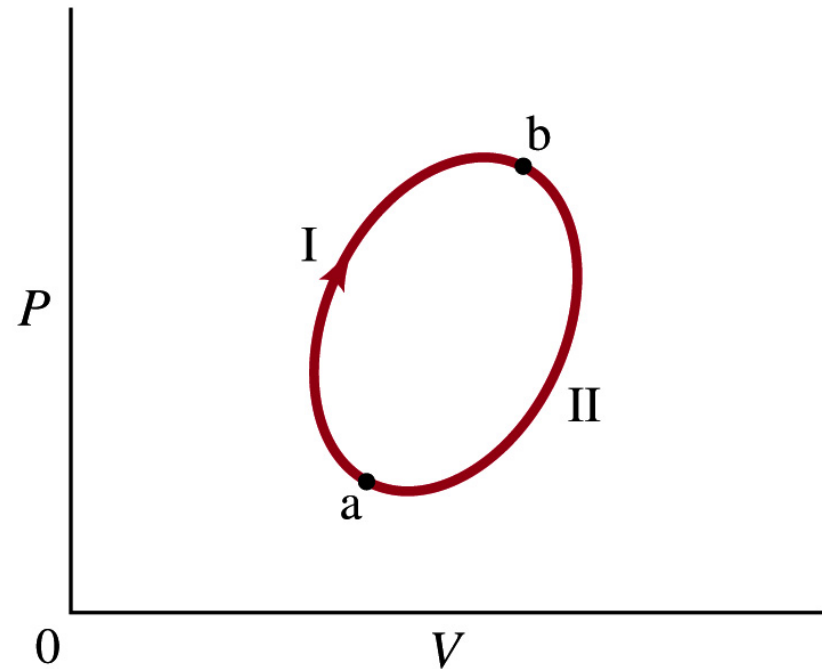where dQ is an infinitesimal heat flow

# Entropy

For any **reversible process** (e.g. Carnot cycle):

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



$$\int_{I\,a}^{b} \frac{dQ}{T} + \int_{II\,b}^{a} \frac{dQ}{T} = 0$$

$$\int_{I\,a}^{b} \frac{dQ}{T} = - \int_{II\,b}^{a} \frac{dQ}{T} = \int_{II\,a}^{b} \frac{dQ}{T}$$

The entropy of a system in a given state is independent of the path taken to get there, and is thus a **state variable**.
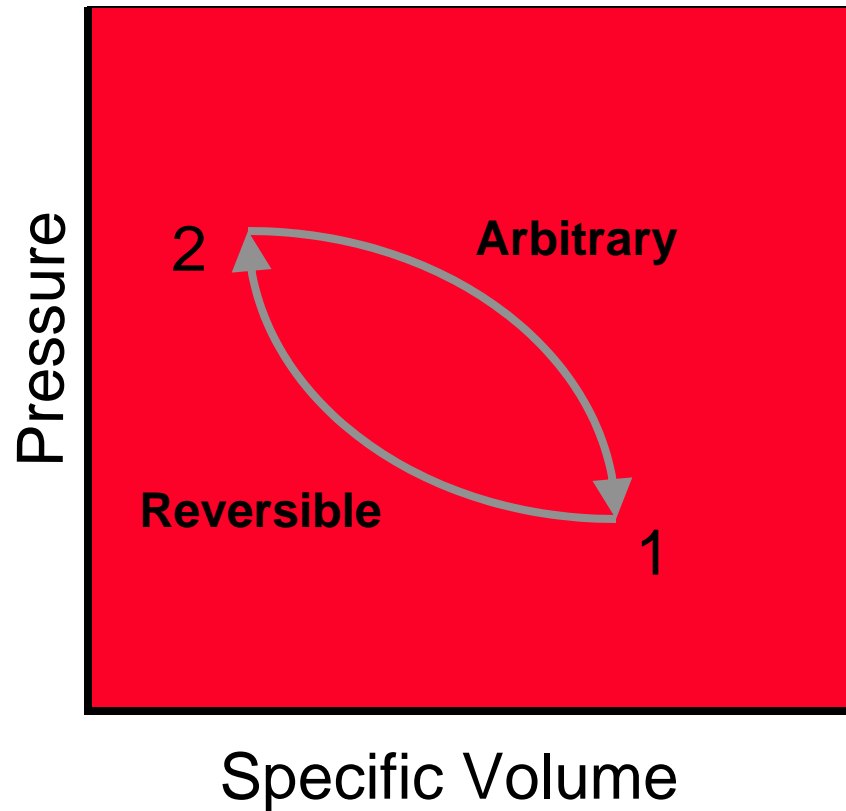
- The entropy difference between two equilibrium states *a* and *b* does not depend on how the system got from *a* to *b*.

$$\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{dQ}{T}$$

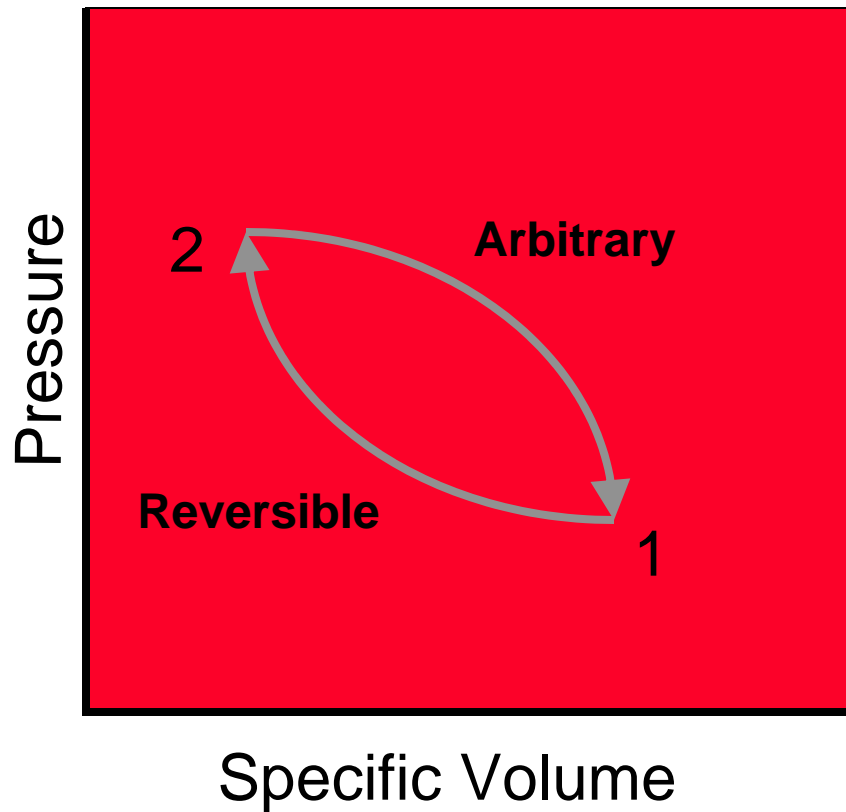**Entropy** is a **state variable** (like $P, V$ and $T$)

# Entropy



Consider a cycle composed of two processes

Process 1 (from state 1 to state 2) is reversible

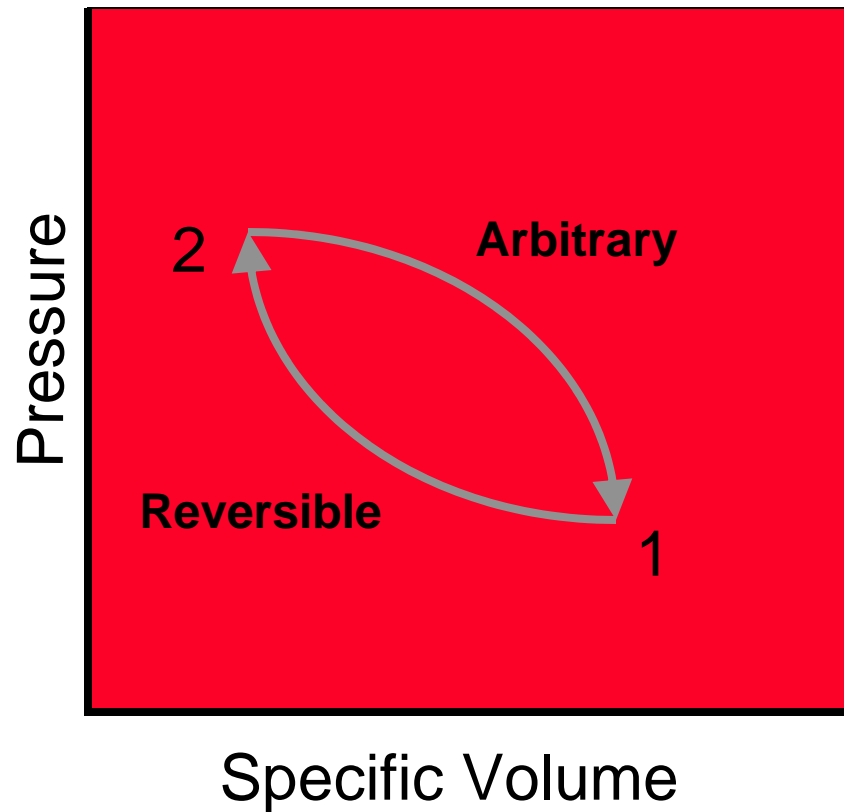Process 2 (from state 2 back to state 1 is arbitrary

# Entropy



Since the process is a cycle, the total change in entropy is 0

The change in entropy from state1 to 2 is

The change in entropy from state 2 to 1 is

$$\int_1^2 \left( \frac{\delta Q_{net}}{T} \right)_{rev} + (S_1 - S_2) = 0$$
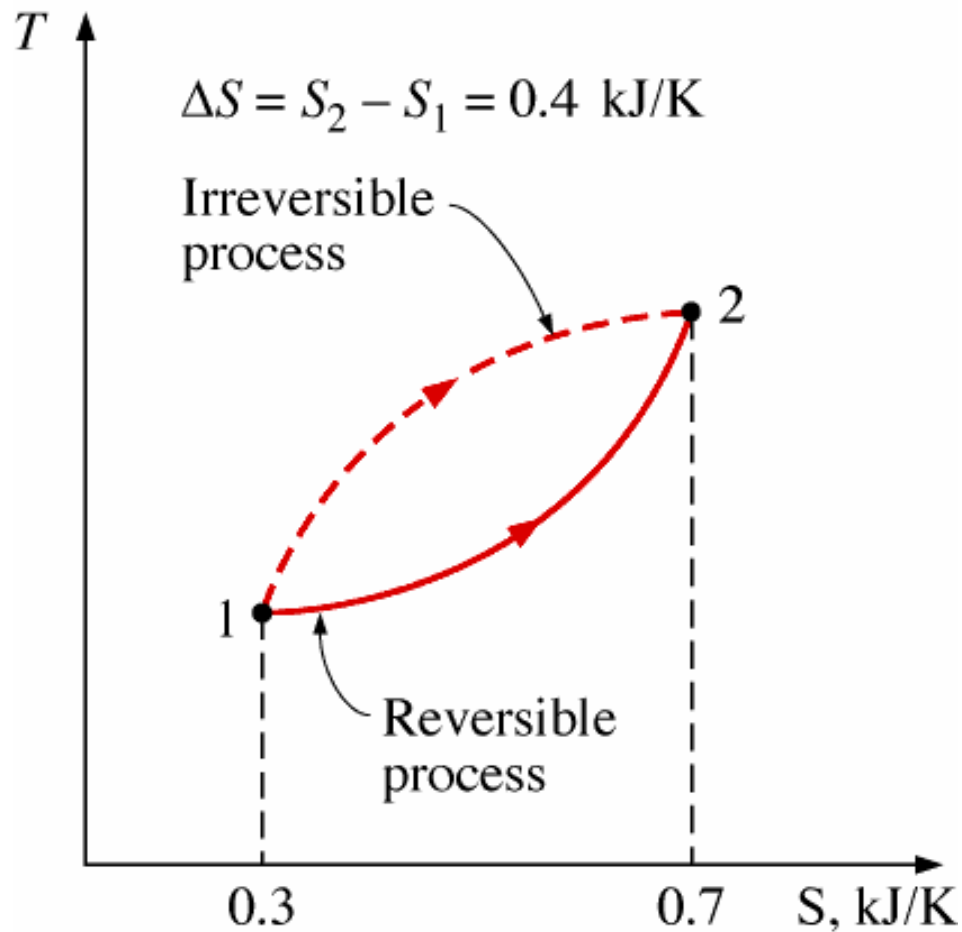
# Entropy



So, the definition of a change in entropy becomes....

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

Or...

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

# Entropy Change

$$\Delta S = S_2 - S_1 = 0.4 \text{ kJ/K}$$

Irreversible process

Reversible process

**The entropy change between two specific states is the same whether the process is reversible or irreversible**

Entropy is a "state function"

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

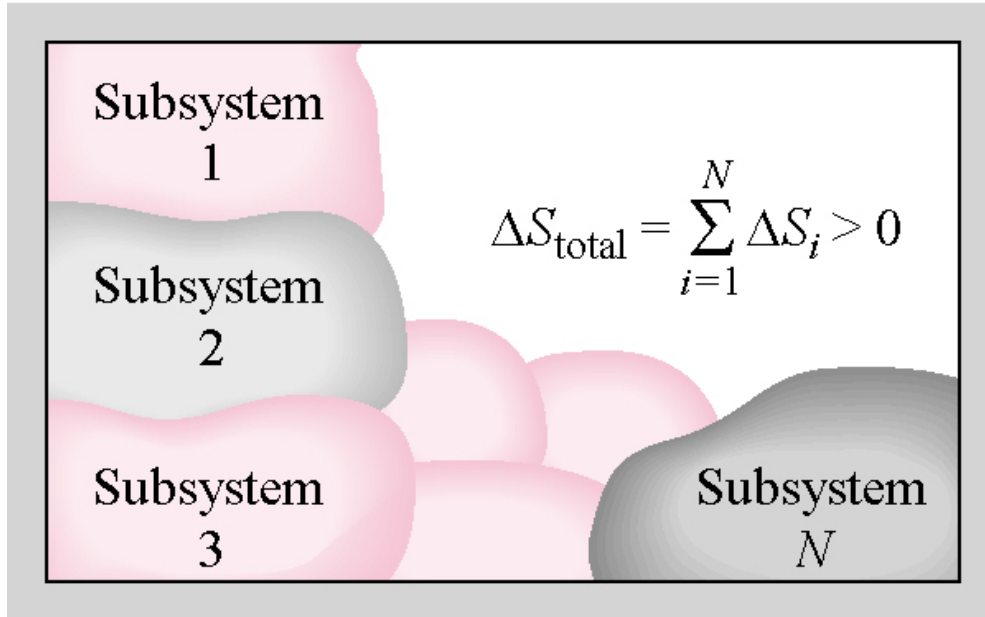Consider an adiabatic reversible process…

$$\delta Q = 0$$

## So… $\Delta$S=0

A reversible, adiabatic process is called isentropic and S is constant.

But what if the process isn't reversible?

$$S_2 - S_1 > \int_1^2 \left( \frac{\delta Q_{net}}{T} \right)_{irreversible}$$

# Isolated Systems

(Isolated)

Subsystem 1

Subsystem 2

Subsystem 3

Subsystem N

$$\Delta S_{total} = \sum_{i=1}^{N} \Delta S_i > 0$$

Consider an isolated system

Because it is isolated, there is no heat transfer or work

$$S_2 - S_1 \geq \int_1^2 \left( \frac{\delta Q_{net}}{T} \right)^{\!0}$$

$$\Delta S \geq 0$$

The equality holds if all the processes inside the system are reversible

## Now consider the universe

- It can be considered to be an isolated system!!

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

**This is the second law of thermodynamics, expressed mathematically!!**

You can consider any system to be isolated, if you draw your system boundaries out far enough



Isolated system boundary

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

System

$m$

$Q, W$
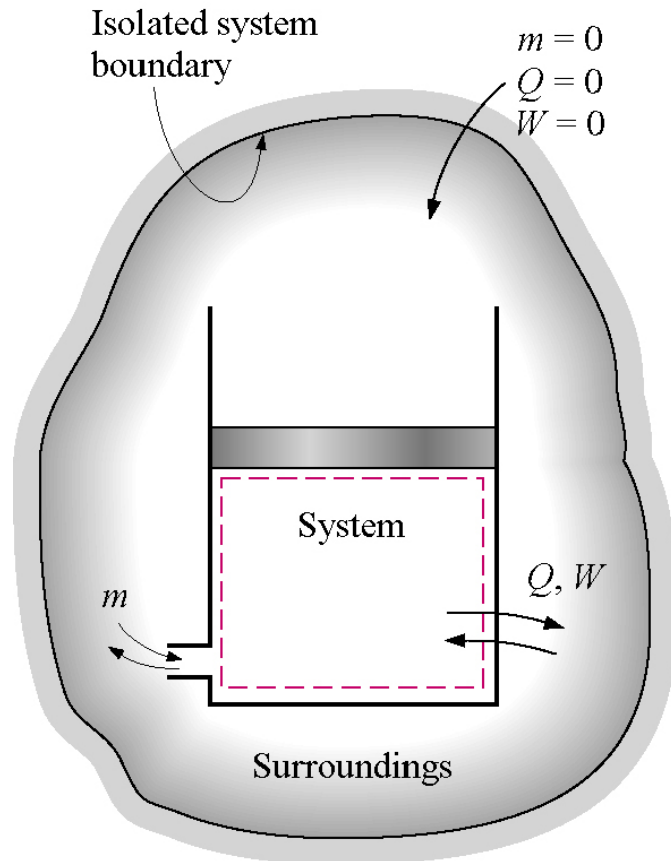
Surroundings

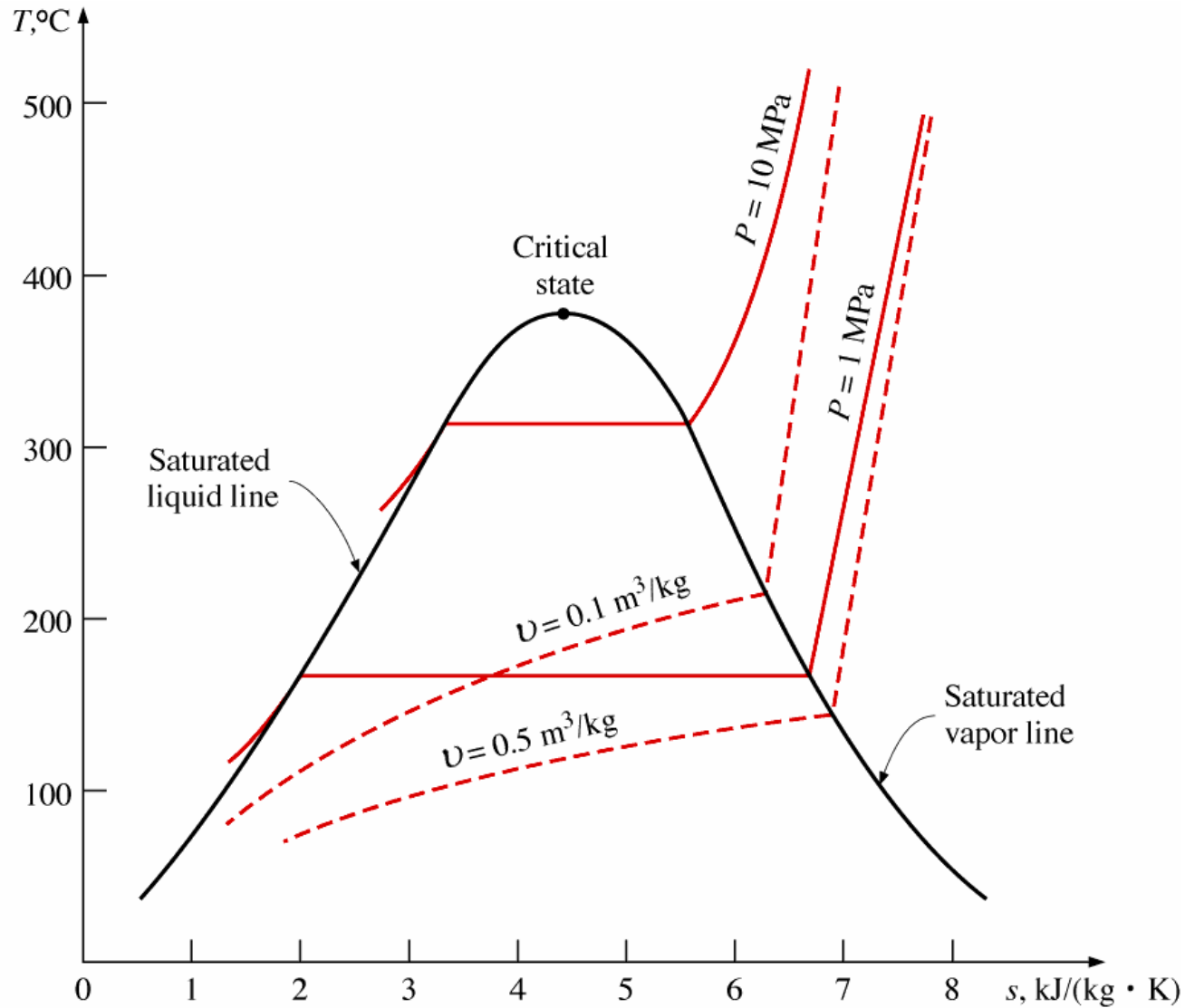$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

# Hopefully you have a better feel for entropy now!

- ## How do you calculate entropy changes for real systems?
  - If it's reversible adiabatic, $\Delta S=0$
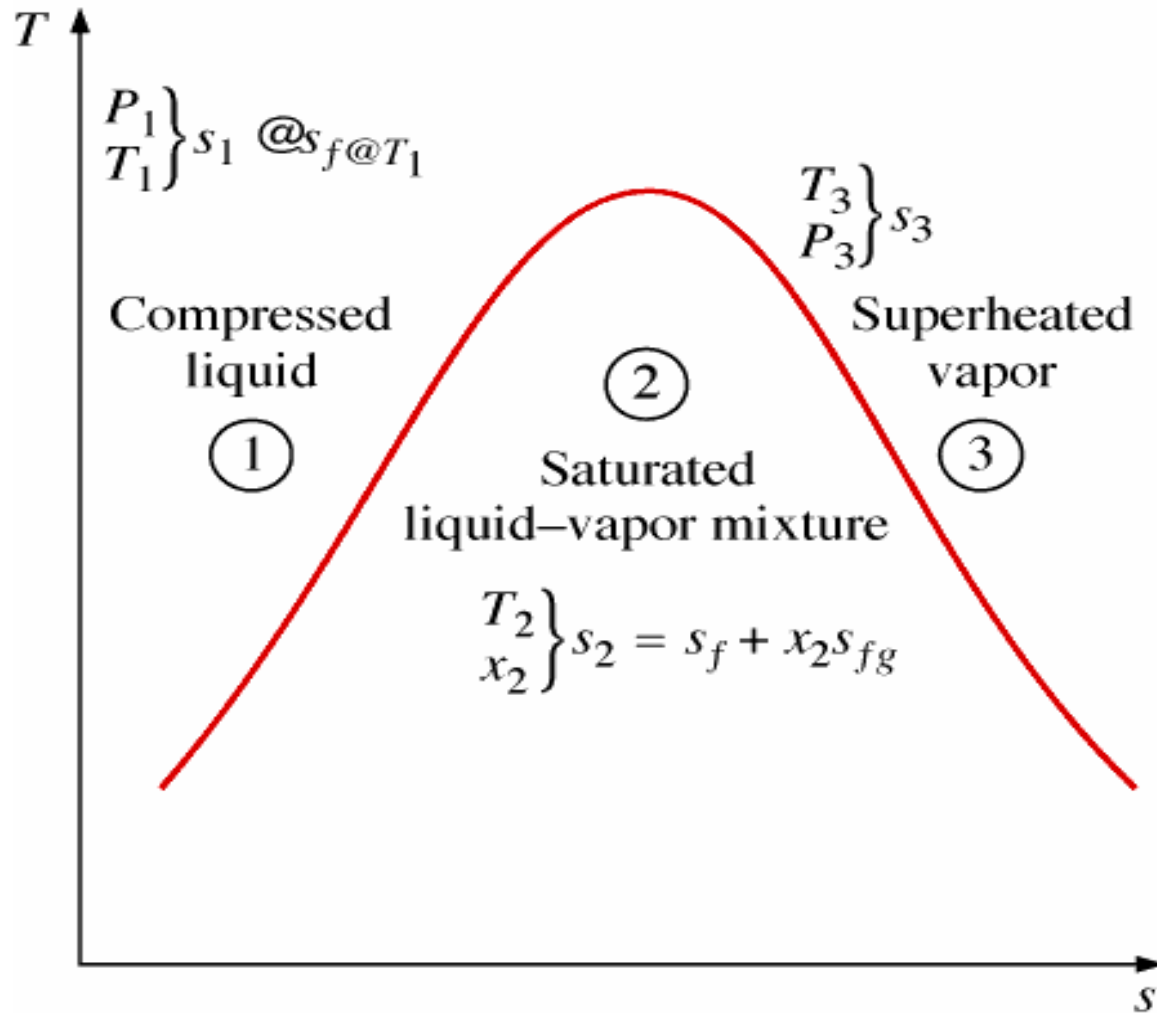  - If it's isothermal heat transfer

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

  - If it's not an ideal gas, just look it up on the property tables

# Entropy is a property

# Entropy is a property



The entropy of a pure substance is determined from the tables, just as for any other property

## Some Remarks about Entropy

- Entropy is a non-conserved property, and there is no such thing as the conservation of entropy principle.  The entropy of the universe is continuously increasing.

- The performance of engineering systems is degraded by the presence of irreversibilities, and entropy generation is a  measure of the magnitudes of the irreversibilities present during that process.

# Engineering Devices
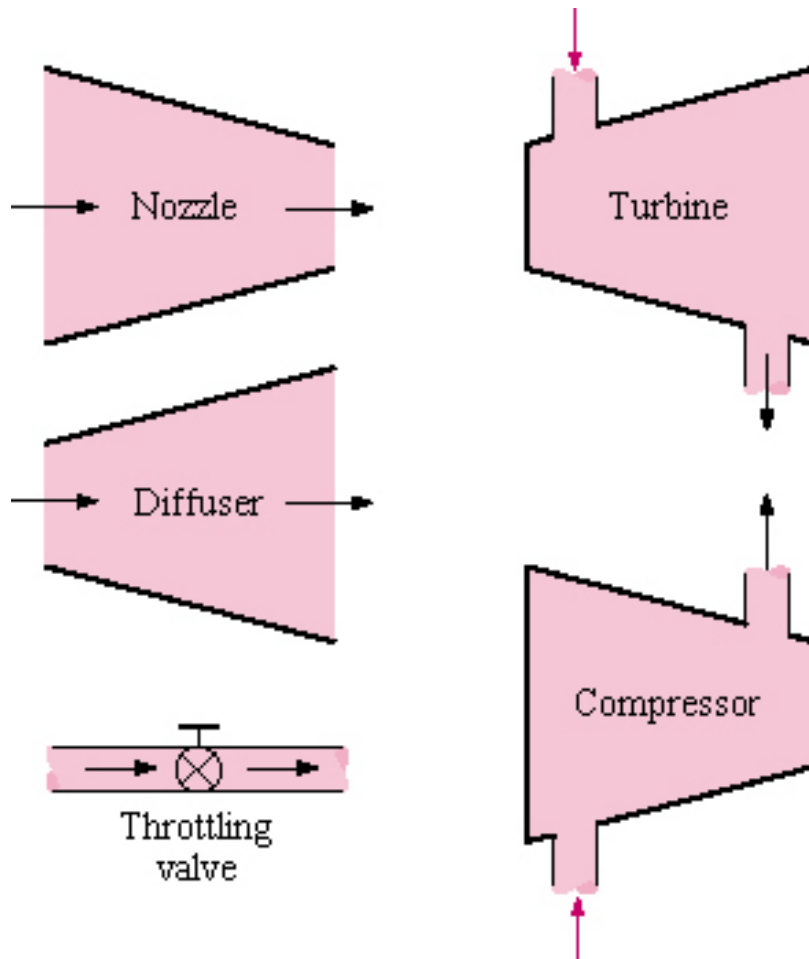


Many engineering devices are essentially adiabatic

- They perform best when irreversibilities are eliminated
- Isentropic model serves as an idealization of a real process
- These devices work best when they are isentropic

Steam

$s_1$

No irreversibilities
(internally reversible)

No heat transfer
(adiabatic)

$s_2 = s_1$
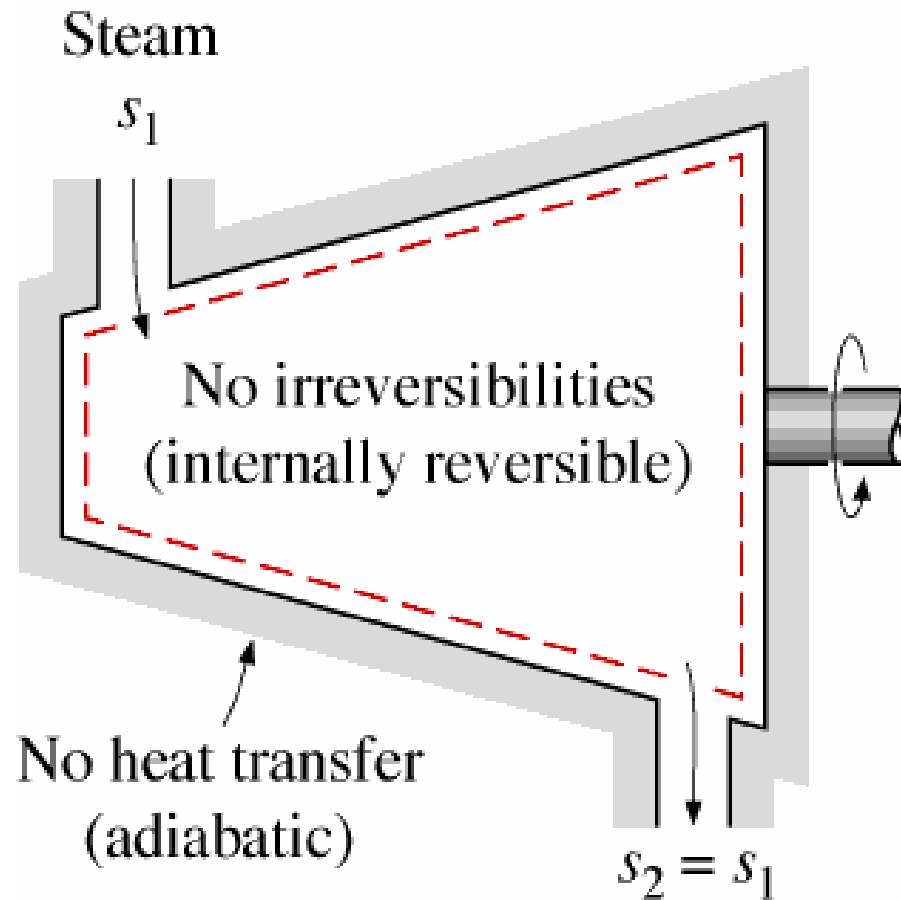
The assumption that a process is isentropic, gives us a connection between the inlet and outlet conditions – just like assuming constant volume, or constant pressure

# Property Diagrams Involving Entropy

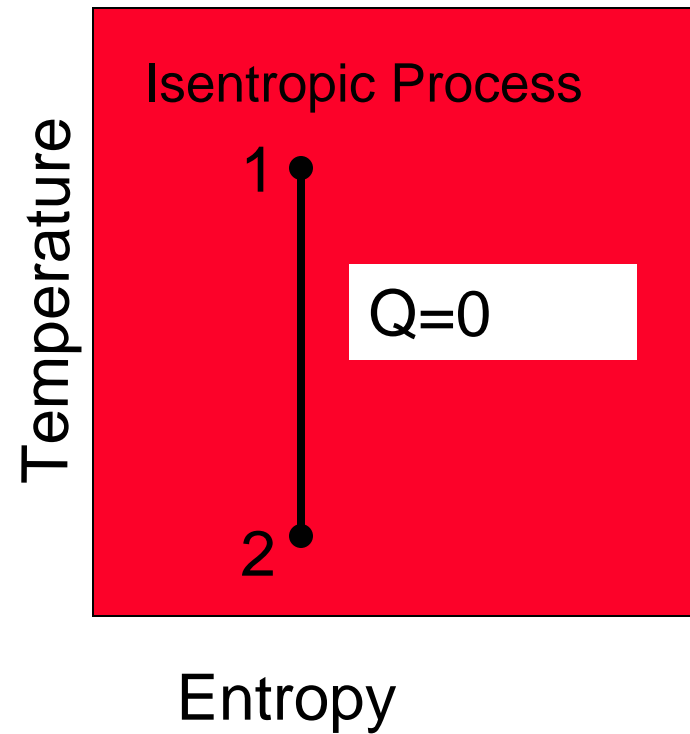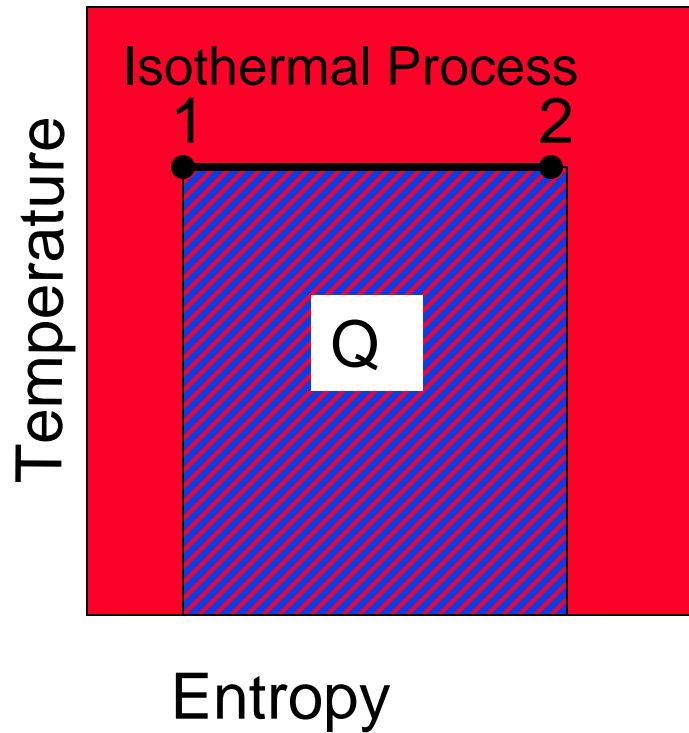$$\delta S = \frac{\delta Q_{\text{int},rev}}{T}$$

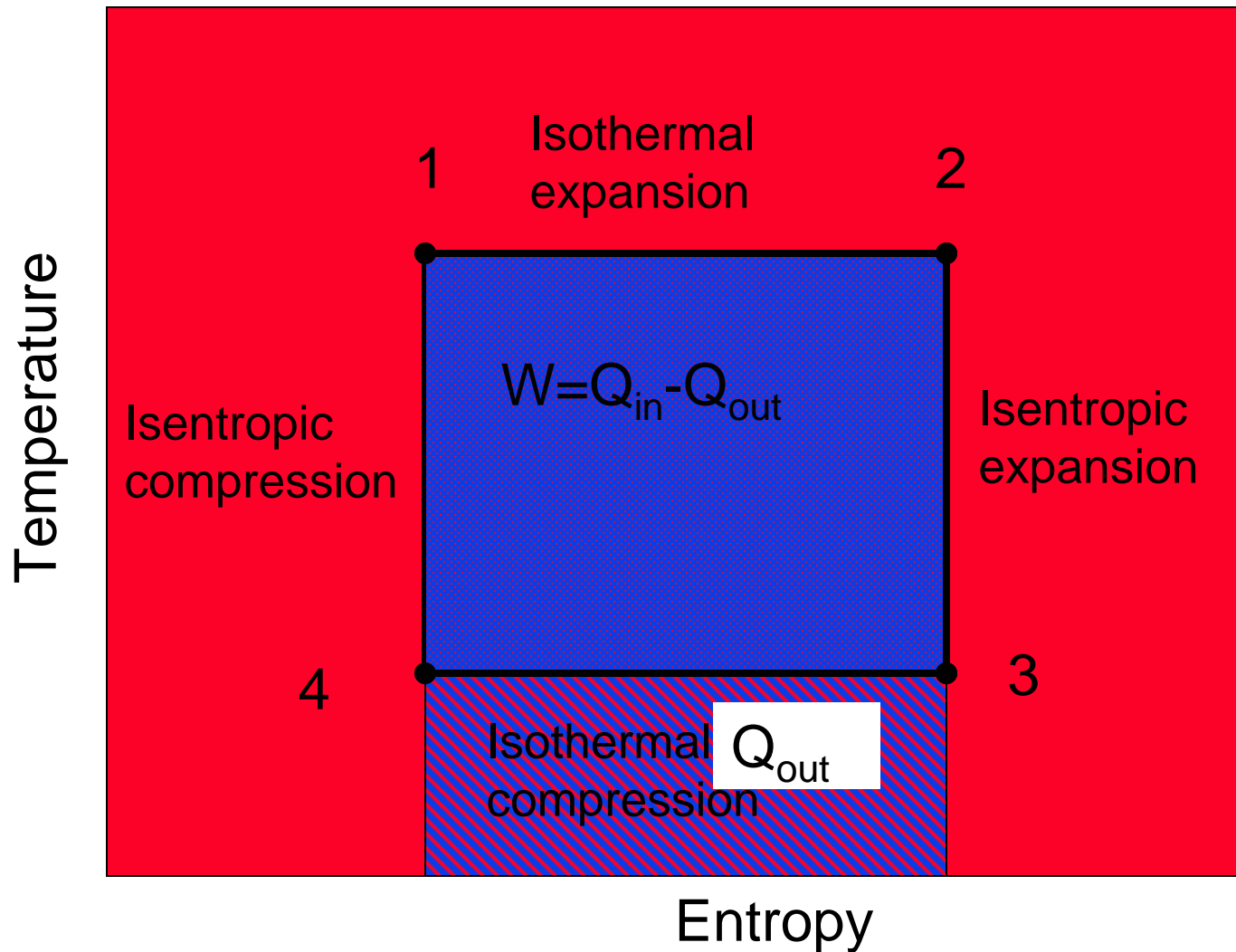$$\delta Q_{\text{int},rev} = TdS$$

$$Q_{\text{int},rev} = \int_1^2 TdS$$
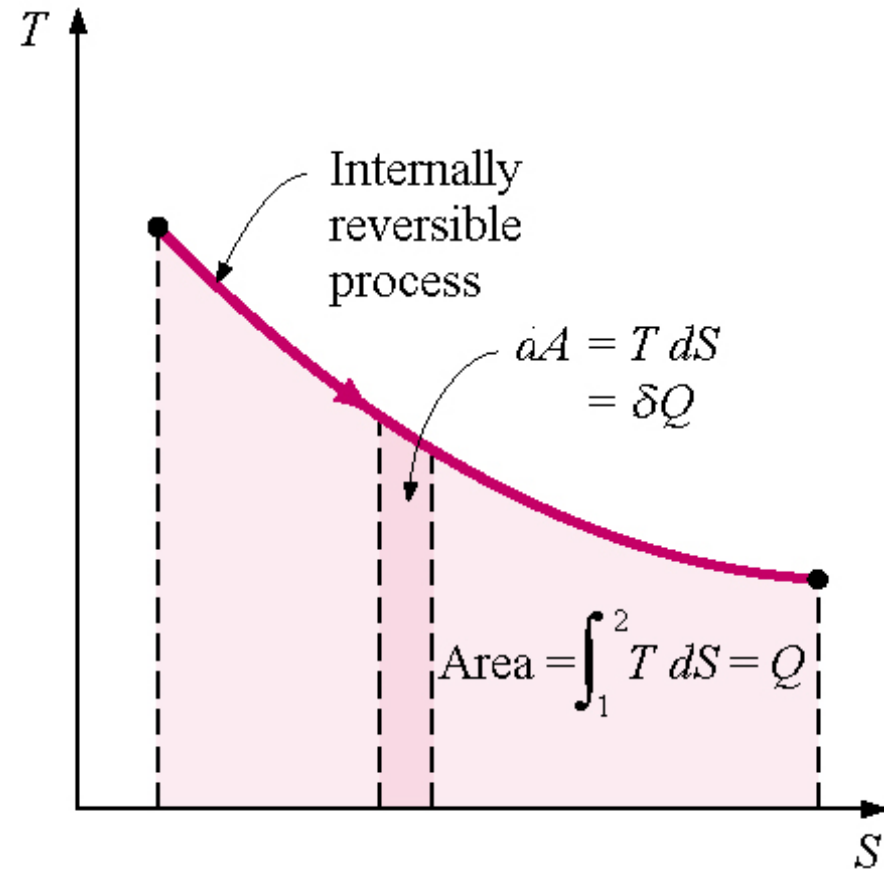


This area has no meaning for irreversible processes

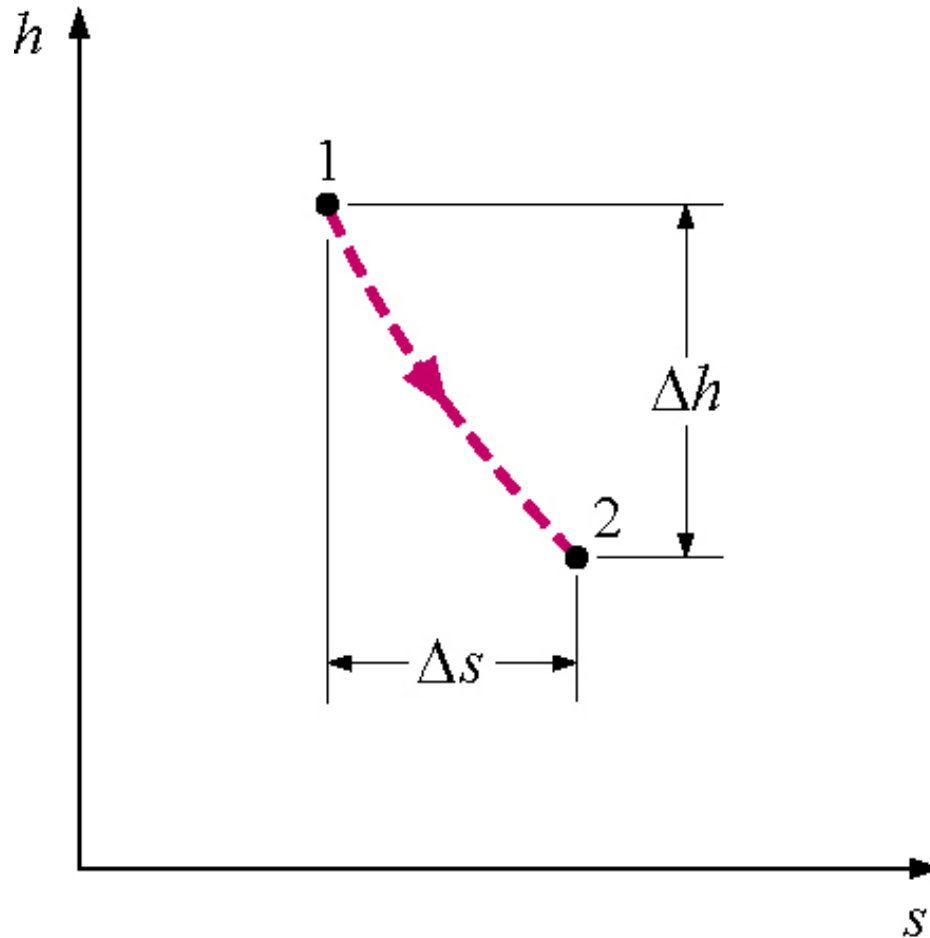# Consider some special cases of the T-s diagram



Isothermal Process
1          2
Q

Temperature
Entropy

Isentropic Process
1
Q=0
2

Temperature
Entropy

# T-s Diagram for the Carnot Cycle

# Mollier Diagrams (h-s Diagrams)



For adiabatic, steady flow devices, Δh is a measure of work, and Δs is a measure of irreversibilities

# Mollier Diagram for Steam