

## 2nd Law

**The Second Law of Thermodynamics:** Processes occur in a certain direction and energy has quality as well as quantity.

**Thermal Energy Reservoirs:** A hypothetical body with a relatively large thermal energy capacity (mass  $\times$  specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature.

## Heat Engines

- Devices that convert heat to work
- Receive heat from high-temp source
- Convert part of this heat to work
- Reject remaining waste heat to low-temperature sink - Kelvin-Planck Statement
- Operate on a cycle
- MUST waste some energy by transferring to low-temperature reservoir in order to complete cycle

Notation:

- $Q_{in} = Q_H$  = amount of heat supplied from a high-temp source
- $Q_{out} = Q_L$  = amount of heat rejected to a low temperature sink
- $W_{out}$  = amount of work delivered out of system by working fluid
- $W_{in}$  = amount of work input to system

$$W_{net,out} = W_{out} - W_{in} \text{ (kJ)}$$

$$W_{net,out} = Q_{in} - Q_{out} \text{ (kJ)}$$

## Thermal Efficiency

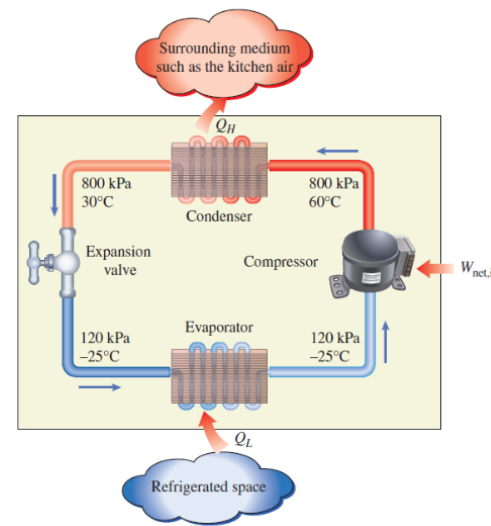
$$\eta = \frac{W_{net,out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{Q_L}{Q_H}$$

## Refrigerators and Heat Pumps

**Coefficient of Performance:** efficiency of a refrigerator.  

$$COP_R = \frac{\text{Desired Output}}{\text{Required Input}} = \frac{Q_L}{W_{net,in}} = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

**Clausius Statement:** It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.



## Reversible and Irreversible Processes

**Reversible Process:** A process that can be reversed without leaving any trace on the surroundings - theoretical to find limits.

**Irreversible Process:** A process that is not reversible.

**Irreversibilities:**

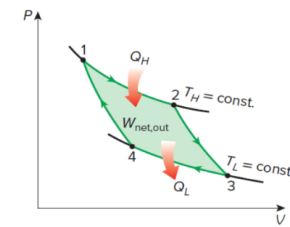
- Friction
- Unrestrained expansion
- Mixing of two fluids
- Heat transfer across a finite temperature difference
- Electric resistance
- Inelastic deformation of solids
- Chemical reactions

## The Carnot Cycle

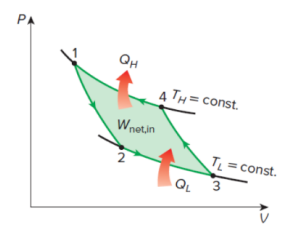
The Carnot Cycle is composed of four reversible processes - two isothermal and two adiabatic - and it can be executed either in a closed or steady-flow system.

- Reversible Isothermal Expansion - process 1-2,  $T_H = \text{constant}$
- Reversible Adiabatic Expansion - process 2-3,  $T_H \rightarrow T_L$
- Reversible Isothermal Compression - process 3-4,  $T_L = \text{constant}$
- Reversible Adiabatic Compression - process 4-1,  $T_L \rightarrow T_H$

The Carnot Cycle is completely reversible - in which case it becomes the Carnot refrigeration cycle.



**FIGURE 7-35**  
 P-V diagram of the Carnot cycle.



**FIGURE 7-36**  
 P-V diagram of the reversed Carnot cycle.

**The Carnot Principles:** The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs and the efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

**The Thermodynamic Temperature Scale:** A temperature scale that is independent of the properties of the substances that are used to measure temperature.

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

## The Carnot Heat Engine

Any heat engine:  $\eta_{th} = 1 - \frac{Q_L}{Q_H}$

Carnot heat engine:  $\eta_{th,rev} = 1 - \frac{T_L}{T_H}$

$$\eta_{th} \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine} \end{cases}$$

Amount of heat rejected per cycle:  $Q_{L,rev} = \frac{T_L}{T_H} Q_{H,rev}$

**Quality of Energy:** The higher the temperature of the thermal energy, the higher its quality. Directly relates to face that you can use temperature to measure efficiency in  $\eta_{th,rev}$ .

## The Carnot Refrigerator and Heat Pump

Any refrigerator or heat pump:

$$COP_R = \frac{1}{Q_H/Q_L - 1} \text{ and } COP_{HP} = \frac{1}{1 - Q_L/Q_H}$$

Carnot refrigerator or heat pump:

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1} \text{ and } COP_{HP,rev} = \frac{1}{1 - T_L/T_H}$$

$$COP_R \begin{cases} < COP_{R,rev} & \text{irreversible refrigerator} \\ = COP_{R,rev} & \text{reversible refrigerator} \\ > COP_{R,rev} & \text{impossible refrigerator} \end{cases}$$

# Entropy

- Processes can only occur in a certain direction and that direction must comply with the increase of entropy principle:  $S_{\text{gen}} \geq 0$ .
- 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.
- Entropy generation is the measure of the magnitudes of the irreversibilities during the performance of engineering systems. It is also used to establish criteria for the performance of engineering devices.

**Clausius Inequality:**  $\oint \frac{\delta Q}{T} \leq 0$

$\delta W_C = \delta Q_R - dE_C$

Reversible cyclic device:

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

For a system undergoing a cycle:  $W_C = T_R \oint \frac{\delta Q}{T}$

$$\oint \left( \frac{\delta Q}{T} \right)_{\text{int,rev}} = 0 \text{ and } dS = \left( \frac{\delta Q}{T} \right)_{\text{int,rev}} \text{ (kJ/K)}$$

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

**Special Case:**

Internally Reversible Isothermal Heat Transfer Process  $\Delta S = \frac{Q}{T_0}$  (kJ/K) where  $T_0$  is the constant temperature of the system and  $Q$  is the heat transfer for the internally reversible process.

**Generated Entropy:**

$$S_{\text{gen}} = \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \rightarrow \Delta S_{\text{sys}} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}}$$

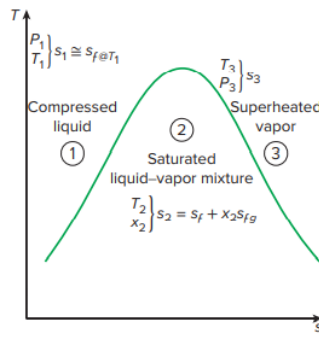
**The Increase of Entropy Principle:**

$$S_{\text{gen}} \begin{cases} < 0 \text{ impossible process} \\ = 0 \text{ reversible process} \\ > 0 \text{ irreversible process} \end{cases}$$

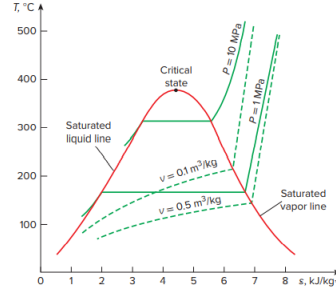
## Entropy Change of Pure Substances

Once the state of the system is fixed the value of entropy is also fixed.

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



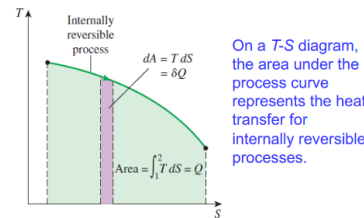
T-s Diagram for water ↓



## Isentropic Processes

$$\Delta S = 0 \text{ or } S_2 = S_1 \text{ (kJ/kgK)}$$

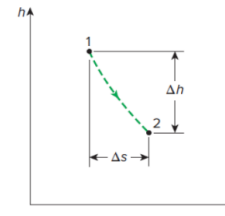
## Property Diagrams involving Entropy



$$\delta Q_{\text{int rev}} = T ds \quad Q_{\text{int rev}} = \int_1^2 T ds$$

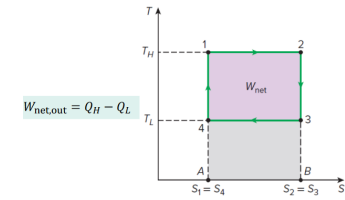
$$\delta q_{\text{int rev}} = T ds \quad q_{\text{int rev}} = \int_1^2 T ds$$

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



**FIGURE 8-18** 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.

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



**FIGURE 8-19** The  $T$ - $S$  diagram of a Carnot cycle

## What is Entropy?

**Boltzmann Relation:**  $S = k \ln W$

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

**Gibb's Formulation:**  $S = -k \sum P_i \log P_i$

**Pure Crystal:**  $T = 0 \text{ K}$  then Entropy = 0

The entropy of a pure crystalline substance at absolute zero temperature is zero (Third Law of Thermodynamics)

## The Tds Relations

**The First Tds or Gibbs Equation:**

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

$$\delta Q_{\text{int,rev}} = Tds \text{ and } \delta W_{\text{int,rev,out}} = PdV$$

$$Tds = dU + PdV \text{ (kJ)}$$

$$Tds = du + PdV$$

**The Second Tds Equation:**

$$h = u + Pv$$

$$dh = du + PdV + v dP \text{ and } Tds = du + PdV$$

$$Tds = dh - v dP$$

**Finally:**

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

## Entropy Change of Liquids and Solids

Liquids and solids can be approximated as incompressible substances.