Marissa Palamara
ASEN 3112
Spring 2021

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 x 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-Plank 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

$W_{net,out} = W_{out} - W_{in}$ (kJ)
$W_{net,out} = Q_{in} - Q_{out}$ (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.
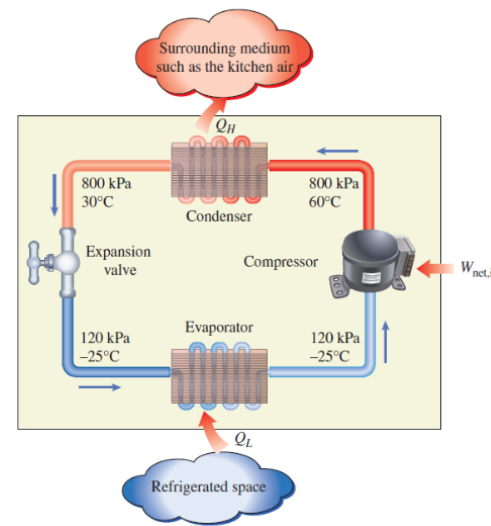
Reversible and Irreversible Processes

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.

Ierreversibilities:

- 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 = constant
- Reversible Adiabatic Expansion - process 2-3, $T_H \to T_L$
- Reversible Isothermal Compression - process 3-4, T_L = constant
- Reversible Adiabtic Compression - process 4-1, $T_L \to T_H$

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

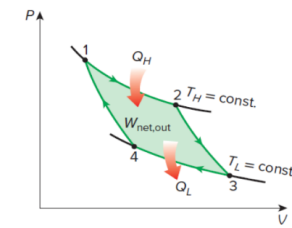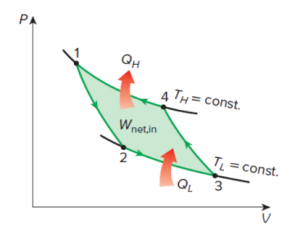**The Carnot Principles**: The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs and the efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

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

Carnot refrigerator or heat pump:
$COP_{R,rev} = \frac{1}{T_H/T_L - 1}$ 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: $\boxed{\oint \frac{\delta Q}{T} \leq 0}$

$\delta W_C = \delta Q_R - dE_C$

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 underoing a cycle: $W_C = T_R \oint \frac{\delta Q}{T}$

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

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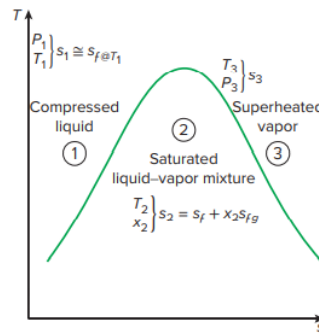
The Increase of Entropy Principle:

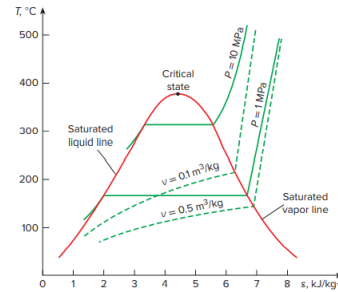$$S_{\text{gen}} \begin{cases} < 0 \text{ impossible process} \\ = 0 \text{ reversible process} \\ > 0 \text{ irreversible process} \end{cases}$$

Entropy Change of Pure Substances

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

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

T-s Diagram for water↓

Isentropic Processes

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

Property Diagrams involving Entropy

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

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

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

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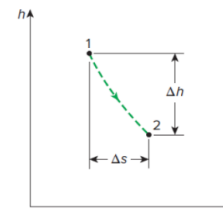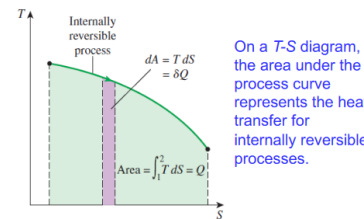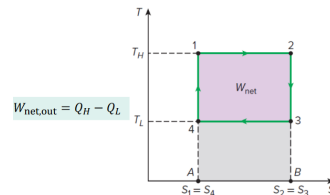

FIGURE 8-18
For adiabatic steady-flow devices, the vertical distance Δh on an h-s diagram is a measure of work, and the horizontal distance Δs is a measure of irreversibilities.

Mollier diagram: The h-s diagram

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

$W_{\text{net,out}} = Q_H - Q_L$

What is Entropy?

Boltzmann Relation: $S = k \ln W$
$k = 1.3806 \times 10^{-23}$ J/K
Gibb's Formulation: $S = -k \sum P_i \log P_i$
Pure Crystal: $T = 0$ 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:
$\delta Q_{\text{int,rev}} - \delta W_{\text{int,rev,out}} = dU$
$\delta Q_{\text{int,rev}} = TdS$ and $\delta W_{\text{int rev,out}} = PdV$
$TdS = dU + PdV$ (kJ)
$\boxed{Tds = du + Pdv}$
The Second Tds Equation:
$h = u + Pv$
$dh = du + Pdv + vdP$ and $Tds = du + Pdv$
$\boxed{Tds = dh - vdP}$
Finally:
$\boxed{ds = \frac{du}{T} + \frac{Pdv}{T} = \frac{dh}{T} - \frac{vdP}{T}}$

Entropy Change of Liquids and Solids

Liquids and solids can be approximated as incompressible substances $\rightarrow dv = 0$.
$ds = \frac{du}{T} = \frac{cdT}{T} \rightarrow c_P = c_v = c$ and $du = cdT$
$\boxed{S_2 - S_1 = \int_1^2 d(T)\frac{dT}{T} = c_{\text{avg}} \ln \frac{T_2}{T_1}}$ (kJ/kgK)
Isentropic: $s_2 - s_1 = c_{\text{avg}} \ln \frac{T_2}{T_1} = 0 \rightarrow T_2 = T_1$

Entropy Change of Ideal Gases

$Pv = RT$
$du = c_v dT$
$dh = c_p dT$
$ds = c_v \frac{dT}{T} + R\frac{dv}{v} \rightarrow s_2 - s_1 = \int_1^2 c_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$
$s_2 - s_1 = \int_1^2 c_p(T)\frac{dT}{T - R\ln\frac{P_2}{P_1}}$

Constant Specific Heats (Approximate Analysis)

$s_2 - s_1 = c_{v,avg} \ln \frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$
$s_2 - s_1 = c_{p,avg} \ln \frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$

Variable Specific Heats (Exact Analysis)

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

Choose absolute zero as reference temperature and define a function s° as:

$s^\circ = int_0^T c_p(T) \frac{dT}{T}$

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

On a unit mass basis:

$s_2 - s_1 = s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1}$ (kJ/kgK)

Isentropic Processes of Ideal Gases

Constant Specific Heats

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

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

$\left(\frac{V_1}{V_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$

Variable Specific Heats

Relative Pressure, $P_r = \exp\left(s^\circ/R\right)$

Relative Specific Volume, T/P_r

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

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

Reverse Steady-Flow Work

$w_{\text{rev}} = -\int_1^2 v dP - \Delta ke - \Delta pe \rightarrow w_{\text{rev}} = -v(P_2 - P_1) - \Delta ke - \Delta pe$

When KE and PE are negligible: $w_{\text{rev}} = -\int_1^2 v dP$

For steady flow of a liquid through a device that involves no work, like a pipe, the work term is zero:

$v(P_2 - P_1) + \frac{V_2^2 - -V_1^1}{2} + g(z_2 - z_1) = 0$

General Knowledge

Isentropic: Constant entropy

Isothermal: Constant temperature

Adiabatic: No Q

Adiabatic and Reversible: Isentropic