Kelvin Planck Statement of the Second Law

It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of heat from a single reservoir and the performance of an equivalent amount of work.

Clausius Statement of the Second Law

It is impossible to have a system operating in a cycle which transfers heat from a cooler to a hotter body without work being done on the system by the surroundings.
Actual Heat Engine

Energy source (such as a furnace)

System boundary

Energy sink (such as the atmosphere)
Actual Refrigeration Machine

- **Condenser:** 800 kPa, 60°C
- **Expansion Valve:** 120 kPa, -25°C
- **Compressor:** 800 kPa, 30°C
- **Evaporator:** 120 kPa, -20°C

**QL**: Refrigerated space

**QH**: Surrounding medium such as the kitchen air

**W_{net, in}**: Work input into the system
Carnot Power Cycle

Reversible constant temperature heat transfer,
process 1 \to 2, \text{ process } 3 \to 4
Reversible adiabatic expansion,
process 2 \to 3, \text{ process } 4 \to 1

\begin{align*}
\text{Efficiency} &= \frac{\text{Desired Effect}}{\text{Required Input}} \\
\eta_{\text{cycle}} &= \frac{Q_H - Q_L}{Q_H} = \frac{\text{Work}}{Q_{\text{in}}} \quad Q_{\text{in}}
\end{align*}
Carnot Refrigeration Cycle

Reversible constant temperature heat transfer,
process 4 $\rightarrow$ 1, process 2 $\rightarrow$ 3
Reversible adiabatic expansion,
process 1 $\rightarrow$ 2 process 3 $\rightarrow$ 4

Coefficient of Performance $= \frac{\text{Desired Effect}}{\text{Required Input}}$

$\text{COP}_{\text{refrigerator}} = \frac{Q_L}{Q_L - Q_H} = \frac{Q_{\text{in}}}{\text{Work}}$

$\text{COP}_{\text{heat pump}} = \frac{Q_H}{Q_L - Q_H} = \frac{Q_{\text{out}}}{\text{Work}}$
NEWCOMEN ATMOSPHERIC ENGINE
Ford Museum, Detroit, 1760, 14 strokes/min
NEWCOMEN ATMOSPHERIC ENGINE

Ford Museum, 1760

14 strokes/min

atmospheric pressure

72 in stroke

15 psia steam

28 in

50 F water

28 in
NEWCOMEN ATMOSPHERIC ENGINE

Ford Museum, 1760
14 strokes/min

atmospheric pressure

F
72 in stroke

50°F

15 psia

28 in

15 psia steam

A = \pi R^2 = \pi (14)^2 = 614 \text{ in}^2

F = p \times A = (14.7 \text{ psia} - 0.18 \text{ psia}) \times 614 \text{ in}^2 = 9114 \text{ lbs}

W = F \times d = 9114 \text{ lbs} \times (72/12) \text{ ft} = 54,684 \text{ ft lb/stroke}

\text{Power} = 54,684 \frac{\text{ft lb/stroke}}{\text{strokes/min}} \times 14 \frac{\text{strokes}}{\text{min}} = 765,000 \frac{\text{ft lb}}{\text{min}}

\text{Power} = \frac{765,000 \text{ ft lb/min}}{33,000 \text{ hp/ft lb/min}} = 23 \text{ HP} \text{ or } 17.5 \text{ kw}

m = \frac{V}{v} \times \text{strokes} = \left( \frac{614 \text{ in}^2/\text{stroke}}{144 \text{ ft}^2/\text{in}^2} \right) \times 14 \frac{\text{strokes}}{\text{min}} / 26.6 \frac{\text{ft}^3}{\text{lb}} = 13.4 \text{ lb/min}
NEWCOMEN ATMOSPHERIC ENGINE

Ford Museum, 1760

14 strokes/min

atmospheric pressure

F

72 in

stroke

50 F

water

15 psia

steam

28 in

15 psia (213 F)

hv=1105.5 BTU/lb

hl=49.08

h_g @ 15, psia = 1150.5 BTU/lbm

h_l @ 80°F = 49.08 BTU/lbm

Q_{in} = m\Delta h

Q_{in} = 13.4 \text{ lb/min}(1150.5 \text{ BTU/lb} - 49.008 \text{ BTU/lb})

Q_{in} = 14,759. BTU/lbm

W = \frac{765,000 \text{ ftlb/min}}{778 \text{ ftlb/BTU}} = 932.3 \text{ BTU/min}

\eta_{CYCLE} = \frac{W}{Q_{in}} = \frac{932.3 \text{ BTU/min}}{14,759. \text{ BTU/lbm}} = 6.3\%

\eta_{CYCLE, CARNOT} = \frac{T_{h} - T_{l}}{T_{h}} = \frac{213 - 80}{460 + 213} = 20\%

\eta = \frac{765,000 \text{ ftlb/min}}{33,000 \text{ hp/ft lb/min}} = 23 \text{ HP or 17.5 kw}

m = \frac{V}{v} \times \text{strokes} = \left( \frac{614 \text{ in}^2/\text{stroke}}{144 \text{ ft}^2/\text{in}^2} \right) \times 14 \text{ strokes/minute} / 26.6 \frac{\text{ft}^3}{\text{lb}} = 13.4 \text{ lb/min}

A = \pi R^2 = \pi 14^2 = 614 \text{ in}^2
Warm environment at $T_H = 300$ K

- Reversible refrigerator $COP_R = 11$
- Irreversible refrigerator $COP_R = 7$
- Impossible refrigerator $COP_R = 13$

Cool refrigerated space at $T_L = 275$ K
Carnot Principles

1. No engine operating between two heat reservoirs, each having a fixed temperature, can be more efficient than a reversible engine operating between the same reservoirs.

\[ \eta_{\text{actual}} \leq \eta_{\text{Carnot}} \]

2. All reversible engines operating between two heat reservoirs, each having its own fixed temperature, have the same efficiency.

3. The efficiency of any reversible engine operating between two reservoirs is independent of the nature of the working fluid and depends only on the temperature of the reservoirs.

4. An absolute temperature scale can be defined in a manner independent of the thermometric material.

\[ \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \]
FIGURE 5-47
Proof of the first Carnot principle.

(a) A reversible and an irreversible heat engine operating between the same two reservoirs (the reversible heat engine is then reversed to run as a refrigerator)

(b) The equivalent combined system
Thermodynamic Temperature Scale

\[ \eta = \text{function}(T_1, T_3) \]

\[ \eta = 1 - \frac{Q_3}{Q_1} \]

\[ \frac{Q_1}{Q_3} = \text{function}(T_1, T_3) \]

from engine schematics

\[ \frac{Q_1}{Q_2} = f(T_1, T_2) \quad \frac{Q_2}{Q_3} = f(T_2, T_3) \quad \frac{Q_1}{Q_3} = f(T_1, T_3) \]

by identity,

\[ \frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \cdot \frac{Q_2}{Q_3} \]

substituting,

\[ f(T_1, T_2) = f(T_2, T_3) \times f(T_1, T_3) \]

this equation can be satisfied only if,

\[ \left( \frac{Q_h}{Q_1} \right) = \frac{T_h}{T_1} \quad \text{and} \quad Q_1 = Q_h \frac{T_1}{T_h} \]

A reversible engine (or a real engine corrected to reversible) can be used to measure temperature difference.

Second Law ⇒ Heat Engine ⇒ Thermodynamic Temperature Scale
SECOND LAW \[ \frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \quad T_2 = T_1 \left( \frac{Q_2}{Q_1} \right) \]

\( T_1 \) and \( T_2 \) - absolute temperatures.

When a reversible engine (or a real engine correctable to reversible) is run between ice and steam temperatures with a constant heat input and \( Q_{\text{out}} \) is measured,

\[ \frac{Q_s}{Q_i} = 1.3661 = \left( \frac{T_s}{T_i} \right) \]

\( T_s = 1.3361T_i \)

Temperature scales can be setup for any arbitrarily selected scale 0 point and Scale Range of degrees between ice and steam.

\( T_s - T_i = \text{Scale Range} \)

substituting for \( T_s \),

\[ 1.3661T_i - T_i = \text{Scale Range} \]

\[ T_i = \frac{\text{Scale Range}}{.3661} \]

For: Celsius Scale

\( 100^\circ \text{ Scale Range} \)

ice as Scale 0

\[ T_i = \frac{100}{.3661} = 273.15^\circ K \]

Celsius 0 = 273.15^\circ K

For: Fahrenheit Scale

\( 180^\circ \text{ Scale Range} \)

32\(^\circ\) less than ice as Scale 0

\[ T_i = \frac{180}{.3661} = 491.68^\circ K \]

Fahrenheit 0 = 491.68 - 32

Fahrenheit 0 = 459.68^\circ R
Carnot Cycle Performance

Using the absolute thermodynamic temperature scale,

$$\left( \frac{Q_H}{Q_L} \right) = \frac{T_H}{T_L}$$

The Carnot efficiency and COP are,

\[ \eta_{ENGINE} = \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H} = \frac{\text{Work}}{Q_{in}} \]

\[ \text{COP}_{REFRIGERATOR} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L} = \frac{Q_{in}}{\text{Work}} \]

\[ \text{COP}_{HEAT PUMP} = \frac{Q_H}{Q_H - Q_L} = \frac{T_H}{T_H - T_L} = \frac{Q_{out}}{\text{Work}} \]
Half the work of an engine operating between 800°C and 20°C is used to power a refrigeration machine absorbing heat at 2°C and rejecting 62,000 kJ/hr at 22°C. How much heat is supplied to the engine?

$$\text{COP}_{\text{heat pump}} = \frac{Q_{\text{out}}}{Q_{\text{out}} - Q_{\text{in}}} = \frac{Q_{\text{out}}}{W_{\text{heat pump}}} = \frac{T_h}{T_h - T_l} = \frac{273.15 + 22}{20} = 14.8$$

$$W_{\text{heat pump}} = \frac{Q_{\text{out}}}{\text{COP}_{\text{heat pump}}} = \frac{62,000 \text{ kJ/hr}}{14.8} = 4189.2 \text{ kJ/kg}$$

$$\eta_{\text{heat engine}} = \frac{T_h - T_l}{T_h} = \frac{780^\circ K}{800 + 273.15} = .725$$

$$Q_{\text{in}} = \frac{2 \times W_{\text{heat pump}}}{\eta} = \frac{2 \times 4189.2}{.725}$$

$$Q_{\text{in}} = 11,556 \text{ kJ/hr}$$
.0103 kg steam executes the following cycle. The absolute high temperature is twice the absolute low temperature and the net work output is 25 kJ. Heat is rejected during a phase change from a vapor to a liquid. What is the rejection temperature?

\[ \frac{T_h - T_l}{T_h} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{W}{Q_{in}} \]

\[ T_h = 2 \times T_l \]

\[ \eta = \frac{2T_l - T_l}{2T_l} = \frac{W}{Q_{in}} = \frac{25 \text{ kJ}}{Q_{in}} = .5 \]

\[ Q_{in} = \frac{25 \text{ kJ}}{.5} = 50 \text{ kJ} \]

\[ Q_{out} = m\Delta H = Q_{in} - W = 25 \text{ kJ} \]

\[ \Delta H = \frac{Q_{out}}{m} = \frac{25 \text{ kJ}}{.0103 \text{ kg}} = 2427.2 \text{ kJ/kg} = h_{fg} \]

\[ T @ h_{fg} = 2427.2 \]

\[ T \quad h_{fg} \]

\[ 35 \quad 2418.6 \]

\[ 31.1 \quad 2427.2 \]

\[ 40 \quad 2430.5 \]

\[ T = 35 - \frac{(2427.2 - 2418.6)}{(2430.5 - 2427.2)} \times 5 = 31.2^\circ C \]
Two Carnot engines operate in series at the same efficiency. The high temperature engine receives heat at 2400 K and the low temperature engine rejects heat at 300. What is the temperature between the engines?

\[ \eta_1 = \eta_2 \]

\[ \eta = \frac{T_h - T_1}{T_h} \]

\[ \frac{2400 - T}{2400} = \frac{T - 300}{T} \]

\[ T(2400 - T) = 2400T - 300 \times 2400 \]

\[ 2400T - T^2 = 2400T - 300 \times 2400 \]

\[ T = (300 \times 400)^{0.5} \]

\[ T = 848.5^\circ K \]
Since
\[
\left( \frac{Q_H}{Q_L} \right) = \frac{T_H}{T_L}
\]
\[
\frac{Q_h}{T_h} = \frac{Q_l}{T_l}
\]
\[
\sum_{\text{cycle}} \frac{Q}{T} = \frac{Q_h}{T_h} - \frac{Q_l}{T_l} = 0
\]
\[
\frac{Q}{T} \text{ may be independent of path, one of the characteristics of a thermodynamic property.}
\]

In First Law,
\[
\oint_{\text{cycle}} (dQ - W) = 0
\]
lead to the definition of energy as a thermodynamic property
\[
Q = \Delta E + W
\]
Ideal Gas Carnot Cycle

Reversible constant temperature heat transfer, process 1 → 2, process 3 → 4

Reversible adiabatic expansion, process 2 → 3, process 4 → 1

\[ Q_{1\rightarrow2} = W_{1\rightarrow2} = RT_1 \ln \left( \frac{p_2}{p_1} \right) = Q_H \]

\[ Q_{3\rightarrow4} = W_{3\rightarrow4} = RT_3 \ln \left( \frac{p_3}{p_4} \right) = Q_L \]

\[ \int W = \int Q = RT_1 \ln \left( \frac{p_2}{p_1} \right) - RT_3 \ln \left( \frac{p_3}{p_4} \right) = W_{\text{net}} \]

for \( pv^n \) = constant

\[ \left( \frac{p_2}{p_3} \right) = \left( \frac{T_2}{T_3} \right)^{n-1} \quad \left( \frac{p_1}{p_4} \right) \Rightarrow \left( \frac{T_1}{T_4} \right)^{n-1} \]

\[ \left( \frac{P_2}{p_3} \right) = \left( \frac{P_1}{p_4} \right) \quad \text{or} \quad \left( \frac{P_2}{p_4} \right) = \left( \frac{P_3}{p_4} \right) \]

\[ \eta = \frac{W_{\text{net}}}{Q_{\text{in}}} = \frac{RT_1 \ln \left( \frac{p_2}{p_1} \right) - RT_3 \ln \left( \frac{p_3}{p_4} \right)}{RT_1 \ln \left( \frac{p_2}{p_1} \right)} = \frac{T_h - T_1}{T_h} \]

Note \( \sum \frac{dQ}{T} = \frac{RT_1}{T_1} \ln \left( \frac{p_2}{p_1} \right) - \frac{RT_3}{T_3} \ln \left( \frac{p_3}{p_4} \right) = 0 \)

\[ \sum \frac{dQ}{T} \] behaves in this reversible cycle like a property
An engineer proposed an attempt to improve the efficiency of a power cycle by transferring heat from the available high temperature source to an alternate higher temperature source using a heat pump. What do you think of this suggestion?

\[
\eta_{\text{engine}} = \frac{Q_3 - Q_1}{Q_3} = \frac{T_3 - T_1}{T_3} = \frac{W_{\text{engine}}}{Q_3}
\]

\[
Q_3 = W_{\text{engine}} \left( \frac{T_3}{T_3 - T_1} \right)
\]

\[
\text{COP}_{\text{heat pump}} = \frac{Q_3}{Q_3 - Q_1} = \frac{T_3}{T_3 - T_1} = \frac{Q_3}{W_{\text{heat pump}}}
\]

\[
Q_3 = W_{\text{heat pump}} \left( \frac{T_3}{T_3 - T_1} \right)
\]

where \(Q_3_{\text{engine}} = Q_3_{\text{heat pump}}\)

\[
W_{\text{engine}} = W_{\text{heat pump}}
\]

there is no net work gain with reversible machines and there would be a net loss with real machines.