Kelvin-Planck: It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir.

Clausius: It is impossible to construct a device that operates in a cycle and produces no other effect than the transfer of heat from a cooler body to a hotter body.

Woud: used to: 1) predict the direction of processes 
2) establish the conditions of final equilibrium 
3) determine best possible theoretical performance of a process

if it is impossible to have a heat engine with 100% efficiency, how high can it go??

define ideal process, termed reversible process: a process that, once having taken place, can be reversed without changing either the system or surroundings

examples irreversible; piston expanding against stop 
reversible; piston expanding by removing and replacing weights; excerpt from VW&S page 166 good description of reversible and irreversible processes

Let us illustrate the significance of this definition for a gas contained in a cylinder that is fitted with a piston. Consider first Fig. 6.8, in which a gas (which we define as the system) at high pressure is restrained by a piston that is secured by a pin. When the pin is removed, the piston is raised and forced abruptly against the stops. Some work is done by the system, since the piston has been raised a certain amount. Suppose we wish to restore the system to its initial state. One way of doing this would be to exert a force on the piston, thus compressing the gas until the pin could again be inserted in the piston. Since the pressure on the face of the piston is greater on the return stroke than on the initial stroke, the work done on the gas in this reverse process is greater than the work done by the gas in the initial process. An amount of heat must be transferred from the gas during the reverse stroke in order that the system have the same internal energy it had originally. Thus the system is restored to its initial state, but the surroundings have changed by virtue of the fact that work was required to force the piston down and heat was transferred to the surroundings. Thus the initial process is an irreversible one because it could not be reversed without leaving a change in the surroundings.

In Fig. 6.9 let the gas in the cylinder comprise the system and let the piston be loaded with a number of weights. Let the weights be slid off horizontally one at a time, allowing the gas to expand and do work in raising the weights that remain on the piston. As the size of the weights is made smaller and their number is increased, we approach a process that can be reversed, for at each level of the piston during the reverse process there will be a small weight that is exactly at the level of the platform and thus can be placed on the platform without requiring work. In the limit, therefore, as the weights become very small, the reverse process can be accomplished in such a manner that both the system and surroundings are in exactly the same state they were initially. Such a process is a reversible process.
Carnot cycle

example steam power plant - working substance steam boiler - heat transferred from high T (constant) reservoir to steam - steam T only infinitesimally lower than reservoir => reversible isothermal heat transfer process. (phase change fluid - vapor is such a process
turbine - reversible adiabatic (no heat transfer) T decreases from \( T_H \) to \( T_L \)
condenser - heat rejected from working fluid to \( T_L \) reservoir (infinitesimal \( \Delta T \)) some steam condensed
pump - temperature raised to \( T_H \) adiabaticly can reverse and act as refrigerator

Carnot cycle four basic processes:
1. reversible isothermal process in which heat is transferred to or from the \( T_H \) reservoir
2. reversible adiabatic process in which the temperature of the working fluid decreases from \( T_H \) to \( T_L \)
3. reversible isothermal process in which heat is transferred to or from the \( T_L \) reservoir
4. reversible adiabatic process in which the temperature of the working fluid increases from \( T_L \) to \( T_H \)

Carnot cycle most efficient, and only function of temperature

\[
\eta_{\text{thermal}} = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}
\]

temperature scale (arbitrary but defined in terms of Carnot efficiency)

\[
\eta_{\text{thermal}} = 1 - \frac{Q_L}{Q_H} = \psi(T_L,T_H) \quad \frac{Q_H}{Q_L} = \frac{f(T_H)}{f(T_L)} = \frac{T_H}{T_L}
\]

proposed by Lord Kelvin \( \eta_{\text{thermal}} = 1 - \frac{T_L}{T_H} \) most efficient

at this point have ratio of absolute temperatures derive scale from non-Carnot heat engine operating at steam \( T_H \) and ice temperature \( T_L \)

if we could measure it would find \( \eta \) to be 26.80%

\[
\eta_{\text{th}} = 0.2680 = 1 - \frac{T_H}{T_L}
\]

if want difference to be 100 as on the Celsius scale \( \Delta T := 100 \)

\[
T_H := 100 \quad T_L := 200
\]

initial values

\[
0.2680 = 1 - \frac{T_L}{T_H} \quad T_H = T_L + \Delta T
\]
\[
\begin{bmatrix}
T_H \\
T_L
\end{bmatrix} = \text{Find}(T_H, T_L)
\]

\[
\begin{bmatrix}
T_H \\
T_L
\end{bmatrix} = \begin{bmatrix} 373.134 \\ 273.134 \end{bmatrix}
\]

\[T_{deg \_C} + 273.134 = T_{deg \_K}\]

VW&S has 273.15 changed to 273.16 to correspond to triple point of water 0.01 deg_C

**Entropy**

inequality of Clausius ...

\[
\int \frac{1}{T} \, dQ \leq 0
\]

for fig 7.1

\[
\int 1 \, dQ = Q_H - Q_L > 0
\]

from definition of absolute temperature scale and \(T_H\) and \(T_L\) constant

\[
\int \frac{1}{T} \, dQ = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0
\]

if .. \[
\int 1 \, dQ \text{ approaches } 0, \text{ } T_H \text{ approaches } T_L, \text{ while reversible } \int \frac{1}{T} \, dQ = 0
\]

\[= \text{for all reversible heat engines} \] \[\int 1 \, dQ \geq 0 \text{ and } \int \frac{1}{T} \, dQ = 0\]

if irreversible, with \(T_H, T_L,\) and \(Q_H\) same ...

\[W_{irrev} < W_{rev}\]

\[Q_H - Q_L = W \text{ for both } Q_H - Q_{L, irrev} < Q_H - Q_{L, rev} \Rightarrow Q_{L, irrev} > Q_{L, rev}\]

\[
\int 1 \, dQ = Q_H - Q_{L, irrev} > 0 \text{ and } \int \frac{1}{T} \, dQ = \frac{Q_H}{T_H} - \frac{Q_{L, irrev}}{T_L} < 0
\]

if heat engine becomes more irreversible such that \(W \Rightarrow 0\),

as \[\int 1 \, dQ = 0 \text{ } \int \frac{1}{T} \, dQ < 0 \Rightarrow \text{all irreversible engines} \]

should do refrigeration cycle as well

**FIGURE 7.1**

Reversible heat engine cycle for demonstration of the inequality of Clausius.
example fig 7.3 - simple steam power plant cycle - not typical - pump handles mixture of liquid and vapor in such proportions that saturated liquid leaves the pump and enters the boiler. The pressures and quality at various points are given in the figure. Does this data satisfy the inequality of Clausius?

\[
\int \frac{1}{T} \, dQ \leq 0
\]

heat is transferred in boiler and condenser, both at constant \(T\)

\[
\int \frac{1}{T} \, dQ = \int \frac{1}{T} \, dQ_{\text{boiler}} + \int \frac{1}{T} \, dQ_{\text{condenser}} = \frac{1}{T_{\text{boiler}}} \int 1 \, dQ_{\text{boiler}} + \frac{1}{T_{\text{condenser}}} \int 1 \, dQ_{\text{condenser}}
\]

on a per unit mass basis

\[
\text{mass} := 1 \text{kg} \quad \text{MPa} := 10^6 \text{Pa} \quad \text{kJ} := 10^3 \text{J} \quad \text{kPa} := 10^3 \text{Pa}
\]

boiler ...

\[
p_1 := 0.7 \text{MPa} \quad h_{fg} := 2066.3 \frac{\text{kJ}}{\text{kg}} \quad T_1 := 164.97 \text{ deg C} \quad \text{steam tables Table A.1.2}
\]

\[
q_{1-2} := h_{fg} \quad q_{1-2} = 2066.3 \frac{\text{kJ}}{\text{kg}} \quad q = \Delta h \quad \text{from first law}
\]

\[
p_{\text{condenser}} = p_3 = p_4 = 15 \text{kPa} \quad h_f := 225.94 \frac{\text{kJ}}{\text{kg}} \quad h_{fg} := 2373.1 \frac{\text{kJ}}{\text{kg}} \quad T_3 := 53.97 \text{ deg C} \quad \text{steam tables Table A.1.2}
\]

\[
x_3 := 0.9 \quad h_3 := h_f + x_3 \cdot h_{fg}
\]

\[
x_4 := 0.1 \quad h_4 := h_f + x_4 \cdot h_{fg} \quad q_{3-4} := h_4 - h_3 \quad q_{3-4} = -1898.48 \frac{\text{kJ}}{\text{kg}}
\]

\[
T_{\text{deg C}} + 273.15 = T_{\text{deg K}}
\]

\[
\int \frac{dQ}{T} := \frac{q_{1-2}}{T_1 + 273.15} + \frac{q_{3-4}}{T_3 + 273.15} \quad \int \frac{dQ}{T} = -1.087 \frac{\text{kJ}}{\text{kg}} \quad \text{deg K} \quad \text{is} < 0
\]
two reversible cycles from 1 to 2 (not labeled)
A - B
and ... A - C

\[ \int \frac{1}{T} \, dQ = 0 \] reversible ...

A - B
\[ \int \frac{1}{T} \, dQ = 0 = \int_{1}^{2} \frac{1}{T_A} \, dQ_A + \int_{2}^{1} \frac{1}{T_B} \, dQ_B \]

subtract second from first =>

\[ \int_{2}^{1} \frac{1}{T_B} \, dQ_B = \int_{2}^{1} \frac{1}{T_C} \, dQ_C \]

so as we did for energy E (e) in first law
\[ \frac{1}{T} \, dQ \text{ is independent of path in reversible process} \Rightarrow \text{is a property of the substance} \]

\[ dS = \frac{\delta Q_{\text{rev}}}{T} \text{ reversible ...} \]

entropy is an extensive property and entropy per unit mass is \( S \)

\[ \int_{2}^{1} \frac{1}{T} \, dQ_{\text{rev.}} = S_2 - S_1 \] (7.3)
entropy change in a reversible process

example Carnot

Carnot cycle four basic processes:
1. reversible isothermal process in which heat is transferred to or from the $T_H$ reservoir
2. reversible adiabatic process in which the temperature of the working fluid decreases from $T_H$ to $T_L$
3. reversible isothermal process in which heat is transferred to or from the $T_L$ reservoir
4. reversible adiabatic process in which the temperature of the working fluid increases from $T_L$ to $T_H$

plot data

1 to 2

\[ \int_{1}^{2} \frac{1}{T} dQ_{\text{rev.}} = S_2 - S_1 = \frac{Q_{1,2}}{T_H} \]

2 to 3 - adiabatic

\[ \int_{2}^{3} \frac{1}{T} dQ_{\text{rev.}} = 0 = S_3 - S_2 \quad S_3 = S_2 \]

3 to 4

\[ \int_{3}^{4} \frac{1}{T} dQ_{\text{rev.}} = S_2 - S_1 = \frac{Q_{3,4}}{T_L} \]

4 to 1 - adiabatic

\[ \int_{4}^{1} \frac{1}{T} dQ_{\text{rev.}} = 0 = S_1 - S_4 \quad S_1 = S_4 \quad i := 4 \ldots 5 \]

total cycle ...

\[ \int_{1}^{5} \frac{1}{T} dQ_{\text{rev.}} = 0 \quad S_1 = S_4 \quad i := 1 \ldots 5 \]

in general .. for reversible process, area under T S curve represents Q
two relationships for simple compressible substance: Gibbs equations in Woud

\[ \delta Q = T \cdot d \quad \delta W = p \cdot dV \]

as .. e.g. a piston ...

\[ \delta W = F \cdot d = p \cdot A \cdot ds = p \cdot dV \]

from first law ..

\[ \delta Q = dE + \delta W \] \hspace{1cm} (5.4)

\[ \delta Q = dU + \delta W \]

without KE or PE

\[ \delta Q = dU + \delta W \]

reversible ...

\[ \delta W = p \cdot dV \]

\[ \delta Q = T \cdot d \]

substitute ...

\[ T \cdot dS = dU + p \cdot d \]

QED \hspace{1cm} (7.5)

since ...

\[ H = U + p \cdot V \]

\[ \delta H = dU + p \cdot dV + V \cdot dp \]

on a per unit mass ...

\[ T \cdot ds = du + p \cdot \delta v \] \hspace{1cm} (7.7)

substitute ...

\[ T \cdot dS = dH - V \cdot dp \]

QED \hspace{1cm} (7.6)

applicable to BOTH reversible and irreversible processes as they are relationships between state variables

entropy change for irreversible process

\[ \begin{align*}
\text{reversible cycle from 1 to 2 to 1 (not labeled) } A - B \\
\text{and ...} \\
\text{irreversible cycle from 1 to 2 to 1 (not labeled) } A - C
\end{align*} \]

\[ \begin{align*}
\text{A - B reversible ...} \\
\int \left( \frac{1}{T} \right) dQ = 0 = \int_{1}^{2} \frac{1}{T_A} dQ_A + \int_{2}^{1} \frac{1}{T_B} dQ_B
\end{align*} \]

\[ \begin{align*}
\text{A - C irreversible} \\
\int \left( \frac{1}{T} \right) dQ = \int_{1}^{2} \frac{1}{T_A} dQ_A + \int_{2}^{1} \frac{1}{T_C} dQ_C < 0 \\
\text{inequality of Clausius}
\end{align*} \]

subtract second from first and rearrange ...

\[ \begin{align*}
\int_{1}^{2} \frac{1}{T_A} dQ_A + \int_{2}^{1} \frac{1}{T_B} dQ_B - \left( \int_{1}^{2} \frac{1}{T_A} dQ_A + \int_{2}^{1} \frac{1}{T_C} dQ_C \right) > 0
\end{align*} \]
\[
\int_{2}^{1} \frac{1}{T_B} \, dQ_B - \int_{2}^{1} \frac{1}{T_C} \, dQ_C > 0 \quad \int_{2}^{1} \frac{1}{T_B} \, dQ_B > \int_{2}^{1} \frac{1}{T_C} \, dQ_C
\]

is a property and although calculated for reversible process, is identical between states for irreversible. substitute into inequality above ...
second law for a control volume

not developed but second law stated in terms of lost work LW

\[
\frac{dS}{dT} = \frac{\delta Q}{T} + \frac{\delta LW}{T}
\]

during \(\delta t\) change in entropy is ...

\[
\frac{S_2 - S_1}{\delta t} = \frac{1}{\delta t} \frac{\delta Q}{T} + \frac{1}{\delta t} \frac{\delta LW}{T}
\]

(7.43)

\[
S_t = \text{entropy in c.v at time } t
\]

\[
S_{t_0} = \text{entropy in c.v at time } t \text{ plus } \delta t
\]

\[
S_1 = S_t + s_i \delta m_i = \text{entropy of system at time } t
\]

\[
S_2 = S_{t_0} + s_c \delta m_c = \text{entropy of system at time } t \text{ plus } \delta t
\]

\[
S_2 - S_1 = S_{t_0} - S_t + s_c \delta m_c - s_i \delta m_i
\]

(7.44)

etc .....

FIGURE 7.18
Schematic diagram for a second law analysis of a control volume.

second law for a control volume

\[
\frac{d}{dt} S_{c.v.} + \sum_{n} (m_{dot_c} \cdot s_c) - \sum_{n} (m_{dot_i} \cdot s_i) \geq \sum_{c.v} \frac{Q_{dot_{c.v}}}{T} \]

(7.49)  \quad = \text{when reversible}

steady state, steady flow process

\[
\frac{d}{dt} S_{c.v.} = 0
\]

(7.50)

\[
\sum_{n} (m_{dot_c} \cdot s_c) - \sum_{n} (m_{dot_i} \cdot s_i) \geq \sum_{c.v} \frac{Q_{dot_{c.v}}}{T}
\]

(7.51)  \quad = \text{when reversible}
uniform state, uniform flow process

rewrite 7.49 as ...
\[
\frac{d}{dt}(m \cdot s)_{c,v} + \sum_{n} (m_{\cdot dot} e \cdot s_{e}) - \sum_{n} (m_{\cdot dot} i \cdot s_{i}) \geq \sum_{c,v} \frac{Q_{\cdot dot}}{T} \tag{7.54} = \text{when reversible}
\]

and integrate ...
\[
\int_{0}^{t} \frac{d}{dt}(m \cdot s)_{c,v} dt = m_{2} \cdot s_{2} - m_{1} \cdot s_{1} \quad \text{in control volume}
\]
\[
\int_{0}^{t} \sum_{n} (m_{\cdot dot} e \cdot s_{e}) dt = \sum_{n} (m_{e} \cdot s_{e})
\]
\[
\int_{0}^{t} \sum_{n} (m_{\cdot dot} i \cdot s_{i}) dt = \sum_{n} (m_{i} \cdot s_{i})
\]

therefore for time \( t \)
\[
m_{2} \cdot s_{2} - m_{1} \cdot s_{1} + \sum_{n} (m_{e} \cdot s_{e}) - \sum_{n} (m_{i} \cdot s_{i}) \geq \int_{0}^{t} \sum_{c,v} \frac{Q_{\cdot dot}}{T} dt \tag{7.55} = \text{when reversible}
\]

since the temperature over the control volume is uniform at any instant of time
\[
\int_{0}^{t} \sum_{c,v} \frac{Q_{\cdot dot}}{T} dt = \int_{0}^{t} \frac{1}{T} \sum_{c,v} Q_{\cdot dot} dt = \int_{0}^{t} \frac{Q_{\cdot dot}}{T} dt
\]
in first integral \( T \) can be a function of space (location in c. v.) U(niform) S(tate)

\( \Rightarrow T \) only dependent on time

and second law for a uniform state, uniform process is ...

uniform state, uniform flow process

\[
m_{2} \cdot s_{2} - m_{1} \cdot s_{1} + \sum_{n} (m_{e} \cdot s_{e}) - \sum_{n} (m_{i} \cdot s_{i}) \geq \int_{0}^{t} \sum_{c,v} \frac{Q_{\cdot dot}}{T} dt \tag{7.56} = \text{when reversible}
\]

steady state, steady flow process

assumptions ...
1. control volume does not move relative to the coordinate frame
2. the mass in the control volume does not vary with time
3. the mass flux and the state of mass at each discrete area of flow on the control surface do not vary with time and the rates at which heat and work cross the control surface remain constant.

example: centrifugal air compressor, operating at constant mass rate of flow, constant rate of heat transfer to the surroundings, and constant input power.

uniform state, uniform flow process USUF

assumptions:
1. control volume remains constant relative to the coordinate frame
2. state of mass within the control volume may change with time, but at any instant of time is uniform throughout the entire control volume - I define this as \( f(t) \) but not of space
3. the state of mass crossing each of the areas of flow on the control surface is constant with time although the mass flow rates may be changing.

example: filling a closed tank with a gas or liquid, discharge from a closed vessel.