# Second Law

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
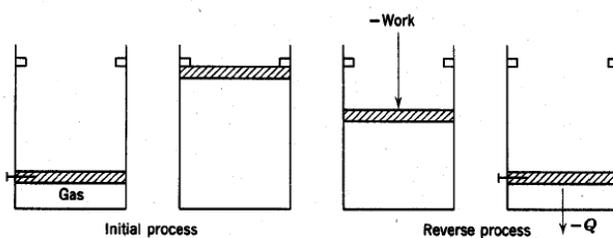


FIGURE 6.8
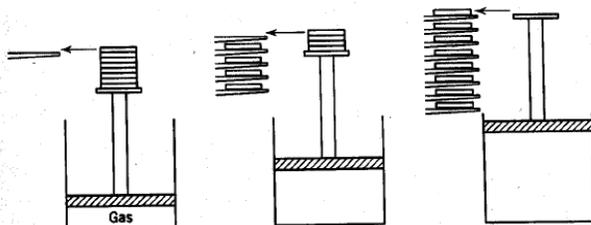**An example of an irreversible process.**



FIGURE 6.9
**An example of a process that approaches being reversible.**

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

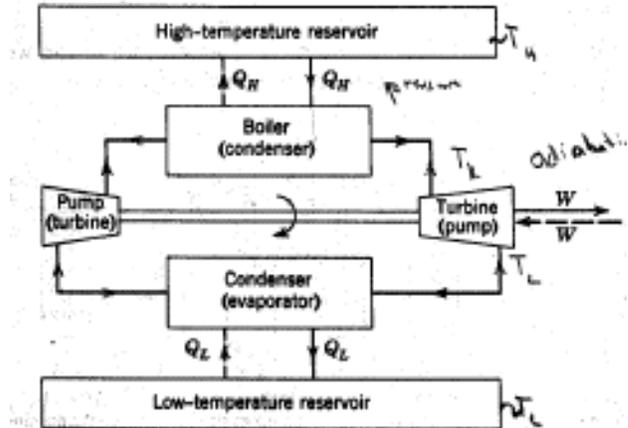can reverse and act as refrigerator



**FIGURE 6.14**
**Example of a heat engine that operates on a Carnot cycle.**

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

efficiency (in heat engine)

$$\eta_{thermal} = \frac{W = energy\_sought}{Q_H = energy\_that\_costs} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

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

$$\eta_{thermal} = 1 - \frac{Q_L}{Q_H} = \psi(T_L, T_H) \qquad \frac{Q_H}{Q_L} = \frac{f(T_H)}{f(T_L)} = \frac{T_H}{T_L} \qquad \text{proposed by Lord Kelvin} \qquad \eta_{thermal} = 1 - \frac{T_L}{T_H} \qquad \text{most efficient}$$

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%

$$\eta_{th} = 0.2680 = 1 - \frac{T_H}{T_L}$$

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

$T_H := 100 \qquad T_L := 200$
initial values $\qquad$ Given $\qquad 0.2680 = 1 - \frac{T_L}{T_H} \qquad T_H = T_L + \Delta T$

$$\begin{pmatrix} T_H \\ T_L \end{pmatrix} := \text{Find}(T_H, T_L) \qquad\qquad \begin{pmatrix} T_H \\ T_L \end{pmatrix} = \begin{pmatrix} 373.134 \\ 273.134 \end{pmatrix}$$

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 ...

$$\int \frac{1}{T}\, dQ \le 0$$

for fig 7.1

$$\int 1\, dQ \mathbf{=} Q_H - Q_L > 0$$

from definition of absolute temperature scale and $T_H$ and $T_L$ constant

**FIGURE 7.1**
Reversible heat engine cycle for demonstration of the inequality of Clausius.

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

if .. $\displaystyle\int 1\, dQ$  approaches 0, $T_H$ approaches $T_L$,  while reversible $\displaystyle\int \frac{1}{T}\, dQ \mathbf{=} 0$

=> for all reversible heat engines ...   $\displaystyle\int 1\, dQ \ge 0$   and ...   $\displaystyle\int \frac{1}{T}\, dQ \mathbf{=} 0$

if irreversible, with $T_H$, $T_L$, and $Q_H$ same  ...        $W_{irrev} < W_{rev}$

$Q_H - Q_L \mathbf{=} W$     for both          $Q_H - Q_{L\_irrev} < Q_H - Q_{L\_rev}$        =>    $Q_{L\_irrev} > Q_{L\_rev}$

$$\int 1\, dQ \mathbf{=} Q_H - Q_{L\_irrev} > 0 \qquad \text{and ...} \qquad \int \frac{1}{T}\, dQ \mathbf{=} \frac{Q_H}{T_H} - \frac{Q_{L\_irrev}}{T_L} < 0$$

if heat engine becomes more irreversible such that W => 0..

as ... $\displaystyle\int 1\, dQ \mathbf{=} 0$      $\displaystyle\int \frac{1}{T}\, dQ < 0$     => all irreversible engines    $\displaystyle\int 1\, dQ \ge 0$     $\displaystyle\int \frac{1}{T}\, dQ < 0$

should do refrigeration cycle as well

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?

inequality of Clausius ...

$$\int \frac{1}{T}\, dQ \leq 0$$

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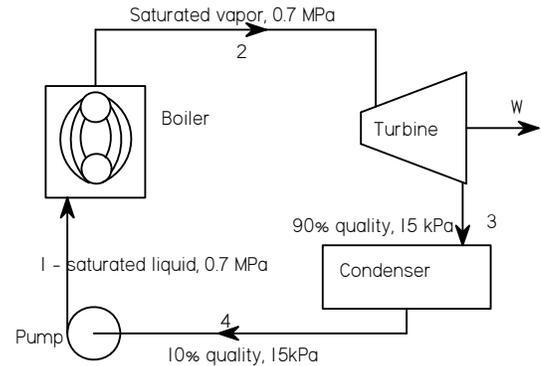


$$\int \frac{1}{T}\, dQ = \int \frac{1}{T}\, dQ_{boiler} + \int \frac{1}{T}\, dQ_{condenser} = \frac{1}{T_{boiler}} \cdot \int 1\, dQ_{boiler} + \frac{1}{T_{condenser}} \cdot \int 1\, dQ_{condenser}$$

on a per unit mass basis        $mass := 1kg$        $MPa := 10^6 Pa$        $kJ := 10^3 J$    $kPa := 10^3 Pa$

boiler ...        $p_1 := 0.7MPa$        $h_{fg} := 2066.3\,\frac{kJ}{kg}$    $T_1 := 164.97$    deg_C        steam tables Table A.1.2

$q_{1\_2} := h_{fg}$        $q_{1\_2} = 2066.3\,\frac{kJ}{kg}$                $q = \Delta h$        from first law

$p_{condenser} = p_3 = p_4 = 15kPa$        $h_f := 225.94\,\frac{kJ}{kg}$        $h_{fg} := 2373.1\,\frac{kJ}{kg}$    $T_3 := 53.97$        steam tables Table A.1.2

$x_3 := 0.9$        $h_3 := h_f + x_3 \cdot h_{fg}$

$x_4 := 0.1$        $h_4 := h_f + x_4 \cdot h_{fg}$    $q_{3\_4} := h_4 - h_3$            $q_{3\_4} = -1898.48\,\frac{kJ}{kg}$

$T\_deg\_C + 273.15 = T\_deg\_K$

$int\_dQ\_over\_T := \frac{q_{1\_2}}{T_1 + 273.15} + \frac{q_{3\_4}}{T_3 + 273.15}$        $int\_dQ\_over\_T = -1.087\,\frac{kJ}{kg}$  deg_K        is < 0

*entropy*

▶ plot data

two **reversible** cycles
from 1 to 2 (not labeled)
A - B
and ... A - C
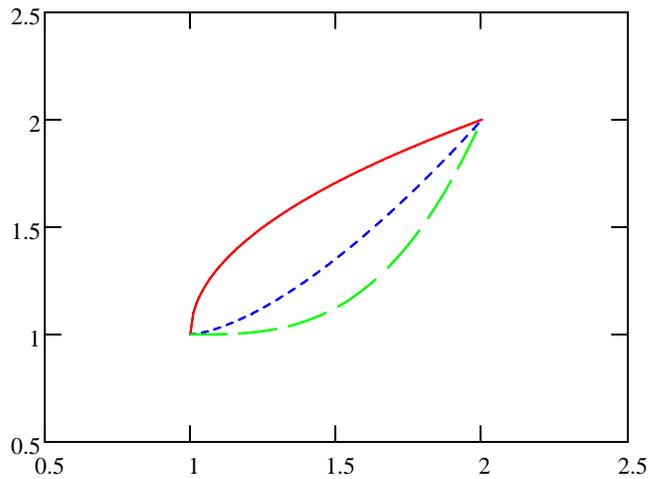


A process ———
B process ----
C process — ·

$$\int \frac{1}{T} dQ = 0 \qquad \text{reversible ...}$$

A -B

$$\int \frac{1}{T} dQ = 0 = \int_1^2 \frac{1}{T_A} dQ_A + \int_2^1 \frac{1}{T_B} dQ_B$$

A - C

$$\int \frac{1}{T} dQ = 0 = \int_1^2 \frac{1}{T_A} dQ_A + \int_2^1 \frac{1}{T_C} dQ_C$$

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 $\int \frac{1}{T} dQ$ is independent of

path in reversible process => is a property of the substance

$$dS = \left( \frac{\delta Q_{rev}}{T} \right) \qquad \text{reversible ...}$$

entropy is an extensive property and
entropy per unit mass is = S

(7.2), W (2.13)

$$\int_1^2 \frac{1}{T} dQ_{rev.} = S_2 - S_1 \qquad (7.3)$$

## *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
$$i := 1..2$$

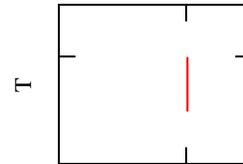$$\int_1^2 \frac{1}{T} dQ_{rev.} = S_2 - S_1 = \frac{Q_{1\_2}}{T_H}$$
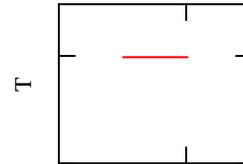
2 to 3 - adiabatic
$$i := 2..3$$

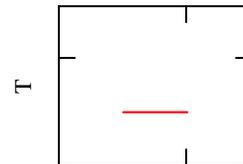$$\int_2^3 \frac{1}{T} dQ_{rev.} = 0 = S_3 - S_2 \qquad S_3 = S_2$$
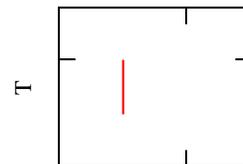
3 to 4
$$i := 3..4$$

$$\int_3^4 \frac{1}{T} dQ_{rev.} = S_2 - S_1 = \frac{Q_{3\_4}}{T_L}$$
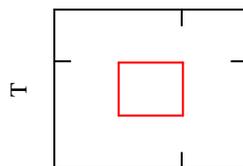
4 to 1 - adiabatic

$$\int_4^1 \frac{1}{T} dQ_{rev.} = 0 = S_1 - S_4 \qquad S_1 = S_4 \qquad i := 4..5$$

total cycle ...
$$i := 1..5$$

in general .. for reversible process, area under T S curve represents Q

**_two relationships for simple compressible substance: Gibbs equations in Woud_**

from first law ..

.

without KE or PE

$\delta Q = dE + \delta W$   (5.4)

$\delta Q = dU + \delta W$

reversible ...    $\delta Q = T \cdot d$     $\delta W = p \cdot dV$    as .. e.g. a piston ...    $\delta W = F \cdot d = p \cdot A \cdot ds = p \cdot dV$

substitute ...    $T \cdot dS = dU + p \cdot d$    QED   (7.5)

since ...    $H = U + p \cdot$     $dH = dU + p \cdot dV + V \cdot dp$    on a per unit mass ...    $T \cdot ds = du + p \cdot \delta v$   (7.7)

substitute ...    $T \cdot dS = dH - V \cdot dp$    QED   (7.6)     $T \cdot ds = dh - v \cdot dp$

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

### _entropy change for irreversible process_

plot data

reversible cycle from 1 to 2 to 1 (not labeled)  A - B and ...
irreversible cycle from 1 to 2 to 1 (not labeled)  A - C
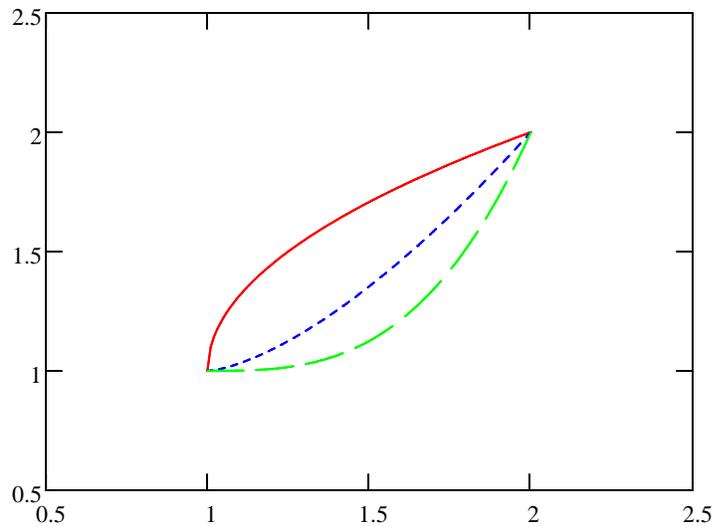


— A process reversible
--- B process reversible
– · C process irreversible

A - B reversible ...

$$\int \frac{1}{T} dQ = 0 = \int_1^2 \frac{1}{T_A} dQ_A + \int_2^1 \frac{1}{T_B} dQ_B$$

A - C irreversible

$$\int \frac{1}{T} dQ = \int_1^2 \frac{1}{T_A} dQ_A + \int_2^1 \frac{1}{T_C} dQ_C < 0 \qquad \text{inequality of Clausius}$$

subtract second from first and rearrange ...

$$\int_1^2 \frac{1}{T_A} dQ_A + \int_2^1 \frac{1}{T_B} dQ_B - \left( \int_1^2 \frac{1}{T_A} dQ_A + \int_2^1 \frac{1}{T_C} dQ_C \right) > 0$$

$$\int_2^1 \frac{1}{T_B}\,dQ_B - \int_2^1 \frac{1}{T_C}\,dQ_C > 0 \qquad\qquad \int_2^1 \frac{1}{T_B}\,dQ_B > \int_2^1 \frac{1}{T_C}\,dQ_C$$

$$\int_2^1 \frac{1}{T_{B\_rev}}\,dQ_{B\_rev} = \int_2^1 1\,dS_{B\_rev} = \int_2^1 1\,dS_C$$

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

$$\int_2^1 1\,dS_C > \int_2^1 \frac{1}{T_C}\,dQ_C \quad \text{or in general ...} \quad dS \geq \frac{\delta Q}{T}$$

$$S_2 - S_1 \geq \int_1^2 \frac{1}{T}\,dQ$$

equality holds when reversible and when irreversible, the change of entropy will be greater than the reversible

(W 2.14)

### *principle of increase in entropy*

consider system at T and surroundings at To, $\delta Q$ transferred from surroundings to system due to above

$$dS_{system} \geq \frac{\delta Q}{T}$$

for the surroundings, $\delta Q$ is negative therefore

$$dS_{surr} = \frac{-\delta Q}{T_0}$$

total net change in entropy is ...

$$dS_{net} = dS_{system} + dS_{surr} \geq \frac{\delta Q}{T} - \frac{\delta Q}{T_0} = \delta Q \cdot \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

since heat is transferred FROM surroundings, To > T therefore ...

$$dS_{net} \geq \delta Q \cdot \left( \frac{1}{T} - \frac{1}{T_0} \right) \geq 0$$

if T > To reverse signs and result holds

thus ...

### *principle of increase in entropy*

$$dS_{net} = dS_{system} + dS_{surr} \geq 0$$

for all processes that a system and its surroundings can undergo
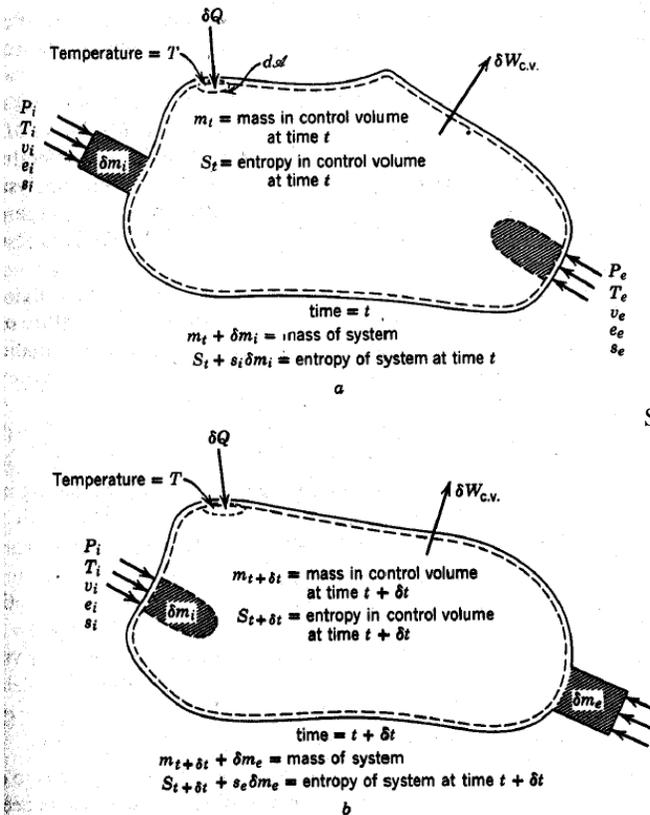
$$dS_{isolated\_system} \geq 0$$

## second law for a control volume

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

$$dS = \frac{\delta Q}{T} + \frac{\delta LW}{T}$$

during $\delta t$ change in entropy is ...

$$\frac{S_2 - S_1}{\delta t} = \frac{1}{\delta t} \cdot \frac{\delta Q}{T} + \frac{1}{\delta t} \cdot \frac{\delta LW}{T} \qquad (7.43)$$



$S_t$ = entropy_in_c_v_at_time_t

$S_{t\_\delta t}$ = entropy_in_c_v_at_time_t_plus_$\delta t$

$S_1 = S_t + s_i \cdot \delta m_i$ = entropy_of_system_at_time_t

$S_2 = S_{t\_\delta t} + s_e \cdot \delta m_e$ = entropy_of_system_at_time_t_plus_$\delta t$

$$S_2 - S_1 = S_{t\_\delta t} - S_t + s_e \cdot \delta m_e - s_i \cdot \delta m_i \qquad (7.44)$$

etc .....

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

## second law for a control volume

$$\frac{d}{dt} S_{c\_v} + \sum_n \left( \text{m\_dot}_e \cdot s_e \right) - \sum_n \left( \text{m\_dot}_i \cdot s_i \right) \geq \sum_{c\_v} \frac{\text{Q\_dot}_{c\_v}}{T} \qquad (7.49) \qquad \text{= when reversible}$$

### steady state, steady flow process

$$\frac{d}{dt} S_{c\_v} = 0 \qquad (7.50)$$

$$\sum_n \left( \text{m\_dot}_e \cdot s_e \right) - \sum_n \left( \text{m\_dot}_i \cdot s_i \right) \geq \sum_{c\_v} \frac{\text{Q\_dot}_{c\_v}}{T} \qquad (7.51) \qquad \text{= when reversible}$$

### *uniform state, uniform flow process*

rewrite 7.49 as ... $\quad \dfrac{d}{dt}(m \cdot s)_{c\_v} + \sum_n \left(m\_dot_e \cdot s_e\right) - \sum_n \left(m\_dot_i \cdot s_i\right) \geq \sum_{c\_v} \dfrac{Q\_dot_{c\_v}}{T}$ (7.54) $\quad$ = when reversible

and integrate ... $\qquad \displaystyle\int_0^t \dfrac{d}{dt}(m \cdot s)_{c\_v}\, dt = m_2 \cdot s_2 - m_1 \cdot s_1 \qquad$ in control volume

$$\int_0^t \sum_n \left(m\_dot_e \cdot s_e\right) dt = \sum_n \left(m_e \cdot s_e\right) \qquad \int_0^t \sum_n \left(m\_dot_i \cdot s_i\right) dt = \sum_n \left(m_i \cdot s_i\right)$$

therefore for time t $\quad m_2 \cdot s_2 - m_1 \cdot s_1 + \sum_n \left(m_e \cdot s_e\right) - \sum_n \left(m_i \cdot s_i\right) \geq \displaystyle\int_0^t \sum_{c\_v} \dfrac{Q\_dot_{c\_v}}{T}\, dt$ $\quad$ (7.55) $\quad$ = when reversible

since the temperature over the control volume is uniform at any instant of time

$$\int_0^t \sum_{c\_v} \dfrac{Q\_dot_{c\_v}}{T}\, dt = \int_0^t \dfrac{1}{T} \cdot \sum_{c\_v} Q\_dot_{c\_v}\, dt = \int_0^t \dfrac{Q\_dot_{c\_v}}{T}\, dt$$

in first integral T can be a function of space (location in c. v.) U(niform) S(tate) => T only dependent on time

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

### *uniform state, uniform flow process*

$$m_2 \cdot s_2 - m_1 \cdot s_1 + \sum_n \left(m_e \cdot s_e\right) - \sum_n \left(m_i \cdot s_i\right) \geq \int_0^t \dfrac{Q\_dot_{c\_v}}{T}\, dt$$

(7.56) $\qquad$ = 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.