## Summary of Thermo

## First Law

first law for cycle $\quad \int 1 \mathrm{dQ}=\int 1 \mathrm{dW}$
from: first_law_rev_2005.mcd, second_law_rev_2005.mcd, availability.mcd
ref: van Wylen \& Sonntag (eqn \#s) Woud (W nn.nn)
first law for system change of state
$\mathrm{Q}_{1 \_2} \quad$ is the heat transferred TO system

$$
Q_{1 \_2}=E_{2}-E_{1}+W_{1 \_2} \quad E_{1} \quad E_{2} \text { are intial and final values of } \begin{gather*}
\text { energy of system and } \ldots \tag{5.5}
\end{gather*}
$$

$\mathrm{W}_{1 \_2} \quad$ is work done BY the system

$$
\begin{equation*}
\delta \mathrm{Q}=\mathrm{dE}+\delta \mathrm{W}=\mathrm{dU}+\mathrm{dKE}+\mathrm{dPE}+\delta \mathrm{W} \tag{5.4}
\end{equation*}
$$

Closed System $\quad \frac{\mathrm{d}}{\mathrm{dt}} \mathrm{U}=\mathrm{Q} \_$dot $-\mathrm{W} \_$dot $\quad \mathrm{d} U=\delta \mathrm{Q}-\delta \mathrm{W} \quad \mathrm{m}_{-} \operatorname{dot}_{\mathrm{e}}=\mathrm{m}_{-} \operatorname{dot}_{\mathrm{i}}=0$
first law as a rate equation

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{Q}=\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{U}+\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{KE}+\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{PE}+\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{~W}=\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{E}+\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{~W} \tag{5.31and5.32}
\end{equation*}
$$

## first law as a rate equation - for a control volume

$$
\begin{array}{ll}
\mathrm{H}=\mathrm{U}+\mathrm{p} \cdot \mathrm{~V} & \text { enthalpy defined }- \text { is } \\
\mathrm{h}=\mathrm{u}+\mathrm{p} \cdot \mathrm{v} & \text { a property (5.12) }
\end{array}
$$

$$
\begin{equation*}
\frac{d}{d t} Q_{c_{-} v}+\sum_{n}\left[m_{-} \operatorname{dot}_{i} \cdot\left(h_{i}+\frac{v_{i}^{2}}{2}+g \cdot z_{i}\right)\right]=\frac{d}{d t} E_{c_{-} v}+\sum_{n}\left[m_{-} \operatorname{dot}_{e} \cdot\left(h_{e}+\frac{v_{e}^{2}}{2}+g \cdot{ }_{\mathrm{z}}^{e}\right)\right]+\frac{d}{d t} W_{c_{-} v} \tag{5.45}
\end{equation*}
$$

Woud assuming energy $\quad E=U+E_{\text {kin }}+E_{\text {pot }} \quad$ and $\ldots \quad E_{\text {kin }}=E_{\text {pot }}=0 \quad E=U$

$$
\frac{d}{d t} U=Q_{-} \operatorname{dot}-W_{-} \operatorname{dot}+m_{-} \operatorname{dot}_{i} \cdot\left(h_{i}+\frac{v_{i}^{2}}{2}+g \cdot z_{i}\right)-m_{-} \operatorname{dot}_{e} \cdot\left(h_{e}+\frac{V_{e}{ }^{2}}{2}+g \cdot z_{e}\right) \quad N . B \cdot \operatorname{dot}=>\text { rate not } d() / d t
$$

steady state, steady flow process ... open stationary

$$
\begin{equation*}
\frac{d}{d t} Q_{c_{-} v}+\sum_{n}\left[m_{-} \operatorname{dot}_{i_{n}} \cdot\left(h_{i}+\frac{v_{i}^{2}}{2}+g \cdot z_{i}\right)\right]=\sum_{n}\left[m_{-} \operatorname{dot}_{e_{n}} \cdot\left(h_{e}+\frac{v_{e}^{2}}{2}+g \cdot z_{e}\right)\right]+\frac{d}{d t} W_{c_{-} v} \tag{5.47}
\end{equation*}
$$

steady state steady flow ... - single flow stream

$$
\mathrm{q}+\mathrm{h}_{\mathrm{i}}+\frac{\mathrm{V}_{\mathrm{i}}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{\mathrm{i}}=\mathrm{h}_{\mathrm{e}}+\frac{\mathrm{V}_{\mathrm{e}}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{\mathrm{e}}+\mathrm{w} \quad \begin{align*}
& \text { this on per unit mass }  \tag{5.50}\\
& \text { basis } \mathrm{q}=\mathrm{Q} / \mathrm{m}_{-} \text {dot }
\end{align*}
$$

## uniform state, uniform flow process

$$
\begin{align*}
Q_{c_{-}-v}+\sum_{n}\left[m_{i_{n}} \cdot\left(h_{i}+\frac{v_{i}^{2}}{2}+g \cdot z_{i}\right)\right]= & \sum_{n}\left[m_{e_{n}} \cdot\left(h_{e}+\frac{v_{e}^{2}}{2}+g \cdot z_{e}\right)\right] \ldots  \tag{5.54}\\
& +m_{2} \cdot\left(u_{2}+\frac{v_{2}^{2}}{2}+g \cdot z_{2}\right)-m_{1} \cdot\left(u_{1}+\frac{v_{1}^{2}}{2}+g \cdot z_{1}\right)+w_{c_{-}-v}
\end{align*}
$$

## Second Law

Carnot cycle most efficient, and only function of temperature
$\eta_{\text {thermal }}=1-\frac{T_{L}}{T_{H}}$ Entropy inequality of Clausius ...
$\int \frac{1}{T} \mathrm{dQ} \leq 0 \quad$ integrals are cyclic $\begin{aligned} & \begin{array}{l}\text { => for all reversible } \\ \text { heat engines } \ldots\end{array}\end{aligned} \quad 1 \mathrm{dQ}=0 \quad \int \frac{1}{\mathrm{~T}} \mathrm{dQ}=0 \quad \begin{aligned} & \text { => all irreversibles } \\ & \text { engines }\end{aligned} \quad \int 1 \mathrm{dQ} \geq 0 \quad \int \frac{1}{\mathrm{~T}} \mathrm{dQ}<0$

$$
\begin{equation*}
\mathrm{dS}=\left(\frac{\delta \mathrm{Q}_{\mathrm{rev}}}{\mathrm{~T}}\right) \quad \text { reversible } \ldots \tag{7.2}
\end{equation*}
$$

$$
\int_{1}^{2} \frac{1}{\mathrm{~T}} \mathrm{~d} \mathrm{Q}_{\mathrm{rev} .}=\mathrm{S}_{2}-\mathrm{S}_{1}
$$

$$
\mathrm{S}_{2}-\mathrm{S}_{1} \geq \int_{1}^{2} \frac{1}{\mathrm{~T}} \mathrm{dQ}
$$

equality holds when reversible and when irreversible, the change of entrpy will be greater than the reversible
so as we did for energy $E(e)$ in first law $\int \frac{1}{T} d Q$ is
independent of path in reversible process => is a porperty of the substance. entropy is an extensive property and entropy per unit mass is $=s$
two relationships for simple compressible substance - Gibbs equations appicable to rev \& irrev processes

$$
\begin{array}{lll}
\mathrm{T} \cdot \mathrm{dS}=\mathrm{dU}+\mathrm{p} \cdot \mathrm{\delta V} & (7.5) & \mathrm{T} \cdot \mathrm{ds}=\mathrm{du}+\mathrm{p} \cdot \delta \mathrm{v}  \tag{7.7}\\
\mathrm{~T} \cdot \mathrm{dS}=\mathrm{dH}-\mathrm{V} \cdot \mathrm{dp} & \text { (7.6) } & \mathrm{T} \cdot \mathrm{ds}=\mathrm{dh}-\mathrm{v} \cdot \mathrm{dp}
\end{array}
$$

second law for a control volume

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{~S}_{\mathrm{c} \_\mathrm{v}}+\sum_{\mathrm{n}}\left(\mathrm{~m}_{-} \operatorname{dot}_{\mathrm{e}} \cdot \mathrm{~s}_{\mathrm{e}}\right)-\sum_{\mathrm{n}}\left(\mathrm{~m}_{-} \operatorname{dot}_{\mathrm{i}} \cdot \mathrm{~s}_{\mathrm{i}}\right) \geq \sum_{\mathrm{c} \_\mathrm{v}} \frac{\mathrm{Q}_{\mathrm{v}} \operatorname{dot}_{\mathrm{c} \_\mathrm{v}}}{\mathrm{~T}} \tag{7.49}
\end{equation*}
$$

= when reversible
steady state, steady flow process

$$
\begin{equation*}
\frac{\mathrm{d}}{\mathrm{dt}} \mathrm{~S}_{\mathrm{c}_{-} \mathrm{v}}=0 \tag{7.50}
\end{equation*}
$$

$$
\begin{equation*}
\sum_{\mathrm{n}}\left(\mathrm{~m}_{-} \operatorname{dot}_{\mathrm{e}} \cdot \mathrm{~s}_{\mathrm{e}}\right)-\sum_{\mathrm{n}}\left(\mathrm{~m}_{\mathrm{n}} \operatorname{dot}_{\mathrm{i}} \cdot \mathrm{~s}_{\mathrm{i}}\right) \geq \sum_{\mathrm{c} \_\mathrm{v}} \frac{\mathrm{Q} \_\operatorname{dot}_{\mathrm{c} \_v}}{\mathrm{~T}} \tag{7.51}
\end{equation*}
$$

= when reversible
uniform state, uniform flow process

$$
\begin{equation*}
m_{2} \cdot s_{2}-m_{1} \cdot s_{1}+\sum_{n}\left(m_{e} \cdot s_{e}\right)-\sum_{n}\left(m_{i} \cdot s_{i}\right) \geq \int_{0}^{t} \frac{\mathrm{Q}^{2} \operatorname{dot}_{\mathrm{c}}}{} \mathrm{v} \text { d } d t \tag{7.56}
\end{equation*}
$$

## Availability

reversible work (maximum) of a control volume that exchanges heat with the surroundings at To

$$
\begin{aligned}
\mathrm{W}_{\mathrm{rev}}= & \sum_{\mathrm{n}}\left[\mathrm{~m}_{\mathrm{i}_{\mathrm{n}}} \cdot\left(\mathrm{~h}_{\mathrm{i}}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{\mathrm{i}}+\frac{\mathrm{V}_{\mathrm{i}}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{\mathrm{i}}\right)\right]-\left[\sum_{\mathrm{n}}\left[\mathrm{~m}_{\left.\mathrm{e}_{\mathrm{n}} \cdot\left(\mathrm{~h}_{\mathrm{e}}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{\mathrm{e}}+\frac{\mathrm{V}_{\mathrm{e}}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{\mathrm{e}}\right)\right]}\right)\right]_{\text {(8.0.7) }} \\
& +-\left[\mathrm{m}_{2} \cdot\left(\mathrm{u}_{2}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{2}+\frac{\mathrm{V}_{2}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{2}\right)-\mathrm{m}_{1} \cdot\left(\mathrm{u}_{1}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{1}+\frac{\mathrm{V}_{1}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{1}\right)\right] \text { c.v. }
\end{aligned}
$$

system (fixed mass

$$
\begin{equation*}
\frac{\mathrm{w}_{\text {rev_1_2 }}}{\mathrm{m}}=\mathrm{w}_{\mathrm{rev} \_1 \_2}=\left(\mathrm{u}_{1}-\mathrm{T}_{0} \cdot \mathrm{~s}_{1}+\frac{\mathrm{v}_{1}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{1}\right)^{-}-\left(\mathrm{u}_{2}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{2}+\frac{\mathrm{v}_{2}^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{2}\right) \tag{8.8}
\end{equation*}
$$

steady-state, steady flow process - rate form

$$
\begin{equation*}
W_{-} \operatorname{dot}_{\text {rev }}=\sum_{n}\left[m_{i_{n}} \cdot\left(h_{i}-T_{0} \cdot s_{i}+\frac{v_{i}^{2}}{2}+g \cdot z_{i}\right)\right]-\left[\sum_{n}\left[m_{e_{n}} \cdot\left(h_{e}-T_{0} \cdot s_{e}+\frac{v_{e}^{2}}{2}+g \cdot z_{e}\right)\right]\right] \tag{8.9}
\end{equation*}
$$

single flow of fluid $\frac{W_{-} \text {dot }_{r e v}}{m_{-} \text {dot }}=w_{r e v}=h_{i}-T_{0} \cdot s_{i}+\frac{v_{i}{ }^{2}}{2}+g \cdot z_{i}-\left(h_{e}-T_{o} \cdot s_{e}+\frac{V_{e}{ }^{2}}{2}+g \cdot z_{e}\right)$

## availablity

steady state, steady flow process ...(e.g. single flow ...availability (per unit mass flow)

$$
\begin{equation*}
\psi=\mathrm{h}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}+\frac{\mathrm{v}_{\mathrm{i}}{ }^{2}}{2}+\mathrm{g} \cdot \mathrm{z}-\left(\mathrm{h}_{\mathrm{o}}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{\mathrm{o}}+\frac{\mathrm{v}_{\mathrm{o}}{ }^{2}}{2}+\mathrm{g} \cdot \mathrm{z}_{\mathrm{o}}\right) \tag{8.16}
\end{equation*}
$$

reversible work between any two states $=$ decrease in availablity between them

$$
\mathrm{w}_{\mathrm{rev}}=\psi_{\mathrm{i}}-\psi_{\mathrm{e}}=\mathrm{h}_{1}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{1}-\mathrm{h}_{2}+\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{2}=\mathrm{h}_{1}-\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{1}-\mathrm{h}_{2}+\mathrm{T}_{\mathrm{o}} \cdot \mathrm{~s}_{2}=\left(\mathrm{h}_{1}-\mathrm{h}_{2}\right)-\mathrm{T}_{\mathrm{o}} \cdot\left(\mathrm{~s}_{1}-\mathrm{s}_{2}\right)
$$

(8.17) extended
can be written for more than one flow ...

$$
\begin{equation*}
w-\operatorname{dot}_{\text {rev }}=\sum_{n}\left(m_{i_{n}} \cdot \psi_{i_{n}}\right)-\sum_{n}\left(m_{e_{n}} \cdot \psi_{e_{n}}\right) \tag{8.18}
\end{equation*}
$$

availability w/o KE and PE per unit mass of system

$$
\begin{equation*}
\phi=\left(u+p_{0} \cdot v-T_{0} \cdot s\right)-\left(u_{o}+p_{0} \cdot v_{o}-T_{0} \cdot s_{o}\right)=u-u_{o}+p_{o} \cdot\left(v-v_{o}\right)-T_{0} \cdot\left(s-s_{o}\right) \tag{8.21}
\end{equation*}
$$

and reversible work maximum between states 1 and 2 is ...

$$
\begin{equation*}
\mathrm{w}_{\mathrm{rev} \mathrm{~L}_{-} \_^{2}}=\phi_{1}-\phi_{2}-\mathrm{p}_{\mathrm{o}} \cdot\left(\mathrm{v}_{1}-\mathrm{v}_{2}\right)+\frac{\mathrm{v}_{1}^{2}-\mathrm{v}_{2}^{2}}{2}+\mathrm{g} \cdot\left(\mathrm{z}_{1}-\mathrm{z}_{2}\right) \tag{8.22}
\end{equation*}
$$

