# The Second Law of Thermodynamics 

Note:
for a reversible process, on $\mathrm{p}-\mathrm{v}$ diagram $\int_{1}^{2} P d v=W_{\text {rev }}$

and If the volume is constant,

$\int_{1}^{2} P d t=0$

- Similarly, for any reversible adiabatic process, $\mathrm{Q}=0$

$$
Q_{r e v}=\int T d s=0
$$

$$
\overbrace{}^{\mathbf{T}_{1}} \begin{aligned}
& S_{2} \\
& S_{1}=S_{2} \\
& Q=0
\end{aligned}
$$

- For any other reversible process

$$
Q_{r e v}=\int_{1}^{2} T d s
$$



- Clausius Inequality:

$$
\oint \frac{\delta Q}{T} \leq 0
$$

- Clausius inequality is valid for all thermodynamic cycles, reversible or irreversible.

$$
\begin{array}{ll}
\oint\left(\frac{\delta Q}{T}\right)_{\text {rev }}=0 & \begin{array}{l}
\text { for internally } \\
\text { reversible cycle }
\end{array} \\
\oint\left(\frac{\delta Q}{T}\right)<0 & \text { for irreversible cycle }
\end{array}
$$

# $\left(\frac{\delta \mathrm{Q}}{\mathrm{T}}\right)_{\mathrm{rev}}$ <br> <br> represents a property change 

 <br> <br> represents a property change}

$$
\begin{aligned}
& \mathrm{dS}=\left(\frac{\delta \mathrm{Q}}{\mathrm{~T}}\right)_{\mathrm{rev}} \\
& \Delta \mathrm{~S}=\mathrm{S}_{2}-\mathrm{S}_{1}=\int_{1}^{2}\left(\frac{\delta \mathrm{Q}}{\mathrm{~T}}\right)_{\mathrm{rev}}
\end{aligned}
$$

- Consider a cycle composed of a reversible and an irreversible process:

- The quantity $\Delta s=s_{2}-s_{1}$ represents the entropy change of the system.
- For a reversible process, entropy transfer with heat

$$
\Delta s=\int_{1}^{2} \frac{\delta Q}{T}
$$

- For an irreversible process

$$
\Delta s_{s y s}=\int_{1}^{2} \frac{\delta Q}{T}+s_{g e n}
$$

- Some entropy is generated during an irreversible process and is always positive quantity. Its value depends on the process, and thus it is not a property of the system.


## Entropy Change for Pure Substances

- The entropy of a pure substance is determined from the tables, just as for any other property.


$$
\begin{gathered}
S=S_{f}+X S_{f g} \\
\Delta S=m\left(s_{2}-s_{1}\right)
\end{gathered}
$$

## - T-s diagram of properties:



$$
Q_{r e v}=T\left(S_{2}-S_{1}\right)
$$

- Entropy of a fixed mass can be changed by:

1) Heat transfer
2) Irreversibilities

- The entropy of a fixed mass will not change during a process that is internally reversible and adiabatic.
- For a reversible, adiabatic process (called Isentropic process)

$$
\Delta s=0 \Rightarrow s_{1}=s_{2}
$$

- If a steam turbine is reversible, and the turbine is insulated (thus the process is reversible and adiabatic)
then $\quad \Delta s=0$
or

- The Tds relations: differential form of the first law:

$$
\delta Q_{r e v}-\delta w_{r e v}=d U
$$

second law: $\quad \delta Q_{\text {rev }}=$ Tds

$$
T d S=P d \forall+d U
$$

$$
T d s=P d v+d u \quad \longleftarrow \quad \text { First Tds relation }
$$

$T d s=d u+P d v$

$$
h=u+P v
$$

$$
d h=d u+P d v+v d P
$$

$T d s=d h-v d P \quad \leftarrow \quad$ Second Tds relation

- Entropy changes for Liquids and solids: Tds $=d u+p d v$

$$
\mathrm{ds}=\frac{d u}{T}+\frac{p d v}{T}
$$

- Liquids and solids are incompressible substances

$$
\begin{gathered}
d v \cong 0 \\
d s=\frac{d u}{T}=\frac{c d T}{T} \quad\left(c_{p}=c_{v}=c\right) \\
s_{2}-s_{1}=\int_{1}^{2} c \frac{d T}{T}=c \ln \frac{T_{2}}{T_{1}} \quad \frac{k J}{k g K}
\end{gathered}
$$

Isentropic process for liquids and solids:

$$
s_{2}-s_{1}=0=c \ln \frac{T_{2}}{T_{1}} \Rightarrow T_{2}=T_{1}
$$

the isentropic process of an incompressible substance is also isothermal.

Note: Tds equations are derived by considering an internally reversible process. An entropy change obtained by integrating these equations is the change for any process.
"Entropy is a property and the change in entropy between any two states is independent of the details of the process linking the states."

## Entropy change of an Ideal gas

Tds equations are used to evaluate the entropy change between two states of an ideal gas.

$$
\begin{aligned}
& d s=\frac{d u}{T}+\frac{P}{T} d v \\
& d s=\frac{d h}{T}-\frac{v}{T} d v
\end{aligned}
$$

For an ideal gas:

$$
\begin{aligned}
& d u=c_{v} d T \\
& d h=c_{p} d T \\
& P v=R T, \quad c_{p}=c_{v}+R \\
& d s=c_{v} \frac{d T}{T}+R \frac{d v}{v} \\
& d s=c_{P} \frac{d T}{T}-R \frac{d P}{P}
\end{aligned}
$$

Now integrating

$$
\begin{aligned}
& s_{2}-s_{1}=\int_{T_{1}}^{T_{2}} c_{v} \frac{d T}{T}+R \ln \frac{v_{2}}{v_{1}} \\
& s_{2}-s_{1}=\int_{T_{1}}^{T_{2}} c_{P} \frac{d T}{T}-R \ln \frac{P_{2}}{P_{1}}
\end{aligned}
$$

To integrate these relations, we must know the temperature dependence of the specific heats.

Using Ideal gas Tables:
Define $\quad s^{o}(T)=\int_{0}^{T} \frac{C_{p}(T)}{T} d T$

Where $s^{o}(T)$ is the specific entropy at a temperature T and a pressure of 1 atm .

Note: The specific entropy is set to zero at the state where the temperature is $0 K$ and the pressure is 1 atm.

Note: Because $S^{o}$ depends only on the temperature, it can be tabulated versus temperature, like $h$ and $u$.

Also,

$$
\int_{T_{1}}^{T_{2}} c_{p} \frac{d T}{T}=\int_{0}^{T_{2}} c_{p} \frac{d T}{T}-\int_{0}^{T_{1}} c_{p} \frac{d T}{T}=s_{2}^{o}-s_{1}^{o}
$$

then ;

$$
\begin{array}{cc}
s_{2}-s_{1}=\left(s_{2}^{o}-s_{1}^{o}\right)-R \ln \frac{P_{2}}{P_{1}} & \frac{\mathrm{KJ}}{\mathrm{Kg} . \mathrm{K}} \\
\bar{s}_{2}-\bar{s}_{1}=\left(\bar{s}_{2}^{o}-\bar{s}_{1}^{o}\right)-R_{u} \ln \frac{P_{2}}{P_{1}} & \frac{\mathrm{KJ}}{\text { Kmole.K }}
\end{array}
$$

Entropy change of an
Incompressible substance: $\quad d u=C(T) d T$
for incompressible
substance, specific heat

$$
\begin{aligned}
& d u=C(T) d T \\
& d s=\frac{d u}{T}+\frac{P}{T} d v \\
& d s=\frac{C(T) d T}{T}+\frac{P}{T} \not 火^{\circ}=C(T) \frac{d T}{T} \\
& S_{2}-S_{1}=\int_{T_{1}}^{T_{2}} C(T) \frac{d T}{T} \leftarrow \text { incompressible }
\end{aligned}
$$

depends solely on
temperature, and

## When the specific

 heat is constant:$$
s_{2}-s_{1}=C \ln \frac{T_{2}}{T_{1}} \leftarrow \text { incompressible, constant } \mathrm{C}
$$

For internally reversible process:

$$
\begin{aligned}
& s_{2}-s_{1}=\int_{1}^{2} c_{p}(T) \frac{d T}{T}-R \ln \frac{P_{2}}{P_{1}} \\
& s_{2}-s_{1}=\int_{1}^{2} c_{v}(T) \frac{d T}{T}-R \ln \frac{V_{2}}{V_{1}}
\end{aligned}
$$

For Isentropic process(Reversible, adiabatic process):

$$
\begin{array}{rl}
S_{2}-S_{1}=0 & 0
\end{array}=\int_{1}^{2} c_{p}(T) \frac{d T}{T}-R \ln \frac{P_{2}}{P_{1}}
$$

$$
\begin{aligned}
0= & c_{p} \ln \frac{T_{2}}{T_{1}}-R \ln \frac{P_{2}}{P_{1}} \\
0= & c_{v} \ln \frac{T_{2}}{T_{1}}+R \ln \frac{V_{2}}{V_{1}} \\
\Rightarrow & \ln \frac{T_{2}}{T_{1}}=-\frac{R}{c_{v}} \ln \frac{V_{2}}{V_{1}}=\ln \left(\frac{V_{1}}{V_{2}}\right)^{\frac{R}{c_{v}}} \\
& \ln \frac{T_{2}}{T_{1}}=\ln \left(\frac{V_{1}}{V_{2}}\right)^{k-1} \quad \text { similarly, } \\
& \left(\frac{T_{2}}{T_{1}}\right)_{\mathrm{s}=\mathrm{constant}}=\left(\frac{V_{1}}{V_{2}}\right)^{k-1} \quad\left(\frac{T_{2}}{T_{1}}\right)_{\mathrm{s}=\mathrm{constant}}=\left(\frac{P_{2}}{P_{1}}\right)^{\frac{k-1}{k}}
\end{aligned}
$$

$$
\begin{array}{cc}
T d s=d u+P d v & \text { Ideal gas, Isentropic Process } \\
(\mathrm{PV}=\mathrm{RT}, \mathrm{ds}=0) \\
d s=\frac{d u}{T}+P \frac{d v}{T} & 0=c_{v} \frac{d T}{T}+R \frac{d v}{v}
\end{array}
$$

Integrate:
Constant $=c_{v} \ln T+R \ln v$
use $P V=R T \Rightarrow \ln \frac{P v}{R}+\frac{R}{C_{v}} \ln v=$ Constant
$\ln P v+\ln v^{k-1}=$ Constant $-\ln R=$ Constant
$\ln \left(P v \times v^{k-1}\right)=$ Constant
$\Rightarrow P v^{k}=$ Constant $\leftarrow$ Isentropic process ideal gas, wi th constant specific heats

$$
\begin{aligned}
s_{2}-s_{1} & =\int_{T_{1}}^{T_{2}} c_{p} \frac{d T}{T}-R \ln \frac{P_{2}}{P_{1}} \\
s_{2}-s_{1} & =s_{2}^{o}-s_{1}^{o}-R \ln \frac{P_{2}}{P_{1}}
\end{aligned}
$$

Isentropic process: $\mathrm{s}_{2}-\mathrm{s}_{1}=0$

$$
\begin{aligned}
s_{2}^{o}-s_{1}^{o} & =R \ln \frac{P_{2}}{P_{1}} \\
\ln \frac{P_{2}}{P_{1}} & =\left(\frac{s_{2}^{o}-s_{1}^{o}}{R}\right) \\
\frac{P_{2}}{P_{1}} & =\exp \frac{s_{2}^{o}-s_{1}^{o}}{R}
\end{aligned}
$$

Relative pressure and relative volume:

$$
\frac{P_{2}}{P_{1}}=\frac{\exp \left(s_{2}^{o} / R\right)}{\exp \left(s_{1}^{o} / R\right)}
$$

The quantity $\exp \left(s^{0} / R\right)$ is a function of temperature only and is given the symbol $\mathrm{P}_{\mathrm{r}}$, define as the relative pressure, and is tabulated for air and other ideal gases

$$
\begin{aligned}
& \frac{P_{2}}{P_{1}}=\frac{P_{r_{2}}}{P_{r_{1}}} \longleftarrow \begin{array}{l}
\text { I sentropic Process } \\
\left(s_{1}=\mathbf{s}_{2}\right) \text { I deal gas } \\
\text { variable specific heats }
\end{array} \\
& \text { where } \mathrm{P}_{\mathrm{r}_{1}}=\mathrm{P}_{\mathrm{r}}\left(\mathrm{~T}_{1}\right) \text { and } \mathrm{P}_{\mathrm{r}_{2}}=\mathrm{P}_{\mathrm{r}}\left(\mathrm{~T}_{2}\right)
\end{aligned}
$$

Note: $P_{r}$ is not truly pressure, and also $P_{r}$ should not be confused with the reduced pressure of compressibility chart.

Similarly a relation between specific volumes and temperatures and for two states having the same entropy can also be developed

$$
\frac{v_{2}}{v_{1}}=\frac{\left(\frac{R T_{2}}{P_{2}}\right)}{\left(\frac{P_{1}}{R T_{1}}\right)} \text { or } \frac{v_{2}}{v_{1}}=\frac{\left(\frac{R T_{2}}{P_{r_{2}}}\right)}{\left(\frac{P_{r_{1}}}{R T_{1}}\right)}
$$

The ratio $\frac{R T}{P_{r}}=v_{r}$ is the relative volume

$$
\frac{v_{2}}{v_{1}}=\frac{v_{r_{2}}}{v_{r_{1}}} \leftarrow \begin{aligned}
& \text { I sentropic process, } \\
& \text { I deal gas variable } \\
& \text { specific heats }
\end{aligned}
$$

In general Isentropic process for ideal gas: $\left(\mathrm{s}_{2}=\mathrm{s}_{1}\right)$

$$
\begin{aligned}
& P v^{k}=C \quad \leftarrow \quad \text { constant specific heat } \\
& \left.\begin{array}{l}
\frac{P_{r_{2}}}{P_{r_{1}}}=\frac{P_{2}}{P_{1}} \\
\frac{v_{r_{2}}}{v_{r_{1}}}=\frac{v_{2}}{v_{1}}
\end{array}\right\} \leftarrow \quad \text { specific heat is a function of temperature }
\end{aligned}
$$

General, reversible (Polytropic) process for an Ideal gas:
$\mathbf{P v}^{\mathbf{n}}=\mathbf{c}$, where $\mathbf{n}$ is constant
$P_{1} v_{1}^{n}=P_{2} v_{2}^{n}$
$\frac{P_{2}}{P_{1}}=\left(\frac{v_{1}}{v_{2}}\right)^{n}$
$W=\int_{1}^{2} P d v$

$=\int_{1}^{2} \frac{c}{v^{n}} d v=\frac{P_{1} v_{1}-P_{2} v_{2}}{n-1}$

## Polytropic process on P-v and T-s diagrams



- The Isentropic process involves no irreversibilities and serves as the ideal process for adiabatic devices.
- The actual process is irreversible and the actual device performance is less than the ideal case.
- The more closely the actual process approximates the idealized isentropic process, the better the device will perform.
- We define the efficiency (isentropic efficiency) of these devices as a measure of deviation of actual processes from the idealized one.


## 1) Isentropic efficiency of Turbines

$$
\dot{w}=h_{1}-h_{2}
$$

$\eta_{\mathrm{t}}=\frac{\text { Actual turbine work }}{\text { Isentropic work }}$
$\eta_{\mathrm{t}}=\frac{w_{a}}{w_{s}}=\frac{h_{1}-h_{2 a}}{h_{1}-h_{2 s}}<100 \%$


## 2) Isentropic efficiency of Compressors and Pumps



$\eta_{c}$ or $\eta_{\mathrm{p}}=\frac{W_{s}}{W_{a}}$
$\eta_{c}$ or $\eta_{p}=\frac{h_{2 s}-h_{1}}{h_{2 a}-h_{1}}$

## 3) Isentropic efficiency of Nozzles

$$
\begin{aligned}
& \eta_{\mathrm{N}}=\frac{\text { Actual K. E. at Nozzle exit }}{\text { Isentropic K.E. at Nozzle exit }} \\
& \eta_{\mathrm{N}}=\frac{V_{2 a}^{2}}{V_{2 s}^{2}} \\
& \text { Note }: h_{1}=h_{2 a}+\frac{V_{2 a}^{2}}{2} \\
& \eta_{\mathrm{N}} \cong \frac{h_{1}-h_{2 a}}{h_{1}-h_{2 s}}
\end{aligned}
$$

