The Second Law of Thermodynamics

## Note:

for a reversible process, on p-v diagram



and If the volume is constant,  $P \begin{bmatrix} 2 \\ -w = 0 \\ v_1 = v_2 \end{bmatrix} \int_{1}^{2} P dv = 0$  • Similarly, for any reversible adiabatic process, Q=0  $T \uparrow S_2 \uparrow$ 

$$Q_{rev} = \int T ds = 0$$

$$S_1 = S_2$$

$$Q = 0$$

$$S_1 = S_2$$

• For any other reversible process



• Clausius Inequality:

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

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

$$\oint \left(\frac{\delta Q}{T}\right)_{rev} = 0$$

for internally reversible cycle

$$\oint \left(\frac{\delta Q}{T}\right) < 0$$

for irreversible cycle





• 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

$$\Delta s_{sys} = \int_{1}^{2} \frac{\delta Q}{T} + s_{gen}$$

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

• 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.



$$s = s_f + x s_{fg}$$
$$\Delta S = m (s_2 - s_1)$$

• T-s diagram of properties:



- 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)

$$\Delta s = 0 \Longrightarrow s_1 = s_2$$

• If a steam turbine is reversible, and the turbine is insulated (thus the process is reversible and adiabatic)



• The Tds relations: differential form of the first law:  $\delta Q_{rev} - \delta W_{rev} = dU$  $\delta Q_{rev} = Tds$ second law: TdS = PdV + dUTds = Pdv + duFirst Tds relation Tds = du + Pdvh = u + Pvdh = du + Pdv + vdPSecond Tds relation Tds = dh - vdP

• Entropy changes for Liquids and solids: Tds=du+pdv

$$ds = \frac{du}{T} + \frac{pdv}{T}$$

• Liquids and solids are incompressible substances

$$dv \cong 0$$

$$ds = \frac{du}{T} = \frac{cdT}{T} \qquad (c_p = c_v = c)$$
$$s_2 - s_1 = \int_1^2 c \frac{dT}{T} = c \ln \frac{T_2}{T_1} \qquad \frac{kJ}{kgK}$$

Isentropic process for liquids and solids:

$$s_2 - s_1 = 0 = c \ln \frac{T_2}{T_1} \Longrightarrow T_2 = T_1$$

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.

$$ds = \frac{du}{T} + \frac{P}{T} dv$$
$$ds = \frac{dh}{T} - \frac{v}{T} dv$$

For an ideal gas:

$$du = c_v dT$$
  

$$dh = c_p dT$$
  

$$Pv = RT, \quad c_p = c_v + R$$
  

$$ds = c_v \frac{dT}{T} + R \frac{dv}{v}$$
  

$$ds = c_p \frac{dT}{T} - R \frac{dP}{P}$$

Now integrating

$$s_{2} - s_{1} = \int_{T_{1}}^{T_{2}} c_{v} \frac{dT}{T} + R \ln \frac{v_{2}}{v_{1}}$$
$$s_{2} - s_{1} = \int_{T_{1}}^{T_{2}} c_{P} \frac{dT}{T} - R \ln \frac{P_{2}}{P_{1}}$$

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

Using Ideal gas Tables:

Define 
$$s^{o}(T) = \int_{0}^{T} \frac{c_{p}(T)}{T} dT$$

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<sup>o</sup> depends only on the temperature, it can be tabulated versus temperature, like h and u.

Also,

$$\int_{T_1}^{T_2} c_p \frac{dT}{T} = \int_{0}^{T_2} c_p \frac{dT}{T} - \int_{0}^{T_1} c_p \frac{dT}{T} = s_2^o - s_1^o$$

then;

$$s_{2} - s_{1} = (s_{2}^{o} - s_{1}^{o}) - R \ln \frac{P_{2}}{P_{1}} \qquad \frac{\text{KJ}}{\text{Kg.K}}$$
  
or  $\overline{s}_{2} - \overline{s}_{1} = (\overline{s}_{2}^{o} - \overline{s}_{1}^{o}) - R_{u} \ln \frac{P_{2}}{P_{1}} \qquad \frac{\text{KJ}}{\text{Kmole.K}}$ 

Entropy change of an Incompressible substance: for incompressible substance, specific heat depends solely on temperature, and

$$du = C(T)dT$$
  

$$ds = \frac{du}{T} + \frac{P}{T}dv$$
  

$$ds = \frac{C(T)dT}{T} + \frac{P}{T}dv = C(T)\frac{dT}{T}$$
  

$$S_2 - S_1 = \int_{T_1}^{T_2} C(T)\frac{dT}{T} \leftarrow \text{incompressible}$$

When the specific heat is constant:

$$s_2 - s_1 = C \ln \frac{T_2}{T_1} \leftarrow \text{incompressible, constant C}$$

For internally reversible process:

$$s_{2} - s_{1} = \int_{1}^{2} c_{p}(T) \frac{dT}{T} - R \ln \frac{P_{2}}{P_{1}}$$
$$s_{2} - s_{1} = \int_{1}^{2} c_{v}(T) \frac{dT}{T} - R \ln \frac{V_{2}}{V_{1}}$$

For Isentropic process(Reversible, adiabatic process):

$$s_{2} - s_{1} = 0 \qquad 0 = \int_{1}^{2} c_{p}(T) \frac{dT}{T} - R \ln \frac{P_{2}}{P_{1}}$$
$$0 = \int_{1}^{2} c_{v}(T) \frac{dT}{T} - R \ln \frac{V_{2}}{V_{1}}$$

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

$$Tds = du + Pdv$$
 Ideal gas, Isentropic Process  

$$ds = \frac{du}{T} + P\frac{dv}{T}$$

$$0 = c_v \frac{dT}{T} + R\frac{dv}{v}$$

Integrate:

Constant  $= c_v \ln T + R \ln v$   $use \ P = RT \implies \ln \frac{Pv}{R} + \frac{R}{c_v} \ln v = \text{Constant}$   $\ln Pv + \ln v^{k-1} = \text{Constant} - \ln R = \text{Constant}$   $\ln(Pv \times v^{k-1}) = \text{Constant}$   $\implies Pv^k = \text{Constant} \leftarrow \text{Isentropic process ideal gas,}$ with constant specific heats

$$s_{2} - s_{1} = \int_{T_{1}}^{T_{2}} c_{p} \frac{dT}{T} - R \ln \frac{P_{2}}{P_{1}}$$

$$s_{2} - s_{1} = s_{2}^{o} - s_{1}^{o} - R \ln \frac{P_{2}}{P_{1}}$$
Isentropic process:  $s_{2} - s_{1} = 0$ 

$$s_{2}^{o} - s_{1}^{o} = R \ln \frac{P_{2}}{P_{1}}$$

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

$$\frac{P_{2}}{P_{1}} = \exp \frac{s_{2}^{o} - s_{1}^{o}}{R}$$

Relative pressure and relative volume:

$$\frac{P_2}{P_1} = \frac{\exp(s_2^o / R)}{\exp(s_1^o / R)}$$

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

$$\frac{P_2}{P_1} = \frac{P_{r_2}}{P_{r_1}} \longleftarrow \qquad \begin{array}{c} \text{Isentropic Process} \\ (s_1 = s_2) \text{ Ideal gas} \\ \text{variable specific heats} \end{array}$$

where  $P_{r_1} = P_r(T_1)$  and  $P_{r_2} = P_r(T_2)$ 

**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





In general Isentropic process for ideal gas:  $(s_2=s_1)$ 

$$Pv^k = C \leftarrow \text{constant specific heat}$$





Polytropic process on P-v and T-s diagrams



# Isentropic Efficiencies of Steady-Flow Devices

- 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

$$\dot{w} = h_1 - h_2$$



### 2) Isentropic efficiency of Compressors and Pumps



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

3) Isentropic efficiency of Nozzles

Actual K. E. at Nozzle exit Isentropic K.E. at Nozzle exit  $\eta_N$  $=\frac{V_{2a}^2}{V^2}$  $\eta_{\rm N}$ Note :  $h_1 = h_{2a} + \frac{V_{2a}^2}{2}$  $P_2$  $2_s$ S  $\eta_{\rm N} \cong \frac{h_1 - h_{2a}}{h_1 - h_2}$