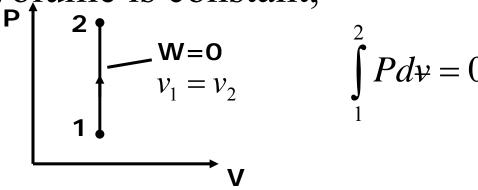
# The Second Law of Thermodynamics

#### Note:

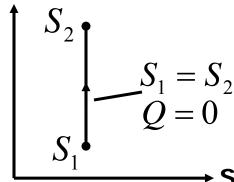
for a reversible process, on p-v diagram

and If the volume is constant,



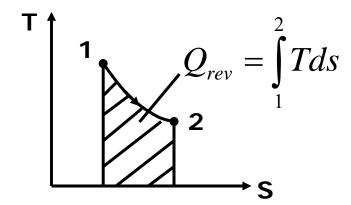
• Similarly, for any reversible adiabatic process, Q=0 T + C

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



For any other reversible process

$$Q_{rev} = \int_{1}^{2} T ds$$



• Clausius Inequality:

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

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

$$\oint \left(\frac{\delta Q}{T}\right)_{rev} = 0 \qquad \text{for internally reversible cycle}$$

$$\oint \left(\frac{\delta Q}{T}\right) < 0 \qquad \text{for irreversible cycle}$$

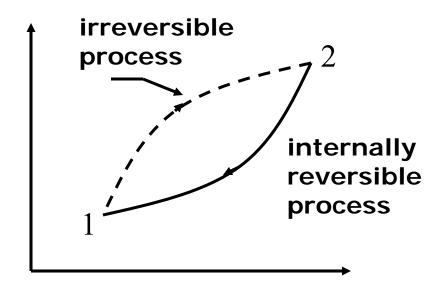
$$\left(\frac{\delta Q}{T}\right)_{rev}$$

represents a property change

$$dS = \frac{\delta Q}{T} \Big|_{rev}$$

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \Big|_{rev}$$

• 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

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

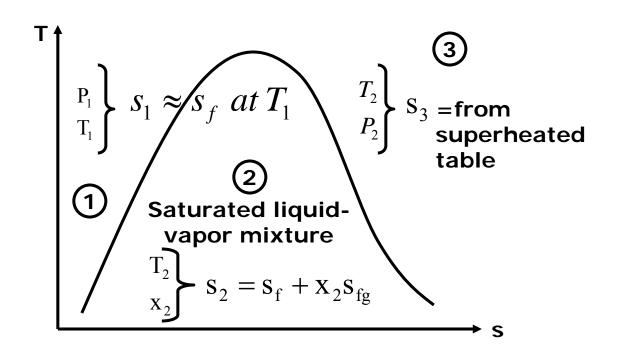
For an irreversible process

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

• 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.

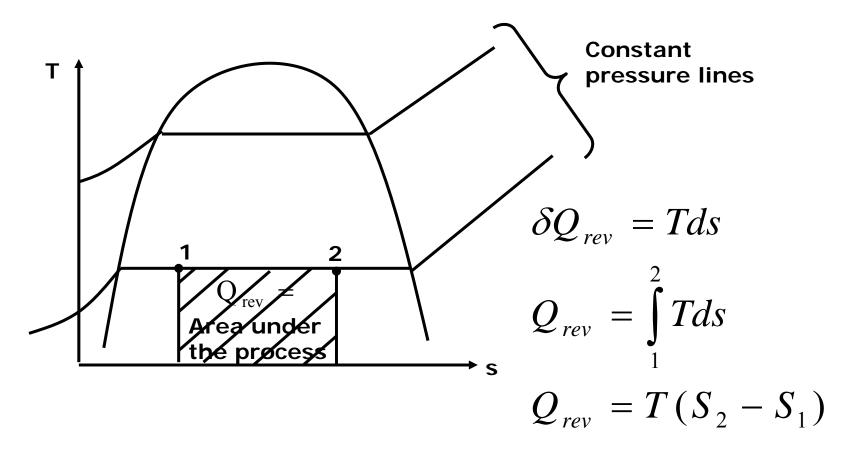
### Entropy Change for Pure Substances

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



$$S = S_f + xS_{fg}$$
$$\Delta S = m(s_2 - s_1)$$

• T-s diagram of properties:



- Entropy of a fixed mass can be changed by:
  - 1) Heat transfer
  - 2) Irreversibilities

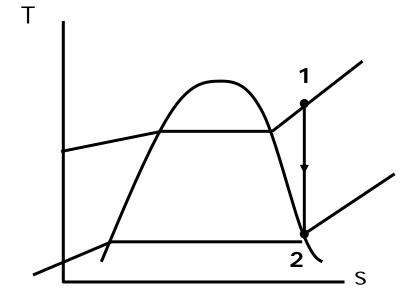
• The entropy of a fixed mass will not change during a process that is internally reversible and adiabatic.

• 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)

then  $\Delta s = 0$ or  $s_1 = s_2$ 



• The Tds relations: differential form of the first law:  $\delta Q_{rev} - \delta w_{rev} = dU$ 

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

$$TdS = PdV + dU$$

$$Tds = du + Pdv$$

$$h = u + Pv$$

$$dh = du + Pdv + vdP$$

$$Tds = dh - vdP \qquad \longleftarrow \quad \text{Second Tds relation}$$

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

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

• Liquids and solids are incompressible substances

$$dv \cong 0$$

$$ds = \frac{du}{T} = \frac{cdT}{T}$$

$$(c_p = c_v = c)$$

$$s_2 - s_1 = \int_1^2 c \frac{dT}{T} = c \ln \frac{T_2}{T_1}$$

$$\frac{kJ}{kgK}$$

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:

$$du = c_{v}dT$$

$$dh = c_{p}dT$$

$$Pv = RT, \quad c_{p} = c_{v} + R$$

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

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

On integration these equations give, respectively

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

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

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;

$$s_{2} - s_{1} = (s_{2}^{o} - s_{1}^{o}) - R \ln \frac{P_{2}}{P_{1}} \qquad \frac{KJ}{Kg.K}$$

$$or \quad \bar{s}_{2} - \bar{s}_{1} = (\bar{s}_{2}^{o} - \bar{s}_{1}^{o}) - R_{u} \ln \frac{P_{2}}{P_{1}} \qquad \frac{KJ}{Kmole.K}$$

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:

$$s_2 - s_1 = C \ln \frac{T_2}{T_1}$$
  $\leftarrow$  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):

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

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

$$0 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$0 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$\Rightarrow \ln \frac{T_2}{T_2} = -\frac{R}{T_2} \ln \frac{V_2}{T_2} = -\frac{R}{T_2} \ln \frac{V_2}{T_2}$$

$$\Rightarrow \ln \frac{T_2}{T_1} = -\frac{R}{c_v} \ln \frac{V_2}{V_1} = \ln \left(\frac{V_1}{V_2}\right)^{\overline{c_v}}$$

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2}\right)^{k-1}$$

$$\left(\frac{T_2}{T_1}\right)_{\text{s=constant}} = \left(\frac{V_1}{V_2}\right)^{k-1}$$

similarly,

$$\left(\frac{T_2}{T_1}\right)_{\text{s=constant}} = \left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{k}}$$

$$Tds = du + Pdv$$

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

Ideal gas, Isentropic Process (PV=RT, ds=0)

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

#### Integrate:

Constant =  $c_v \ln T + R \ln v$ 

$$use \ PV = RT \implies \ln \frac{Pv}{R} + \frac{R}{c_v} \ln v = Constant$$

 $\ln Pv + \ln v^{k-1} = \text{Constant } - \ln R = \text{Constant}$ 

$$ln(Pv \times v^{k-1}) = Constant$$

 $\Rightarrow Pv^k = \text{Constant} \leftarrow \text{Isentropic process ideal gas,}$  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  $\exp(s^o/R)$  is a function of temperature only and is given the symbol  $P_r$ , define as the relative pressure, and is tabulated for air and other ideal gases

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

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

$$\frac{v_2}{v_1} = \frac{\left(\frac{RT_2}{P_2}\right)}{\left(\frac{P_1}{RT_1}\right)} \quad \text{or} \quad \frac{v_2}{v_1} = \frac{\left(\frac{RT_2}{P_{r_2}}\right)}{\left(\frac{P_{r_1}}{RT_1}\right)}$$

The ratio  $\frac{RT}{P_r} = v_r$  is the relative volume

$$\frac{v_2}{v_1} = \frac{v_{r_2}}{v_{r_1}} \leftarrow \begin{array}{c} \text{Isentropic process,} \\ \text{Ideal gas variable} \\ \text{specific heats} \end{array}$$

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

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

$$\frac{P_{r_2}}{P_{r_1}} = \frac{P_2}{P_1}$$

$$\frac{v_{r_2}}{v_{r_1}} = \frac{v_2}{v_1}$$
specific heat is a function of temperature

General, reversible (Polytropic) process for an Ideal gas:

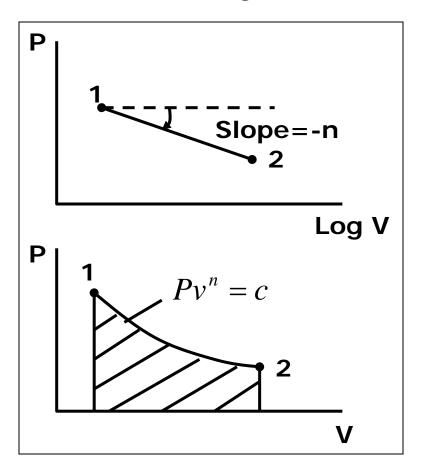
#### Pv<sup>n</sup>=c, where n is constant

$$P_1 v_1^n = P_2 v_2^n$$

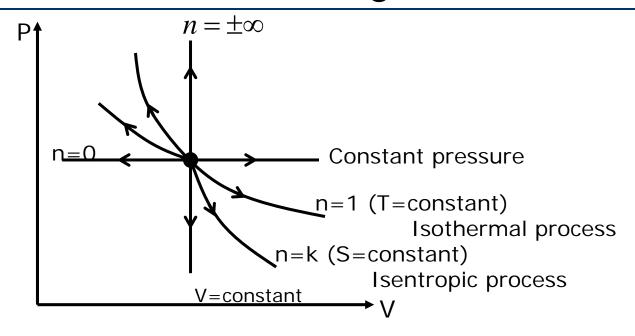
$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^n$$

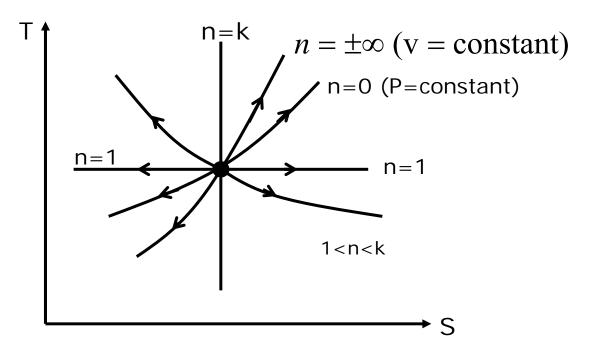
$$W = \int_{1}^{2} P dv$$

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



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





## Isentropic Efficiencies of Steady-Flow Devices

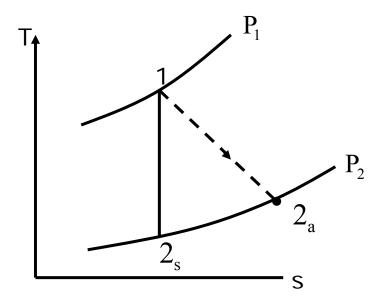
- The Isentropic process involves no irreversibilities and serves as the ideal process for adiabatic devices.
- The actual process is irreversible and the actual device performance is less than the ideal case.
- The more closely the actual process approximates the idealized isentropic process, the better 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

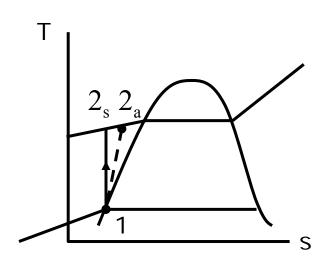
$$\dot{w} = h_1 - h_2$$

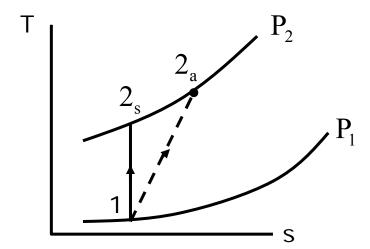
$$\eta_t = \frac{Actual turbine work}{Isentropic work}$$

$$\eta_{t} = \frac{w_{a}}{w_{s}} = \frac{h_{1} - h_{2a}}{h_{1} - h_{2s}} < 100\%$$



## 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

$$\eta_{N} = \frac{\text{Actual K. E. at Nozzle exit}}{\text{Isentropic K.E. at Nozzle exit}}$$

$$\eta_{\mathrm{N}} = \frac{V_{2a}^2}{V_{2s}^2}$$

Note: 
$$h_1 = h_{2a} + \frac{V_{2a}^2}{2}$$

$$\eta_{\rm N} \cong \frac{h_{\rm l} - h_{2a}}{h_{\rm l} - h_{2s}}$$

