

# Entropy

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ME 203: Engineering Thermodynamics

<http://zahurul.buet.ac.bd/ME203/>

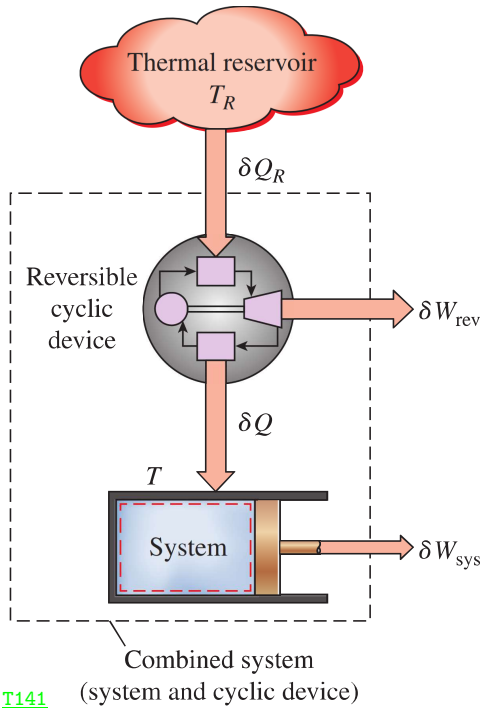


## Consequences of Second Law of Thermodynamics

- If a system is taken through a cycle and produces work, it must be exchanging heat with at least two reservoirs at 2 different temperatures.
- If a system is taken through a cycle while exchanging heat with a single reservoir, work must be zero or negative.
- Heat can never be converted continuously and completely into work, but work can always be converted continuously and completely into heat.
  - ▶ Work is a more valuable form of energy than heat.
  - ▶ For a cycle and single reservoir,  $W_{net} \leq 0$ .



# Clausius Inequity



T141

## Clausius Inequality

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

$$\Rightarrow \delta W_{net} \equiv (\delta W_{rev} + \delta W_{sys}) = \delta Q_R - dU$$

$$\Rightarrow \frac{\delta Q_R}{\delta Q} = \frac{T_R}{T}$$

$$\Rightarrow \delta W_{net} = T_R \frac{\delta Q}{T} - dU$$

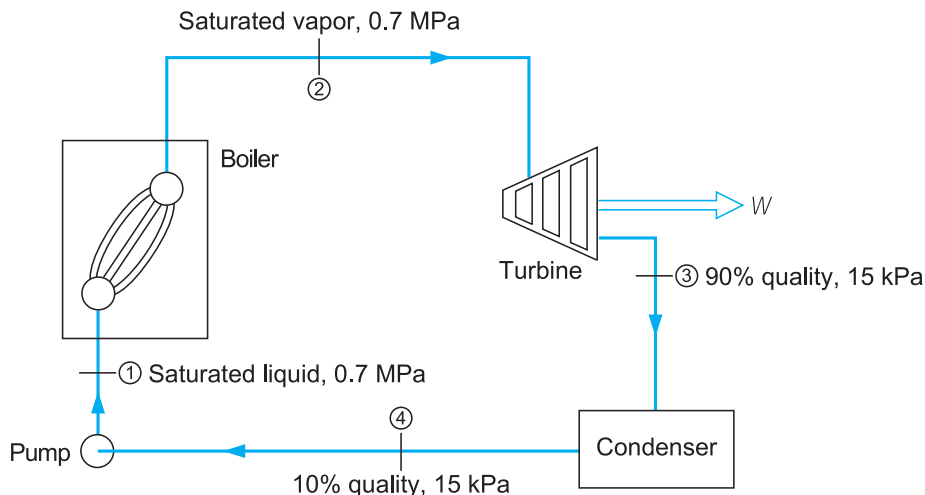
$$\Rightarrow W_{net} = T_R \oint \frac{\delta Q}{T}$$

$$\Rightarrow \oint \frac{\delta Q}{T} \leq 0 \quad \text{as } W_{net} \leq 0$$

$$\oint \frac{\delta Q}{T} \begin{cases} = 0 & \text{reversible process} \\ < 0 & \text{irreversible process} \end{cases}$$



## Example: Clausius Inequality: Steam Power Plant:



T037

- At 0.7 MPa  $T_{sat} = T_H = 164.95^\circ\text{C}$

- At 15 kPa  $T_{sat} = T_L = 53.97^\circ\text{C}$

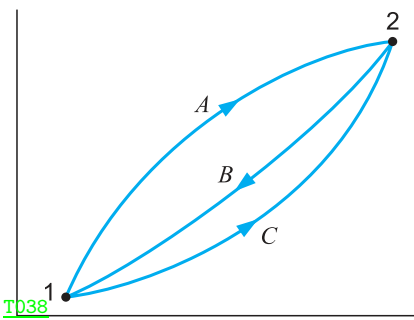
- $Q_H = Q_{12} = h_2 - h_1 = 2.066 \text{ MJ/kg}$

- $Q_L = Q_{34} = h_4 - h_3 = -1.898 \text{ MJ/kg}$

$$\Rightarrow \oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = -1.086 \text{ kJ/kg} < 0$$



# Entropy (S): A Thermodynamic Property



For reversible process:  $\oint \frac{\delta Q}{T} = 0$

$$\Rightarrow \oint \frac{\delta q}{T} = \int_1^2 \left( \frac{\delta q}{T} \right)_A + \int_2^1 \left( \frac{\delta q}{T} \right)_B = 0 \quad \text{①}$$

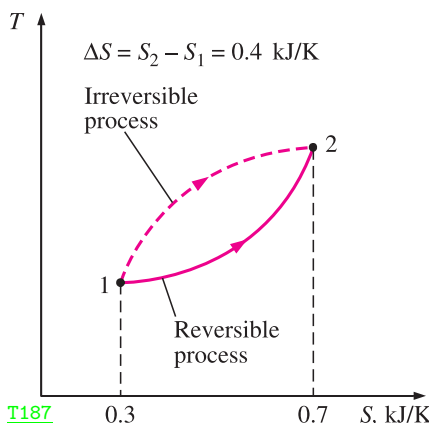
$$\Rightarrow \oint \frac{\delta q}{T} = \int_1^2 \left( \frac{\delta q}{T} \right)_C + \int_2^1 \left( \frac{\delta q}{T} \right)_B = 0 \quad \text{②}$$

$$\bullet \text{ ①} - \text{②} \Rightarrow \int_1^2 \left( \frac{\delta q}{T} \right)_A = \int_1^2 \left( \frac{\delta q}{T} \right)_C = \dots$$

Since  $\int \delta q/T$  is same for all reversible processes/paths between state 1 & 2, this quantity is independent of path and is a function of end states only. This property is called **Entropy, S**.

$$ds \equiv \left( \frac{\delta q}{T} \right)_{rev} \implies \Delta s = s_2 - s_1 = \int_1^2 \left( \frac{\delta q}{T} \right)_{rev}$$

$$\delta q_{rev} = T ds$$



T187

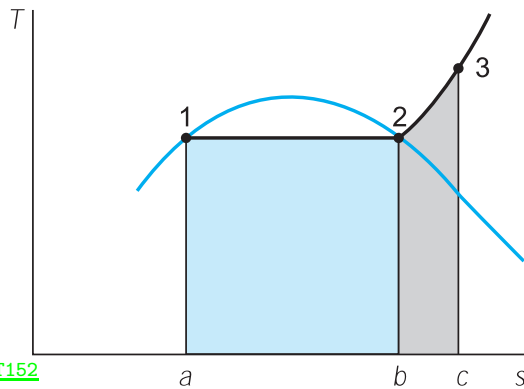
- Entropy is a property, hence change in entropy between two end states is same for all processes, both reversible and irreversible.
- If no irreversibilities occur within the system boundaries of the system during the process, the system is internally reversible.

For an internally reversible process, the change in the entropy is due solely for heat transfer. So, heat transfer across a boundary associated with it the transfer of entropy as well.

$$\int_1^2 \left( \frac{\delta q}{T} \right)_{rev} \equiv \text{Entropy transfer (or flux)}$$



Example: ▷ Steam generation in Boiler.



T152

- $q_{12} = T_{sat}(s_2 - s_1) = \text{area } (1 - 2 - b - a)$
- $q_{23} = \int_2^3 T ds = \text{area } (2 - 3 - c - b)$
- $q_{net} = q_{12} + q_{23} = \text{area } (1 - 2 - 3 - c - a)$

$$\bullet \quad s_2 - s_1 = \int_1^2 \left( \frac{\delta q}{T} \right)_{rev} = \frac{\int_1^2 \delta q}{T_{sat}}$$

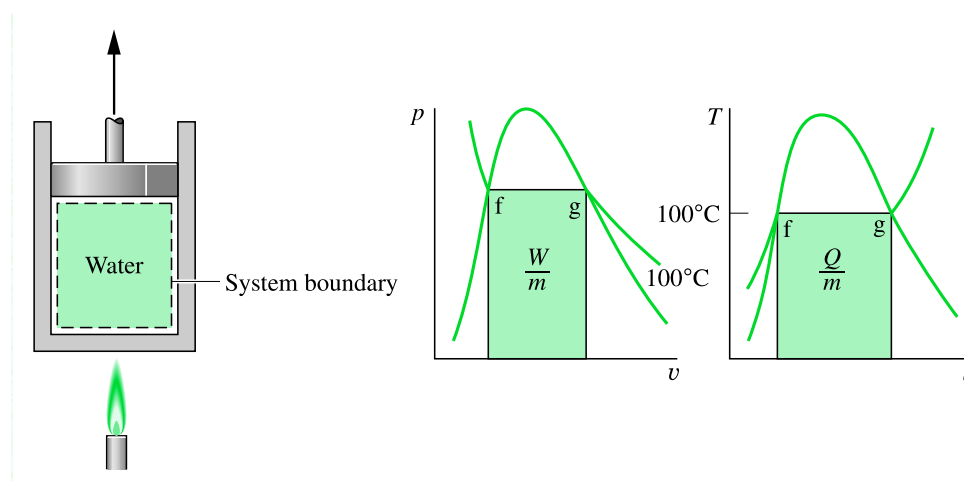
$$\Rightarrow s_2 - s_1 = \frac{q_{12}}{T_{sat}} = \frac{h_2 - h_1}{T_{sat}} = \frac{h_{fg}}{T_{sat}}$$

$$\Rightarrow \boxed{h_{fg} = s_{fg} T_{sat}}$$

$$\bullet \quad q_{23} = \int_2^3 \delta q = \int_2^3 T ds$$



Moran Ex. 6.1: ▷ Internally reversible heating in a piston-cylinder assembly.



T169

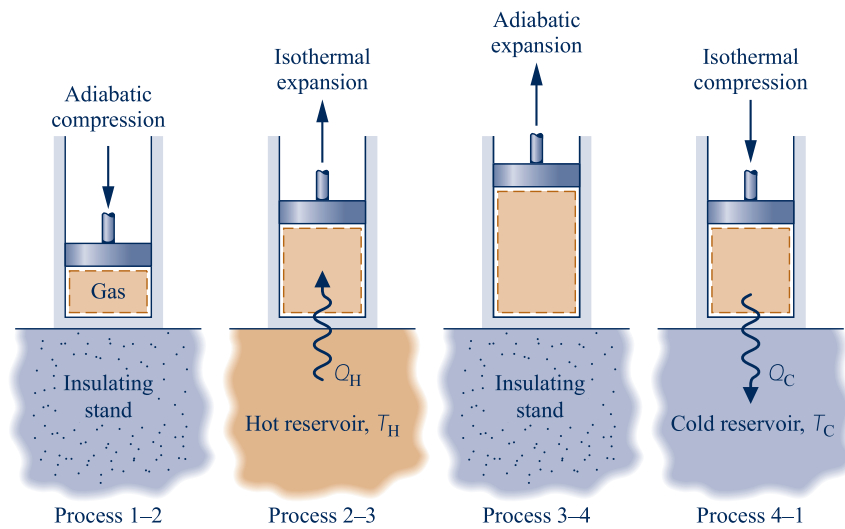
$$\Rightarrow w = \int_f^g P dv = P(v_g - v_f) = 101.325(1.673 - 0.001044) = 170 \text{ kJ/kg} \triangleleft$$

$$\Rightarrow q = \int_f^g T ds = T(s_g - s_f) = T s_{fg} = 373.15 \cdot 6.0486 = 2256.8 \text{ kJ/kg} \triangleleft$$

Also note that,  $h_{fg} = 2257 \text{ kJ/kg} \triangleleft$



## Carnot Cycle



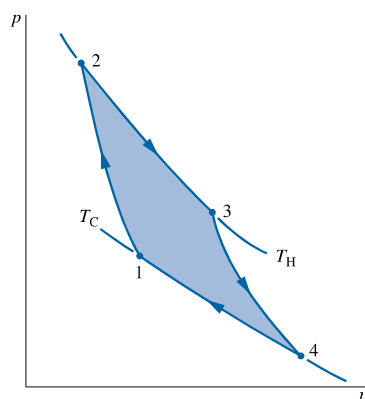
T153

1-2 : Isentropic compression.

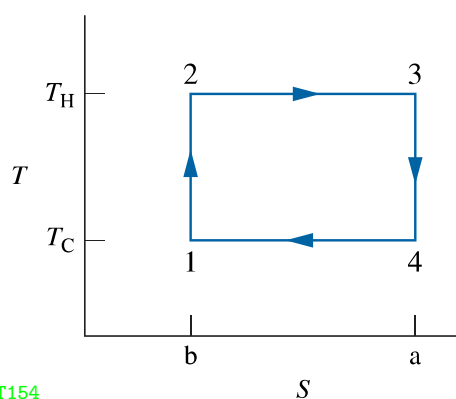
2-3 : Isothermal heat addition and expansion.

3-4 : Isentropic expansion.

4-1 : Isothermal heat rejection and compression.



T156



T154

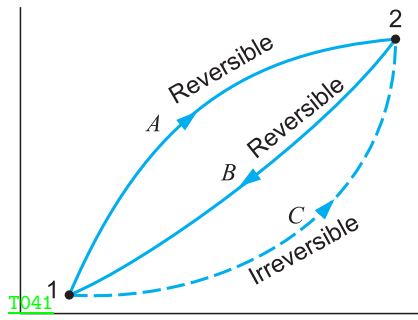
$$\delta q = T ds$$

- $q_{23} = \int_2^3 T ds = T_H \int_2^3 ds = T_H (s_3 - s_2) = T_H \Delta s$
- $q_{41} = \int_4^1 T ds = T_L \int_4^1 ds = T_L (s_1 - s_4) = -T_L \Delta s$
- $w_{net} = q_{net} = q_{23} + q_{41} = (T_H - T_L) \Delta s$
- $q_{in} = q_{23}$

$$\eta_{Carnot} \equiv \frac{w_{net}}{q_{in}} = \frac{(T_H - T_L) \Delta s}{T_H \Delta s} = 1 - \frac{T_L}{T_H}$$



# Entropy Change for Irreversible CM Process



T041

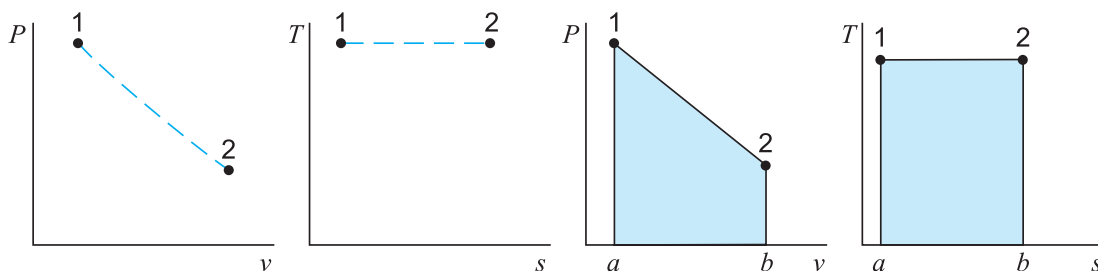
- For reversible process:  $\oint \frac{\delta q}{T} = 0$   
 $\Rightarrow \int_1^2 \left(\frac{\delta q}{T}\right)_A + \int_2^1 \left(\frac{\delta q}{T}\right)_B = 0$  ①
- For irreversible process:  $\oint \frac{\delta q}{T} < 0$   
 $\Rightarrow \int_1^2 \left(\frac{\delta q}{T}\right)_C + \int_2^1 \left(\frac{\delta q}{T}\right)_B < 0$  ②
- ① - ②  $\Rightarrow \int_1^2 \left(\frac{\delta q}{T}\right)_A > \int_1^2 \left(\frac{\delta q}{T}\right)_C$

- Since path A is reversible, and since entropy is a property

$$\int_1^2 \left(\frac{\delta q}{T}\right)_A = \int_1^2 ds_A = \int_1^2 ds_C \Rightarrow \int_1^2 ds_C > \int_1^2 \left(\frac{\delta q}{T}\right)_C$$

- Since path C is arbitrary, for irreversible process

$$ds > \frac{\delta q}{T} \Rightarrow s_2 - s_1 > \int_1^2 \left(\frac{\delta q}{T}\right)_{irrev}$$



T170

Irreversible Process

Reversible Process

- For irreversible process:

$$w_{12} \neq \int_1^2 P dv \quad : \quad q_{12} \neq \int_1^2 T ds$$

So, the area underneath the path does not represent work and heat on the  $P - v$  and  $T - s$  diagrams, respectively.

- In irreversible processes, the exact states through which a system undergoes are not defined. So, irreversible processes are shown as dashed lines and reversible processes as solid lines.



# Entropy Generation

$$dS \geq \frac{\delta Q}{T} \implies \delta\sigma \equiv dS - \frac{\delta Q}{T} \geq 0$$

$\sigma \triangleq$  Entropy produced (generated) by internal irreversibilities.

$$S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right)_b + \sigma$$

entropy change	entropy transfer	entropy production
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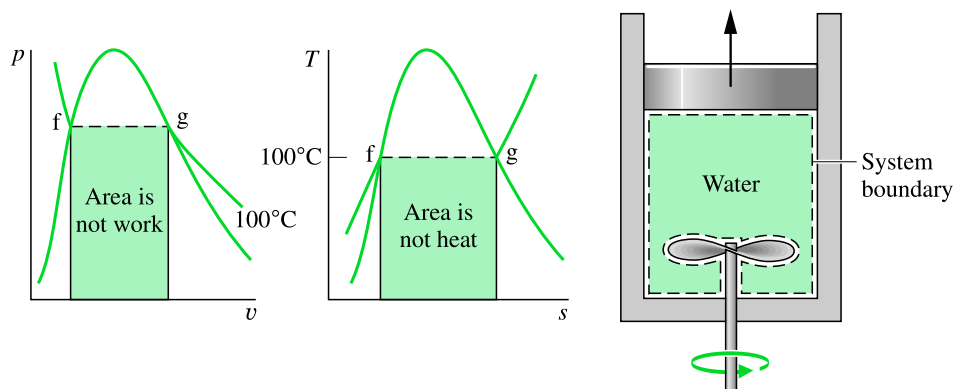
$$\sigma : \begin{cases} > 0 & \text{irreversible process} \\ = 0 & \text{internally reversible process} \\ < 0 & \text{impossible process} \end{cases}$$

T173

- The entropy of a system can increase in only two ways, either by heat addition or by the presence of irreversibility.
- The entropy of a system can decrease only by heat removal.
- Reversible process:  $ds = \delta q/T$  & adiabatic process:  $\delta q = 0 \implies s = \text{constant}$ : for reversible adiabatic process.
- All isentropic processes are not necessarily reversible and adiabatic. Entropy can remain constant during a process if the heat removal balances the irreversibility.



Moran Ex. 6.2: ▷ Irreversible process of water.



T172

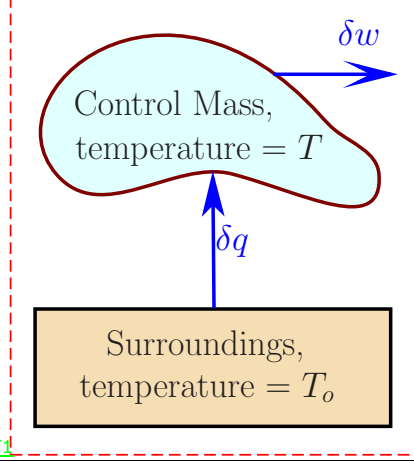
- $du + dKE + dPE = \delta q - \delta w \implies du = -\delta w$
- $\implies \frac{W}{m} = -\int_f^g du = -(u_g - u_f) = -2087.56 \text{ kJ/kg} \triangleleft$   
Note that, the work input by stirring is greater in magnitude than the work done by the water as it expands (170 kJ/kg).
- $\delta(\sigma/m) = ds - \frac{\delta q}{T} = ds - 0 = ds$
- $\implies \frac{\sigma}{m} = s_g - s_f = 6.048 \text{ kJ/kg.K} \triangleleft$



# Principle of Increase of Entropy

$$ds \geq \frac{\delta q}{T}$$

Adiabatic or isolated system

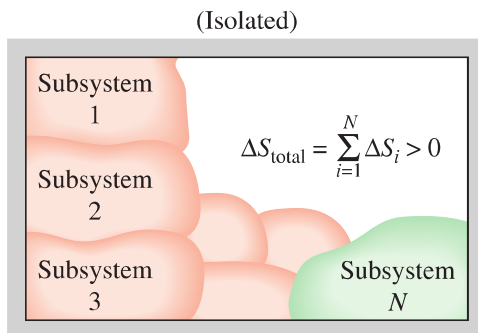


T171

- For control mass:  
 $\Rightarrow ds_{CM} \geq \frac{\delta q}{T}$
- For the surroundings at  $T_o$ ,  $\delta q < 0$ , and reversible heat transfer:  
 $\Rightarrow ds_{surr} = \frac{-\delta q}{T_o}$
- $\Rightarrow ds_{net} = ds_{sys} + ds_{surr} \geq \delta q \left[ \frac{1}{T} - \frac{1}{T_o} \right]$
- If  $T > T_o \Rightarrow \delta q < 0 \Rightarrow ds_{net} \geq 0$
- If  $T < T_o \Rightarrow \delta q > 0 \Rightarrow ds_{net} \geq 0$

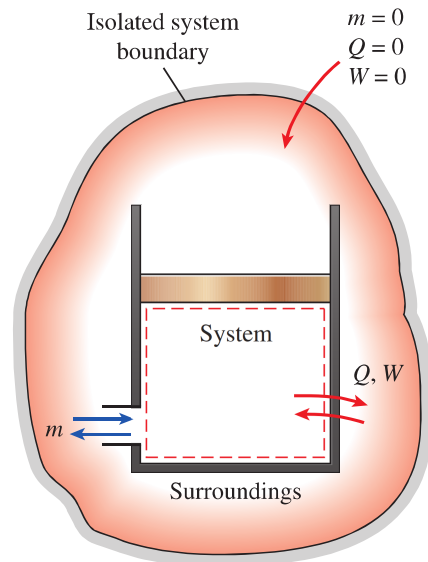
$$ds_{net} \geq 0$$

Entropy change for an isolated system cannot be negative.



T188

*Entropy change of an isolated system is the sum of the entropy changes of its components, and is never less than zero.*



T189

*A system and its surroundings form an isolated system.*

$$ds_{isolated} \geq 0$$





**Example:** ▷ Suppose that 1 kg of saturated water vapor at 100°C is to a saturated liquid at 100°C in a constant-pressure process by heat transfer to the surrounding air, which is at 25°C. What is the net increase in entropy of the water plus surroundings?

$$\Delta s_{net} = \Delta s_{sys} + \Delta s_{surr}$$

- $\Delta s_{sys} = -s_{fg} = -6.048 \text{ kJ/kg.K}$

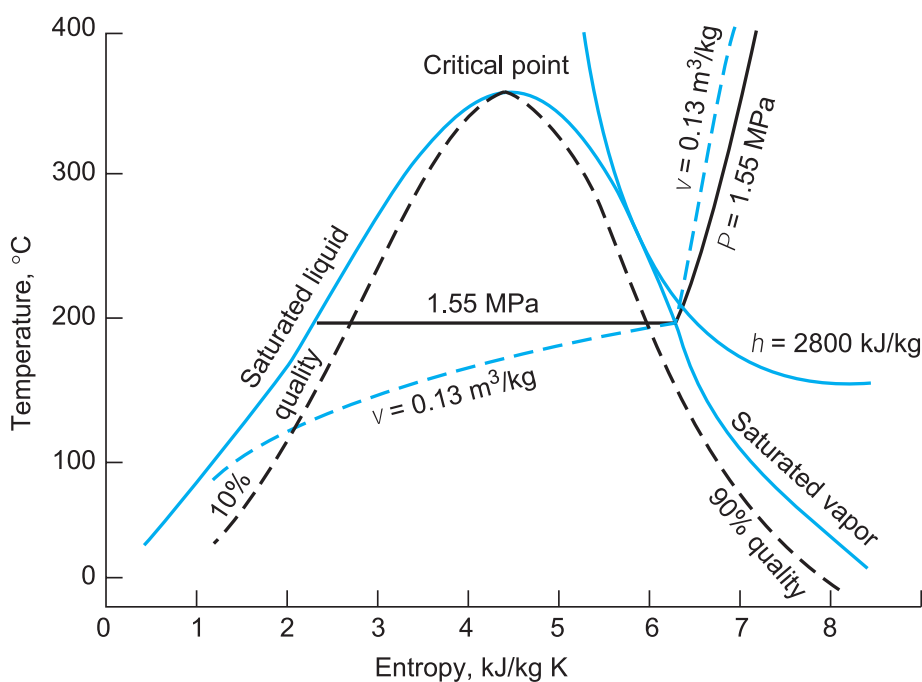
- $\Delta s_{surr} = \frac{q}{T_o} = \frac{h_{fg}}{T_o} = \frac{2257}{298} = 7.574 \text{ kJ/kg.K}$

$$\Rightarrow \Delta s_{net} = 1.533 \text{ kJ/kg.K} <$$

So, increase in net entropy.



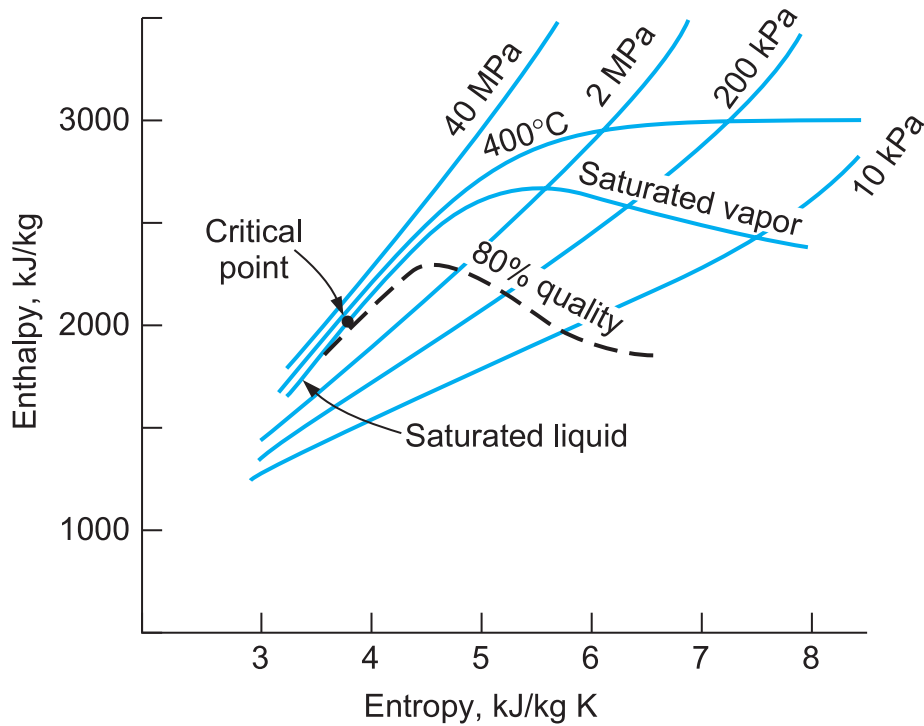
## Entropy of a Pure Substance



T150

*Temperature-entropy diagram for steam.*





T151

*Enthalpy-entropy diagram (Mollier diagram) for steam.*



## Entropy of Ideal Gas

- **First Law:**  $\delta q - \delta w = du$
- **Reversible process:**  $\delta w = Pdv$  :  $\delta q = Tds$
- **Ideal gas:**  $Pv = RT$  :  $du = c_v dT$  :  $dh = c_p dT$

$$\Rightarrow du = -Pdv + Tds \Rightarrow \boxed{Tds = du + Pdv} : 1^{st} Tds \text{ Equation.}$$

$$\Rightarrow ds = c_v \frac{dT}{T} + \frac{P}{T} dv = c_v \frac{dT}{T} + R \frac{dv}{v} : \text{For ideal gas.}$$

$$\Rightarrow \boxed{s(T_2, v_2) - s(T_1, v_1) = \int_{T_1}^{T_2} c_v \frac{dT}{T} + R \ln \left( \frac{v_2}{v_1} \right)}$$

$$\Rightarrow \boxed{s_2 - s_1 = c_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right)} : \text{Ideal gas with } c_v = \text{constant.}$$

$$\Rightarrow h = u + Pv \Rightarrow dh = du + Pdv + vdP = \delta q_{rev} + vdP = Tds + vdP$$

$$\Rightarrow dh = Tds + vdP \Rightarrow \boxed{Tds = dh - vdP} : 2^{nd} Tds \text{ Equation.}$$

$$\Rightarrow \boxed{s(T_2, P_2) - s(T_1, P_1) = \int_{T_1}^{T_2} c_p \frac{dT}{T} - R \ln \left( \frac{P_2}{P_1} \right)}$$

$$\Rightarrow \boxed{s_2 - s_1 = c_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right)} : \text{Ideal gas with } c_p = \text{constant.}$$



Isentropic Process:  $s = \text{constant} \Rightarrow \Delta s = 0$ 

$$\bullet s_2 - s_1 = c_P \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right)$$

$$\Rightarrow \ln \left( \frac{T_2}{T_1} \right) = -\frac{R}{c_V} \ln \left( \frac{v_2}{v_1} \right) = -(k-1) \ln \left( \frac{v_2}{v_1} \right) = \ln \left( \frac{v_1}{v_2} \right)^{(k-1)}$$

$$\Rightarrow \boxed{\frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{(k-1)} \quad (\text{ideal gas, } s_1 = s_2, \text{ constant } k)}$$

$$\bullet s_2 - s_1 = c_P \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right)$$

$$\Rightarrow \ln \left( \frac{T_2}{T_1} \right) = \frac{R}{c_P} \ln \left( \frac{P_2}{P_1} \right) = \frac{(k-1)}{k} \ln \left( \frac{P_2}{P_1} \right) = \ln \left( \frac{P_2}{P_1} \right)^{\frac{(k-1)}{k}}$$

$$\Rightarrow \boxed{\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{(k-1)}{k}} \quad (\text{ideal gas, } s_1 = s_2, \text{ constant } k)}$$

$$\Rightarrow \boxed{Pv^k = \text{constant} \quad (\text{ideal gas, } s_1 = s_2, \text{ constant } k)}$$



$$Pv^n = \text{constant}$$

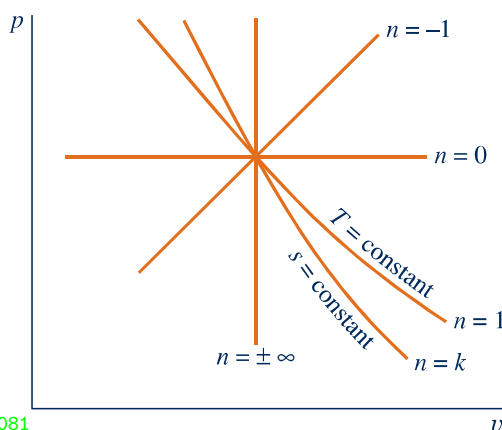
Isobaric process:  $n = 0, \quad P = \text{constant}$

Isothermal process:  $n = 1, \quad T = \text{constant}$

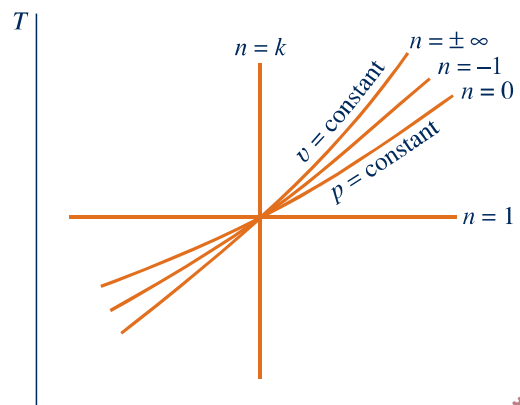
Isentropic process:  $n = k, \quad s = \text{constant}$

Isochoric process:  $n = \infty, \quad v = \text{constant}$

T1653

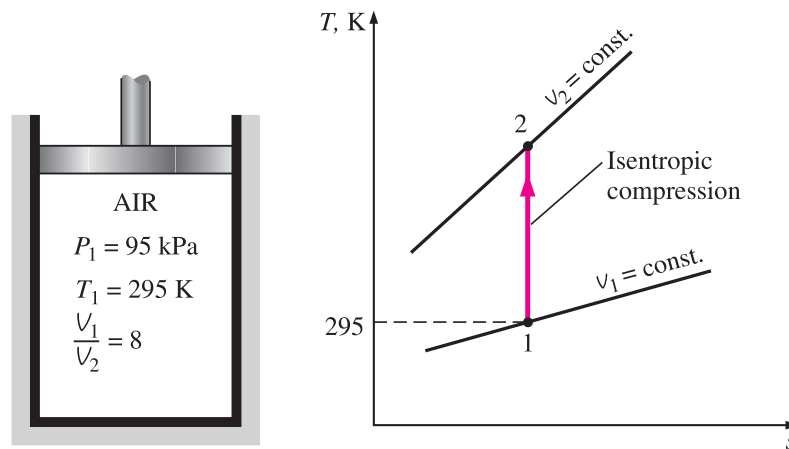


T1081



**Cengel Ex. 7.2:** ▷ Air is compressed in a car engine from 22°C and 95 kPa in a reversible and adiabatic manner. If the compression ratio,  $r_c = V_1/V_2$  of this engine is 8, determine the final temperature of the air.

T190



$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{(k-1)} \Rightarrow T_2 = T_1 \left(\frac{v_1}{v_2}\right)^{(k-1)} = 295(8)^{1.4-1} = 677.7 \text{ K} \triangleleft$$



**Example:** ▷ Determine the change in specific entropy, in KJ/kg-K, of air as an ideal gas undergoing a process from 300 K, 1 bar to 400 K, 5 bar. Because of the relatively small temperature range, we assume a constant value of  $c_p = 1.008 \text{ KJ/kg-K}$ .

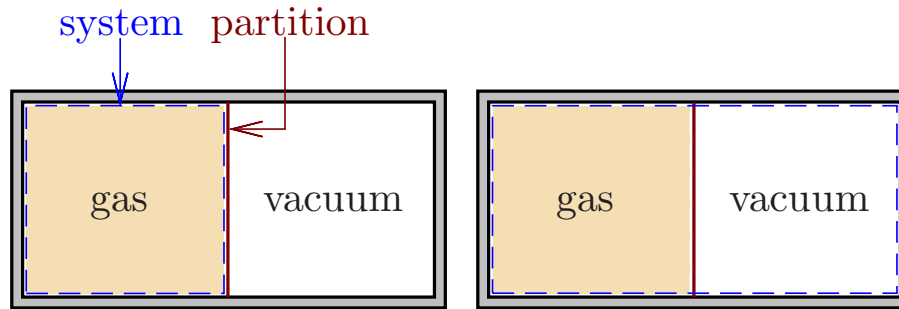
$$\begin{aligned} \Delta s &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\ &= \left(1.008 \frac{\text{kJ}}{\text{kg}\cdot\text{K}}\right) \ln \left(\frac{400\text{K}}{300\text{K}}\right) - \left(\frac{8.314 \text{ kJ}}{28.97 \text{ kg}\cdot\text{K}}\right) \ln \left(\frac{5\text{bar}}{1\text{bar}}\right) \\ &= -0.1719 \text{ kJ/kg}\cdot\text{K} \triangleleft \end{aligned}$$

Note that, for isentropic compression,  $T_{2s} = T_1(P_2/P_1)^{(k-1)/k} = 475 \text{ K}$ .

Hence, entropy change is (-) ve because of cooling of air from 475 K to 400 K.



**Example:** ▷ Air is contained in one half of an insulated tank. The other side is completely evacuated. The membrane is punctured and air quickly fills the entire volume. Calculate the specific entropy change of the isolated system.



T022

- (a) (b)
- $du = \delta q - \delta w$
  - $s_2 - s_1 = c_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right)$
  - ⇒  $w = 0, q = 0 \Rightarrow du = 0 \Rightarrow c_V dT = 0 \Rightarrow T_2 = T_1.$
  - ⇒  $s_2 - s_1 = c_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2}{v_1} \right) = 0 + 287 \ln(2) = 198.93 \text{ kJ/kg.K} \triangleleft$
  - Note that:  $s_2 - s_1 = 198.93 \text{ kJ/kg.K} > \underbrace{\left( \frac{\delta q}{T} \right)}_{=0} \Rightarrow \Delta s > 0$

