

MENG541

Advanced

Thermodynamics

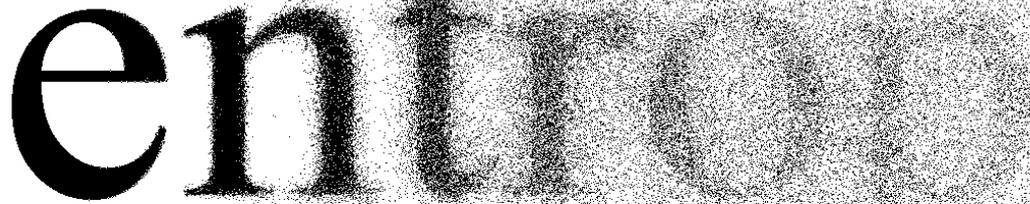
CHAPTER 3 - INTRODUCTION TO ENTROPY

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Definition of Entropy

- Entropy is a measure of disorder of a system
- Entropy is created during a process
- Entropy can not be destroyed



entropy

The Clausius Inequality

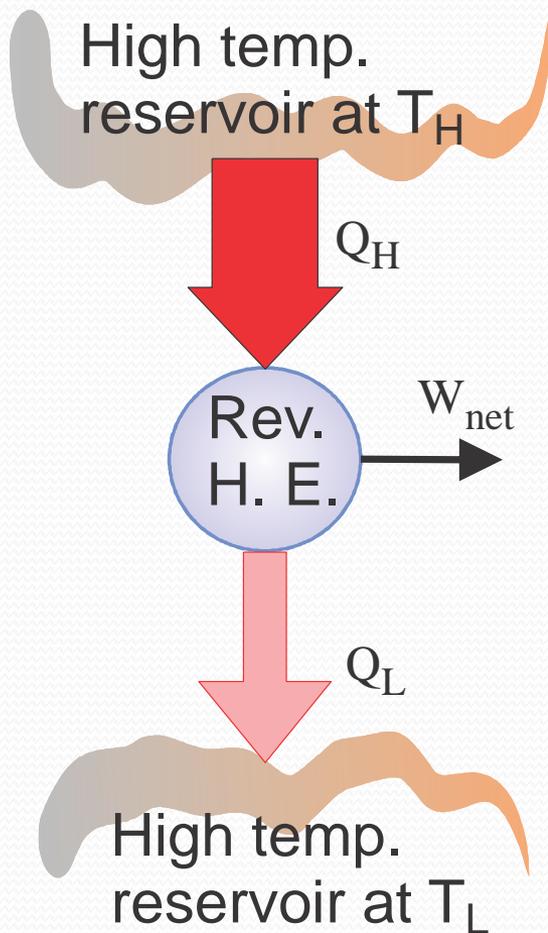
$$\oint \frac{\delta Q}{T} \leq 0 \quad \longrightarrow \quad \text{This inequality is valid for all cycles, reversible or irreversible}$$

Cyclic integral $\left\{ \begin{array}{l} = \text{ for reversible} \\ < \text{ for irreversible} \end{array} \right\}$

The cyclic integral of $\delta Q/T$ can be viewed as the sum of all the differential amounts of heat transfer divided by the temperature at the boundary.

Reversible Cycles

Using the Kelvin temperature scale



For reversible cycles:

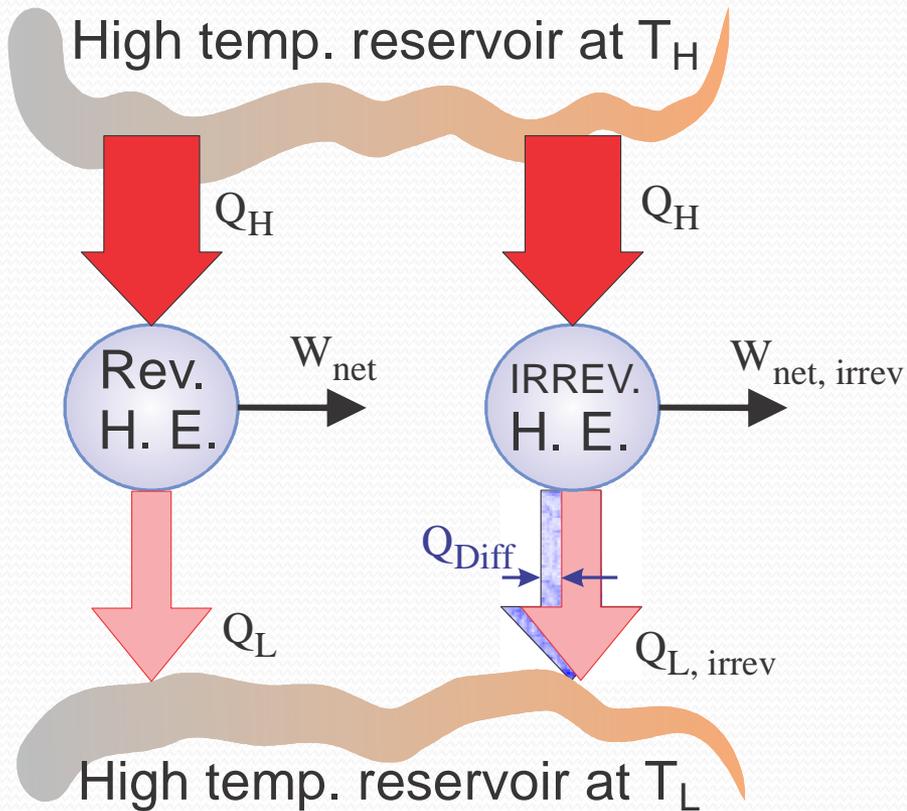
$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \rightarrow \frac{Q_L}{T_L} = \frac{Q_H}{T_H}$$

$$\oint \left(\frac{\delta Q}{T} \right)_{rev} = \int \frac{\delta Q_H}{T_H} - \int \frac{\delta Q_L}{T_L}$$

$$= \frac{1}{T_H} \int \delta Q_H - \frac{1}{T_L} \int \delta Q_L$$

$$= \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

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



For irreversible cycles:

$$Q_{L,irrev} > Q_L \quad \text{or} \quad Q_{L,irrev} = Q_L + Q_{Diff}$$

$$\oint \left(\frac{\delta Q}{T} \right)_{irrev} = \frac{Q_H}{T_H} - \frac{Q_{L,irrev}}{T_L} =$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} - \frac{Q_{Diff}}{T_L} = 0 - \frac{Q_{Diff}}{T_L}$$

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

For all cycles, the two results are combined:

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

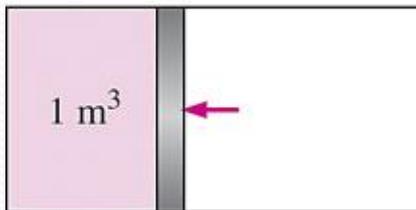
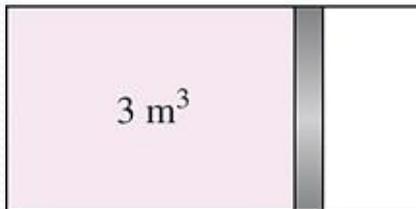
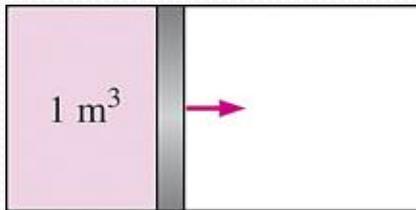
Note: $\oint \frac{\delta Q}{T} > 0$ violates the 2nd law of thermodynamics

$\oint \frac{\delta Q}{T}$ has to be always negative.

Entropy is a property

$$\oint dV = 0$$

Internally reversible

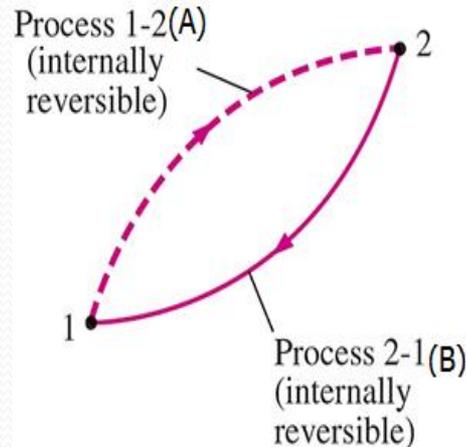


$$\oint dV = \Delta V_{\text{cycle}} = 0$$

The net change in volume (a property) during a cycle is always zero.

→ Any property change during a cycle is zero.

Since $\oint \left(\frac{\delta Q}{T} \right)_{\text{int rev}} = 0$, $\left(\frac{\delta Q}{T} \right)_{\text{int rev}}$ must represent a property in the differential form.



$$\oint \left(\frac{\delta Q}{T} \right)_{\text{int rev}} = \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_B = 0$$

$$\rightarrow \int_1^2 \left(\frac{\delta Q}{T} \right)_A = \int_1^2 \left(\frac{\delta Q}{T} \right)_B$$



The value of the integral depends on the end states only and not the path followed



This represents the change of a property



This property is called entropy, S .

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \quad (\text{kJ/K})$$

Entropy is an extensive property.

The entropy change of a system:

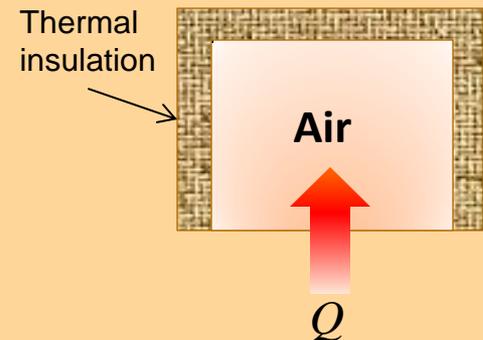
$$\Delta S = S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} \quad (\text{kJ/K})$$

Example: air temperature is raised from T_1 to T_2

$$\delta Q - \overset{0}{\cancel{\delta W}} = dU$$

$$\delta Q = dU = mC_v dT$$

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = \int_1^2 \frac{mC_v dT}{T} = mC_v \ln \frac{T_2}{T_1}$$



Special Case:

Internally Reversible Isothermal heat transfer processes:

Particularly useful for determining the entropy changes of thermal energy reservoirs that can absorb or supply heat indefinitely at constant temperature.



$$Q = 750 \text{ kJ}$$

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T}\right)_{\text{int rev}} = \int_1^2 \left(\frac{\delta Q}{T_C}\right)_{\text{int rev}} = \frac{1}{T_C} \int_1^2 (\delta Q)_{\text{int rev}}$$

$$\Delta S = \frac{Q}{T_C} \quad (\text{kJ/K})$$

Constant absolute temperature

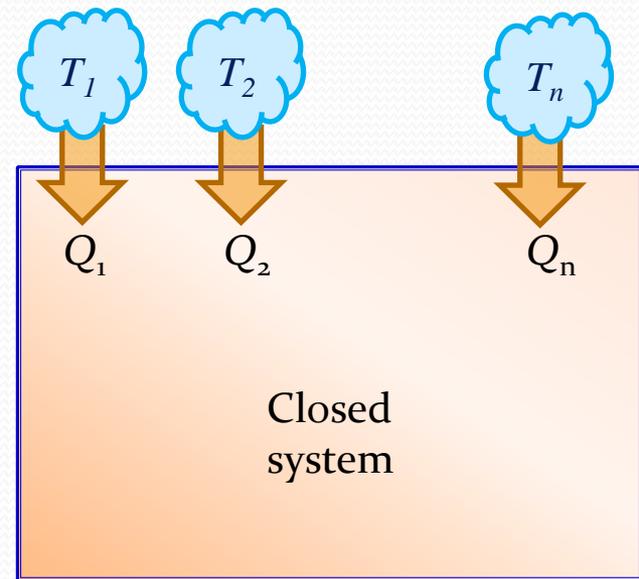
Increase of Entropy Principle: Entropy Generation

- The inequality $dS \geq \delta Q/T$ implies that for irreversible cases dS is greater than $\delta Q/T$
- Therefore $dS - \delta Q/T > 0$ and this quantity is known as *entropy generation*
- For any closed system:

$$dS_{sys} = \frac{dQ}{T} + S_{gen}$$

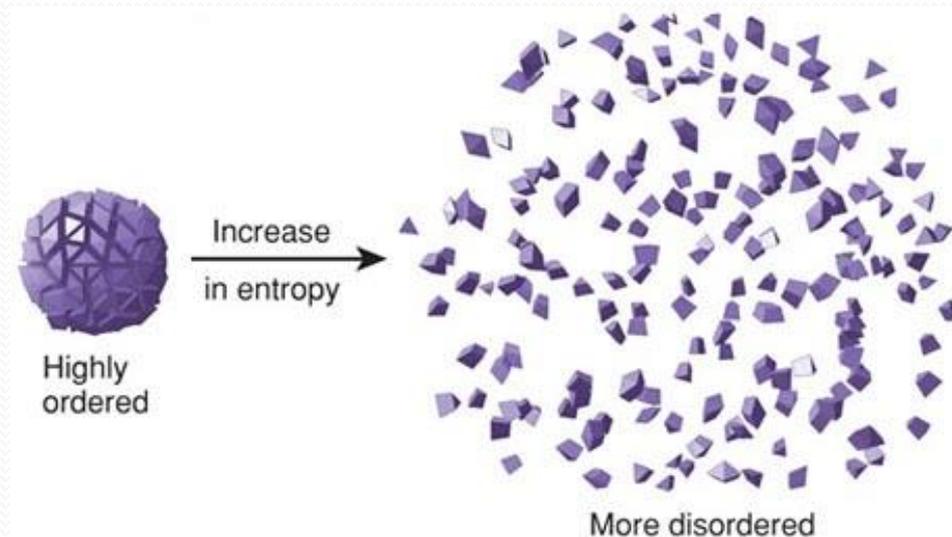
or if there are several heat transfer positions on the boundary :

$$dS_{sys} = \sum_{i=1}^n \frac{dQ_i}{T_i} + S_{gen}$$



Increase of Entropy Principle: Entropy Generation

- Consider equation $S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$
- For an isolated system $\Delta S_{Q=0} \geq 0$
- The entropy of an isolated system always increases (due to irreversibilities) or if reversible, remains constant.



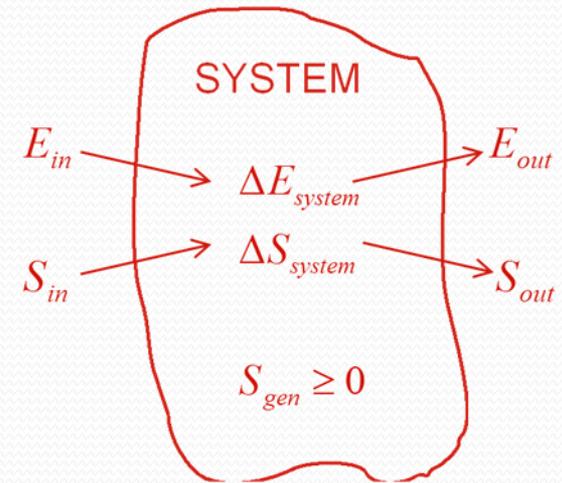
Entropy Balance

- The property *entropy* is a measure of molecular disorder or randomness of a system.
- Entropy can be created but it cannot be destroyed

$$\left(\begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{entering} \end{array} \right) - \left(\begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{leaving} \end{array} \right) + \left(\begin{array}{c} \text{Total} \\ \text{entropy} \\ \text{generated} \end{array} \right) = \left(\begin{array}{c} \text{Change in the} \\ \text{total entropy} \\ \text{of the system} \end{array} \right)$$

or

$$S_{in} - S_{out} + S_{gen} = \Delta S_{system}$$



$$\Delta E_{system} = E_{in} - E_{out}$$

$$\Delta S_{system} = S_{in} - S_{out} + S_{gen}$$

Entropy Change of a System ΔS_{sys}

Entropy change of a system = Entropy at final state – Entropy at initial state

$$\Delta S_{sys} = S_{final} - S_{initial}$$

Note: $\Delta S_{sys} = 0$ during steady state operation.

When the properties of the system are not uniform, the entropy of the system can be determined by :

$$S_{sys} = \int s \delta m = \int s \rho dV$$

density volume

Entropy Change of Pure Substances

- TdS relations:

- $$\left. \begin{aligned} h = u + Pv \rightarrow dh = du + Pdv + vdP \\ TdS = \delta Q \rightarrow Tds = du + Pdv \end{aligned} \right\} Tds = dh - vdP$$

- Hence useful relations can be obtained for ds :

- $$ds = \frac{du}{T} + \frac{Pdv}{T} \quad \text{and} \quad ds = \frac{dh}{T} - \frac{vdP}{T}$$

- We must know the relationship between du or dh and T

- $du = c_v dT$ or for ideal gases $dh = c_p dT$

- For ideal gases: $Pv = RT$ and hence:

- $$ds = c_v \frac{dT}{T} + R \frac{dv}{v} \quad \text{or} \quad ds = c_p \frac{dT}{T} - R \frac{dP}{P}$$

- For liquids and solids assume incompressible hence $dv \cong 0$

- Hence for liquids and solids: $ds = \frac{du}{T} = \frac{cdT}{T}$ since $c_p = c_v = c$
and $du = c dT$

Entropy Change of Ideal Gases

- Specific heats vary with temperature

- Therefore

$$ds = c_p \frac{dT}{T} - R \frac{dP}{P} \rightarrow s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \frac{dP}{P}$$

- Choose absolute zero as reference T and define:

$$s^\circ = \int_0^T c_p(T) \frac{dT}{T}$$

- Table A17 in Çengel* tabulate s°

- Therefore $\int_1^2 c_p(T) \frac{dT}{T} = s^\circ_2 - s^\circ_1$

- Hence $s_2 - s_1 = s^\circ_2 - s^\circ_1 - R \frac{dP}{P}$

Mechanisms of entropy transfer, S_{in} and S_{out}

- Entropy can be transferred by the following two mechanisms:

- **Heat transfer**



Heat is a chaotic form of energy and some chaos (entropy) flows with heat

- **Mass flow**



Mass contains entropy and entropy is carried with it. Entropy increases with mass

- No entropy is transferred by work

Entropy transfer by heat transfer

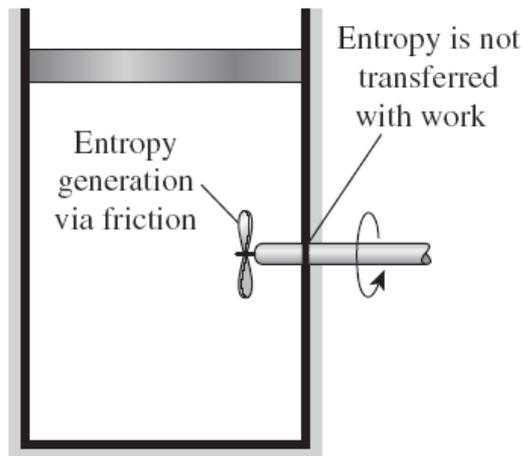
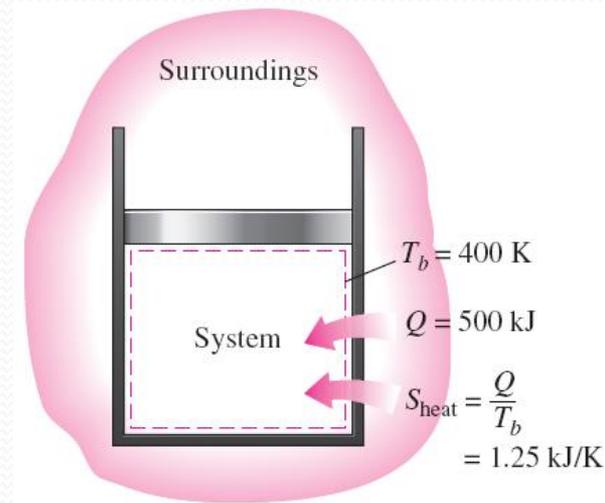
$$S_{\text{heat}} = \frac{Q}{T} \quad (T = \text{constant})$$

$$S_{\text{heat}} = \int_1^2 \frac{\delta Q}{T} \cong \sum \frac{Q_k}{T_k}$$

When temperature is not constant or different throughout the boundary

Entropy transfer by work:

$$S_{\text{work}} = 0$$



Heat transfer is always accompanied by entropy transfer in the amount of Q/T , where T is the boundary temperature.

No entropy accompanies work as it crosses the system boundary. But entropy may be generated within the system as work is dissipated into a less useful form of energy.

Entropy transfer by mass flow

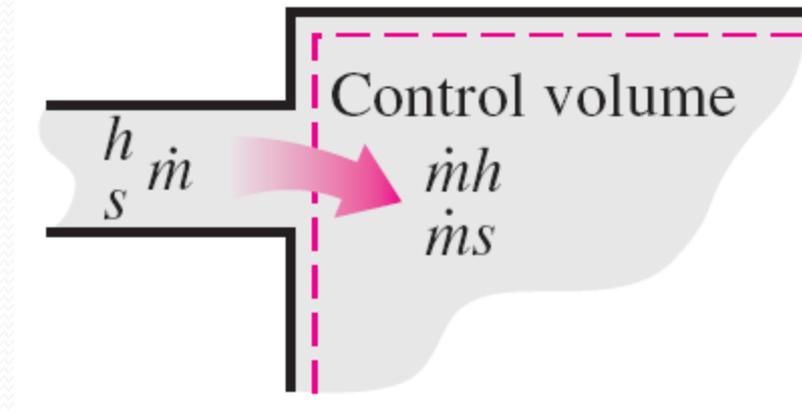
Entropy transfer by mass:

$$S_{\text{mass}} = ms$$

When the properties of the mass change during the process

$$\dot{S}_{\text{mass}} = \int_{A_c} s \rho V_n dA_c$$

$$S_{\text{mass}} = \int s \delta m = \int_{\Delta t} \dot{S}_{\text{mass}} dt$$



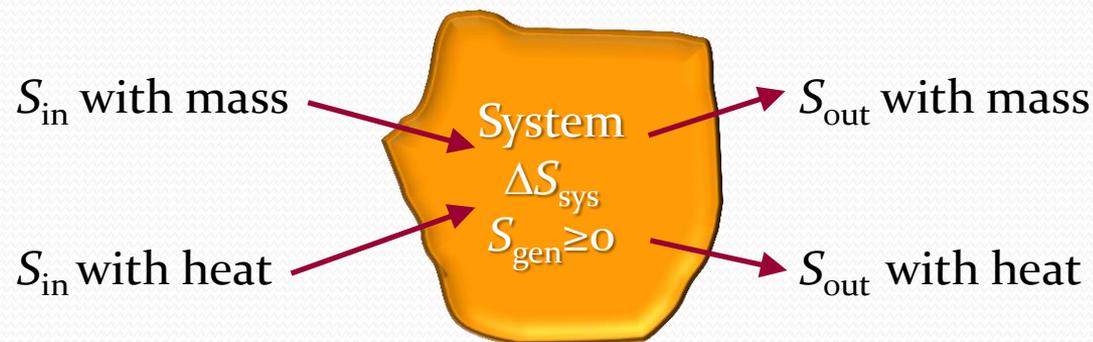
Mass contains entropy as well as energy, and thus mass flow into or out of system is always accompanied by energy and entropy transfer.

Entropy generation, S_{gen}

$$\underbrace{S_{in} - S_{out}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{gen}}_{\text{Entropy generation}} = \underbrace{\Delta S_{system}}_{\text{Change in entropy}} \quad (\text{kJ/K})$$

$$\underbrace{\dot{S}_{in} - \dot{S}_{out}}_{\text{Rate of net entropy transfer by heat and mass}} + \underbrace{\dot{S}_{gen}}_{\text{Rate of entropy generation}} = \underbrace{dS_{system}/dt}_{\text{Rate of change in entropy}} \quad (\text{kW/K})$$

$$(s_{in} - s_{out}) + s_{gen} = \Delta s_{system} \quad (\text{kJ/kg} \cdot \text{K})$$

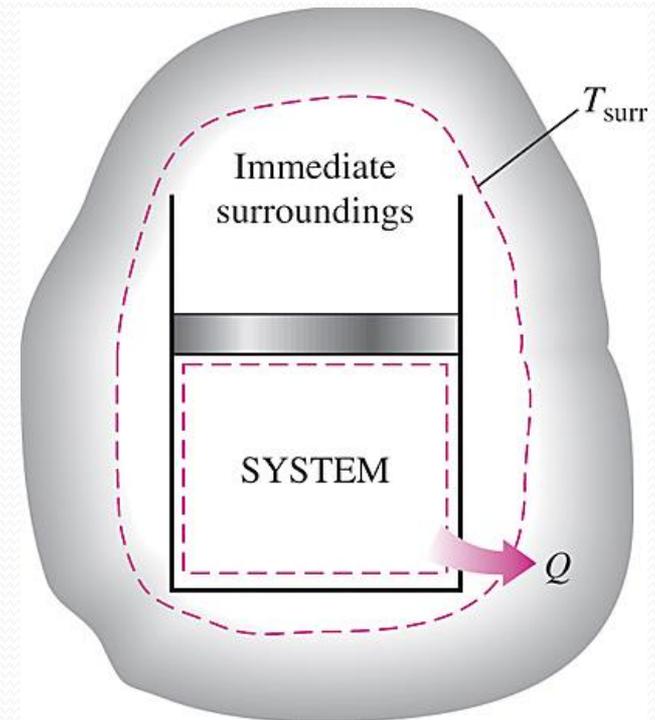


For a reversible process
 $S_{gen} = 0$

Entropy generation, S_{gen}

- The term S_{gen} represents the entropy within the system boundary only
- External irreversibilities are not accounted for in the term S_{gen} .

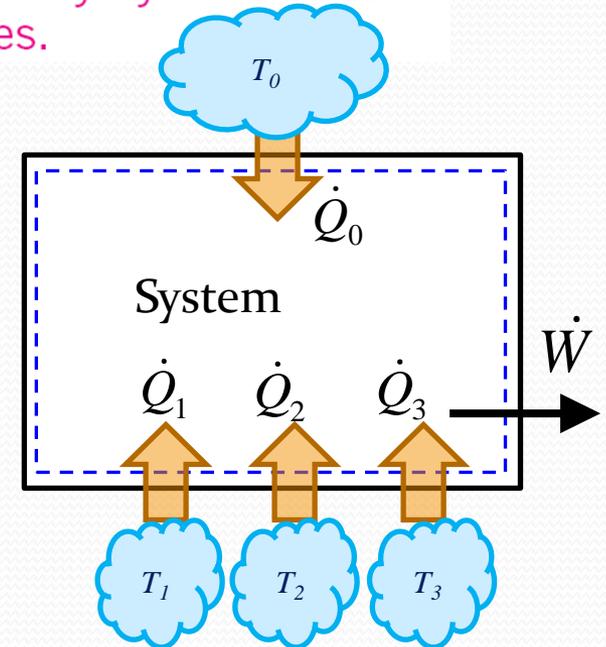
Entropy generation outside system boundaries can be accounted for by writing an entropy balance on an extended system that includes the system and its immediate surroundings.



Entropy balance of control masses (closed systems)

The entropy change of a closed system during a process is equal to the sum of the net entropy transferred through the system boundary by heat transfer and the entropy generated within the system boundaries.

$$\underbrace{\Delta S_{sys}}_{\text{Entropy change of a closed system}} = \underbrace{\sum \frac{Q_k}{T_k}}_{\text{Sum of net entropy transfer through the system boundary by heat transfer}} + \underbrace{S_{gen}}_{\text{Entropy generated}} \quad (\text{kJ/K})$$



Adiabatic closed system:

$$S_{gen} = \Delta S_{\text{adiabatic system}}$$

System + Surroundings:

$$S_{gen} = \sum \Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

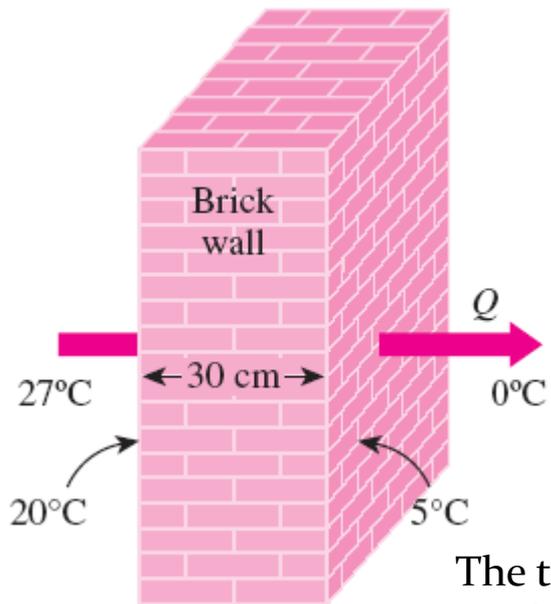
$$\Delta S_{\text{system}} = m(s_2 - s_1)$$

$$\Delta S_{\text{surr}} = Q_{\text{surr}}/T_{\text{surr}}$$

Example:

Entropy generation in a wall

Determine the rate of entropy generation in a wall of 5-m x 7-m and thickness 30 cm. The rate of heat transfer through the wall is 1035 W.



$$\underbrace{\dot{S}_{in} - \dot{S}_{out}}_{\text{Rate of net entropy transfer by heat and mass}} + \underbrace{\dot{S}_{gen}}_{\text{Rate of entropy generation}} = \underbrace{\frac{dS_{sys}}{dt}}_{\text{Rate of change in entropy}} \quad 0 \text{ (steady heat flow)}$$

$$\left(\frac{\dot{Q}}{T}\right)_{in} - \left(\frac{\dot{Q}}{T}\right)_{out} + \dot{S}_{gen} = 0$$

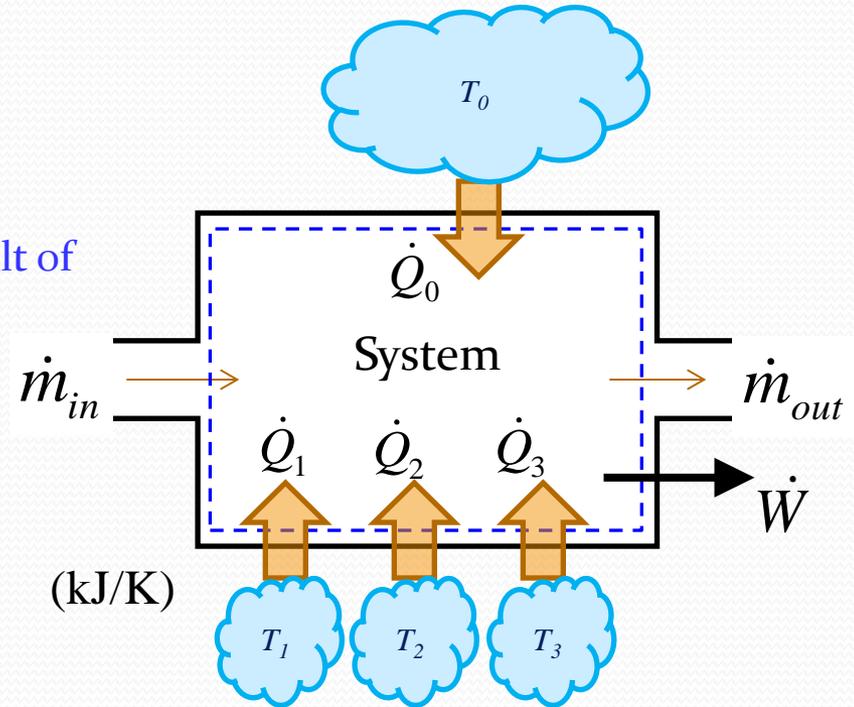
$$\frac{1035 \text{ W}}{293 \text{ K}} - \frac{1035 \text{ W}}{278 \text{ K}} + \dot{S}_{gen} = 0 \quad \Rightarrow \text{therefore } \dot{S}_{gen, wall} = 0.191 \text{ W/K}$$

The total rate of entropy generation (including the indoors and outdoors) can be found by taking into account the indoors and outdoors temperatures (extended system):

$$\frac{1035 \text{ W}}{300 \text{ K}} - \frac{1035 \text{ W}}{273 \text{ K}} + \dot{S}_{gen} = 0 \quad \Rightarrow \text{therefore } \dot{S}_{gen, total} = 0.341 \text{ W/K}$$

Entropy balance of control volumes (open systems)

The entropy of a control volume changes as a result of mass flow as well as heat transfer.



$$\sum \frac{Q_k}{T_k} + \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + S_{gen} = \underbrace{(S_2 - S_1)_{CV}}_{\Delta S_{CV}} \quad (\text{kJ/K})$$

or in the rate form :

$$\underbrace{\sum \frac{\dot{Q}_k}{T_k}}_{\text{Entropy transfer rate by heat transfer}} + \underbrace{\sum \dot{m}_i s_i - \sum \dot{m}_e s_e}_{\text{Net entropy flow rate out of the control volume via mass flow}} + \underbrace{\dot{S}_{gen}}_{\text{Entropy generation rate}} = \underbrace{\frac{dS_{CV}}{dt}}_{\text{Rate of entropy accumulation in the control volume}} \quad (\text{kW/K})$$

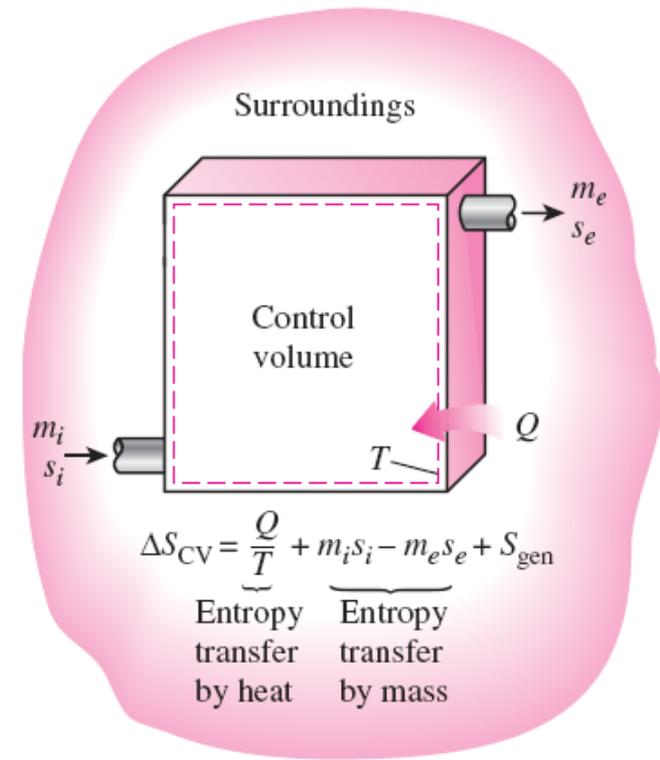
Entropy balance of control volumes (open systems)

$$\sum \frac{\dot{Q}_k}{T_k} + \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \dot{S}_{gen} = \frac{dS_{CV}}{dt}$$

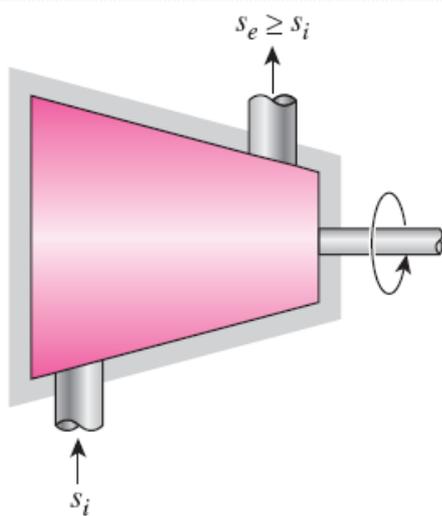
Steady-flow:
$$\dot{S}_{gen} = \sum \dot{m}_e s_e - \sum \dot{m}_i s_i - \sum \frac{\dot{Q}_k}{T_k}$$

Steady-flow, single-stream:
$$\dot{S}_{gen} = \dot{m}(s_e - s_i) - \sum \frac{\dot{Q}_k}{T_k}$$

Steady-flow, single-stream, adiabatic:
$$\dot{S}_{gen} = \dot{m}(s_e - s_i)$$



The entropy of a control volume changes as a result of mass flow as well as heat transfer.



The entropy of a substance always increases (or remains constant in the case of a reversible process) as it flows through a single-stream, adiabatic, steady-flow device.

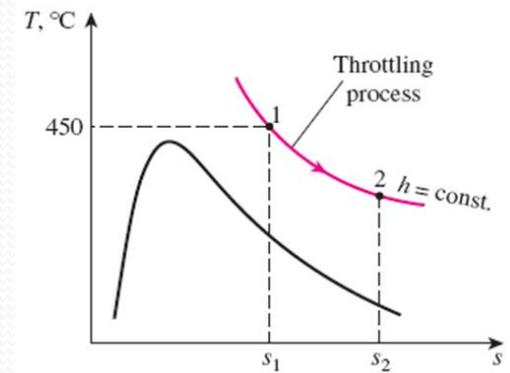
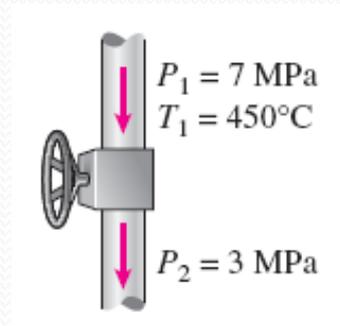
Example: Entropy generation during a throttling process

Determine the rate of entropy generation in a steady-state throttling process of steam shown in the diagram.

Use the tables to determine the entropy at the inlet and the exit states:

$$\text{State 1: } \left. \begin{array}{l} P_1 = 7 \text{ MPa} \\ T_1 = 450^\circ\text{C} \end{array} \right\} h_1 = 3288.3 \text{ kJ/kg}, s_1 = 6.6353 \text{ kJ/kg.K}$$

$$\text{State 2: } \left. \begin{array}{l} P_2 = 3 \text{ MPa} \\ h_2 = h_1 \end{array} \right\} s_2 = 7.0046 \text{ kJ/kg.K}$$



$$\sum \frac{\dot{Q}_k}{T_k} + \sum \dot{m}_i s_i - \sum \dot{m}_e s_e + \dot{S}_{gen} = \frac{dS_{CV}}{dt}$$

0 (negligible heat transfer) 0 (steady flow process)

$$\underbrace{\dot{S}_{in} - \dot{S}_{out}}_{\text{Rate of entropy transfer by mass flow}} + \underbrace{\dot{S}_{gen}}_{\text{Rate of entropy generation}} = \underbrace{\frac{dS_{sys}}{dt}}_{\text{Rate of change in entropy in the control volume}}$$

$$\dot{m}s_1 - \dot{m}s_2 + \dot{S}_{gen} = 0$$

$$\dot{S}_{gen} = \dot{m}(s_2 - s_1)$$

Dividing by mass flow rate :

$$s_{gen} = s_2 - s_1 = 7.0046 - 6.6353 = 0.3693 \text{ kJ/kg.K}$$

Example: Entropy generation in a compressor

$$\underbrace{\dot{S}_{in} - \dot{S}_{out}}_{\text{Rate of net entropy transfer by heat and mass}} + \underbrace{\dot{S}_{gen}}_{\text{Rate of entropy generation}} = \underbrace{\frac{dS_{sys}}{dt}}_{\text{Rate of change in entropy}} \quad 0 \text{ (steady flow process)}$$

$$\dot{m}s_1 - \dot{m}s_2 - \frac{\dot{Q}_{out}}{T_{b,surr}} + \dot{S}_{gen} = 0$$

$$\dot{S}_{gen} = \dot{m}(s_2 - s_1) + \frac{\dot{Q}_{out}}{T_{b,surr}}$$

For ideal gases: $s_2 - s_1 = s_2^0 - s_1^0 - R \ln \frac{P_2}{P_1}$

$$\dot{m}(s_2 - s_1)_{air} = 0.853 \text{ kg/s} (2.40902 - 1.66802) \frac{\text{kJ}}{\text{kg.K}} - 0.287 \ln \frac{1000 \text{ kPa}}{100 \text{ kPa}}$$

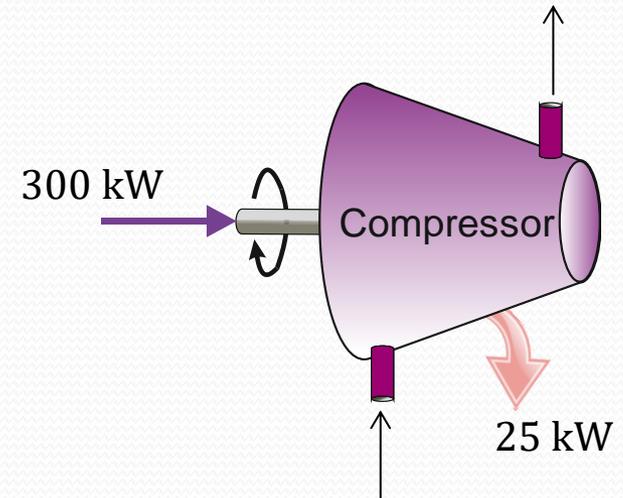
$$= 0.0684 \text{ kW/K}$$

$$\dot{S}_{gen} = 0.0684 \text{ kW/K} + \frac{25 \text{ kW}}{290 \text{ K}} = 0.155 \text{ kW/K}$$

$$P_1 = 1 \text{ MPa}$$

$$T_1 = 327^\circ\text{C}$$

$$s_2^0 = 2.40902 \text{ kJ/kg.K}$$



Air

$$\dot{m}_1 = 0.853 \text{ kg/s}$$

$$P_1 = 100 \text{ kPa}$$

$$T_1 = T_{amb} = 17^\circ\text{C}$$

$$s_1^0 = 1.66802 \text{ kJ/kg.K}$$

Example: Entropy transfer associated with heat transfer

A frictionless piston-cylinder contains saturated liquid vapor mixture at 100°C. 600kJ is lost to the environment at constant pressure leading to condensation of some vapor.

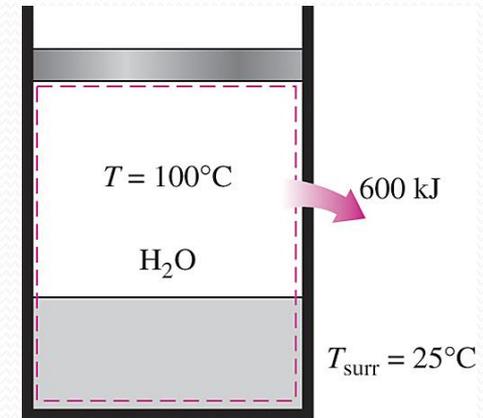
The entropy change of water :

$$\Delta S_{sys} = \frac{Q}{T_{sys}} = \frac{-600 \text{ kJ}}{(100 + 273)\text{K}} = -1.61 \text{ kJ/K}$$

$$\underbrace{S_{in} - S_{out}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{gen}}_{\text{Entropy generation}} = \underbrace{\Delta S_{sys}}_{\text{Entropy change of the system}}$$

Considering the extended system for total entropy change :

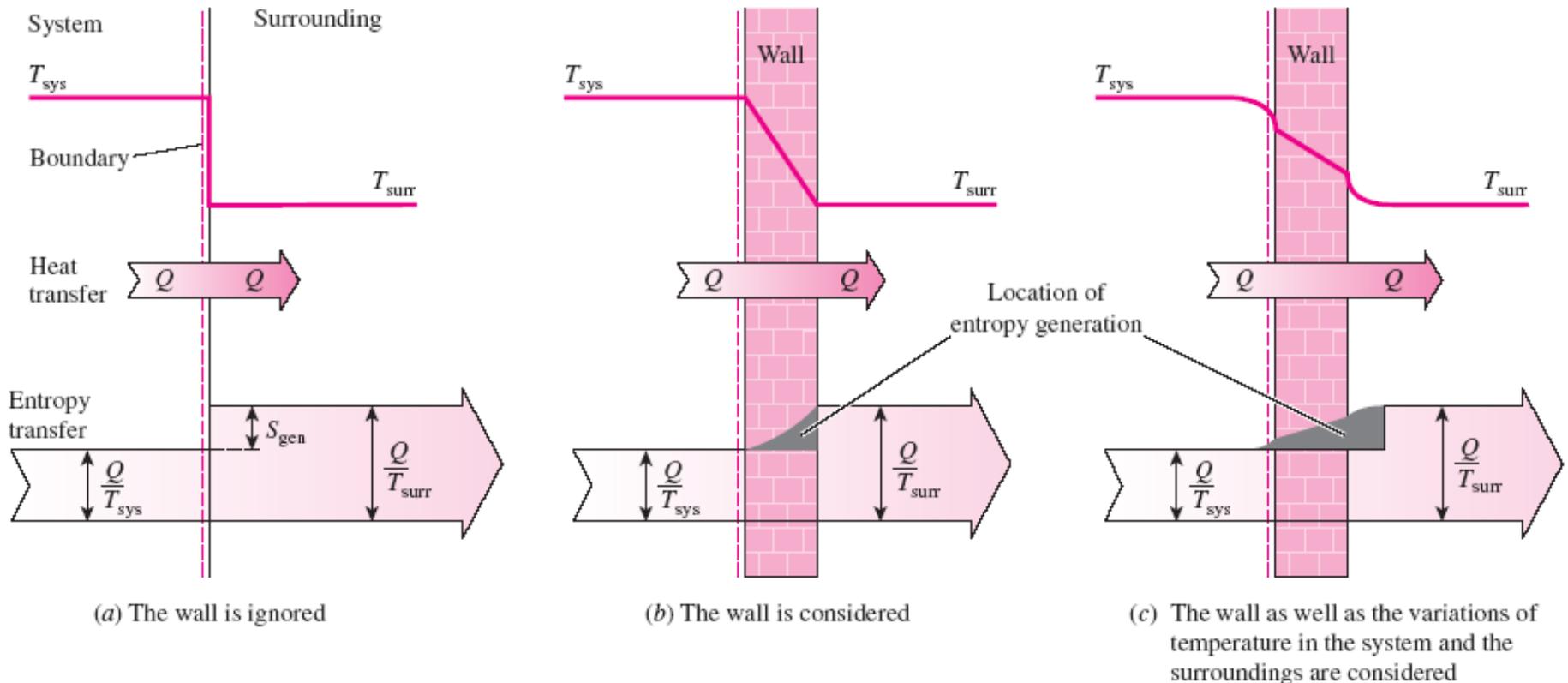
$$\begin{aligned} -\frac{Q_{out}}{T_b} + S_{gen} &= \Delta S_{sys} \Rightarrow S_{gen} = \frac{Q_{out}}{T_b} + \Delta S_{sys} \\ &= \frac{600 \text{ kJ}}{(25 + 273) \text{ K}} + (-1.61 \text{ kJ/K}) = 0.40 \text{ kJ/K} \end{aligned}$$



The *extended system* includes the water, the piston-cylinder device and the surroundings just outside the system that undergoes a temperature change. The boundary of the extended system is at T_{surr} .

Entropy generation associated with a heat transfer process

Pinpointing the **location** of **entropy generation**: Be more precise about the *system*, the *boundary* and the *surroundings*.



Homework

- Steam expands in a turbine steadily at a rate of 40,000 kg/h, entering at 8 MPa and 500°C and leaving at 40 kPa as saturated vapor. If the power generated by the turbine is 8.2 MW, determine the rate of entropy generation for this process. Assume the surrounding medium is at 25°C.

