

Second Law of - Thermodynamics

Entropy

Introduction

The second law often leads to expressions that involve inequalities.

$$\eta_{th} \begin{cases} < \eta_{th,rev} \\ = \eta_{th,rev} \end{cases}$$

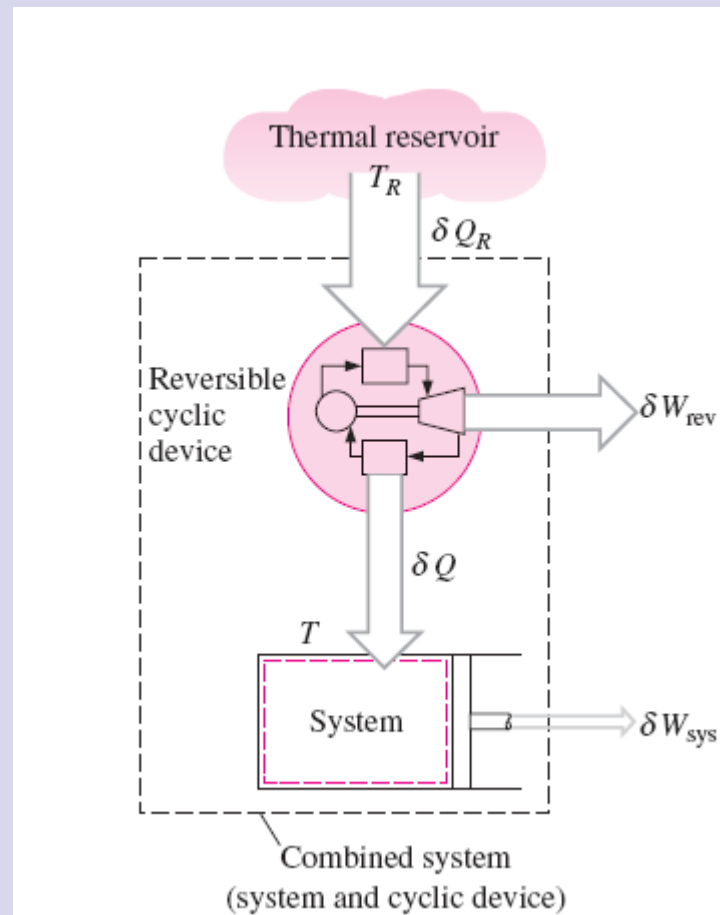
$$\eta_{th} \leq \eta_{th,rev}$$

The Inequality of Clausius

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

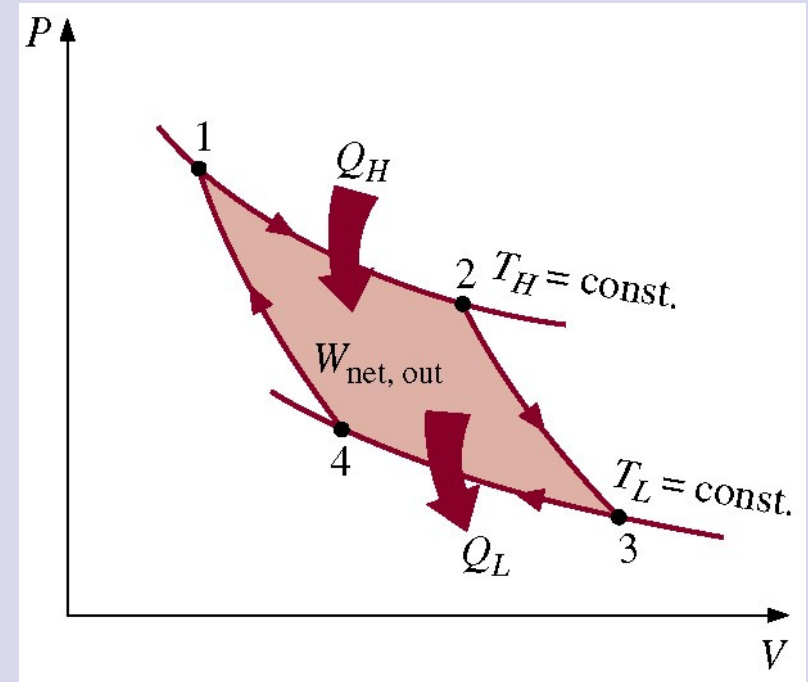
- The inequality of Clausius is a consequence of the second law of thermodynamics.
- **Q** is the heat transfer to or from the system.
- **T** is the absolute temperature at the boundary.
- The symbol $\oint$ is the cyclic integral

The Inequality of Clausius



The cyclic integral

- The cyclic integral indicates that the integral should be performed over the entire cycle and over all parts of the boundary.



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

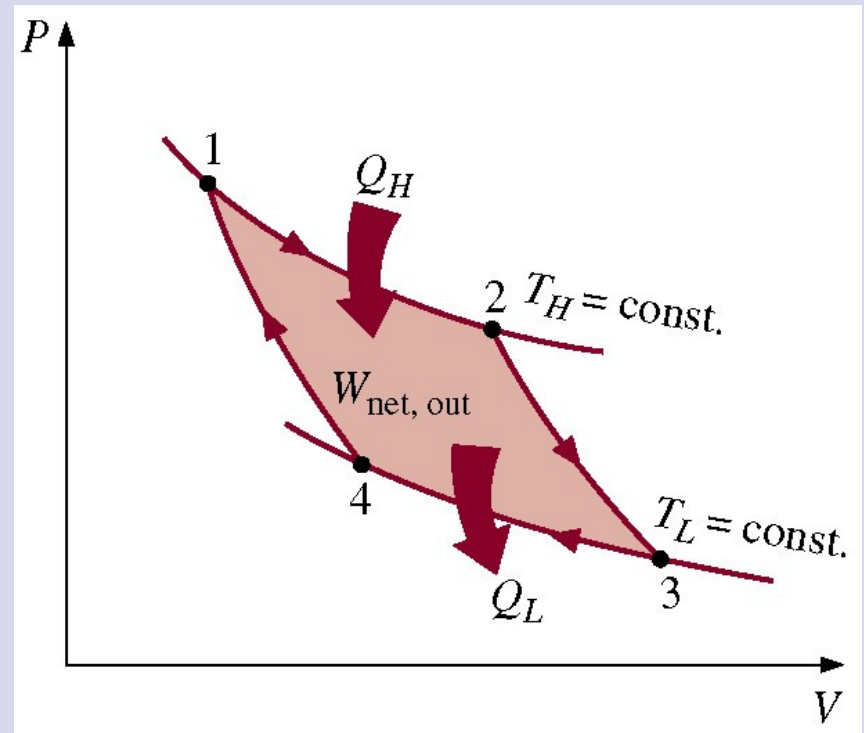
$$= \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

The cyclic integral

$$\oint \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

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

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



Derivation of Clausius Inequality

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

Irreversible	Reversible	
		Heat Engine
		Refrigeration

The cyclic integral of Reversible Heat Engine

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

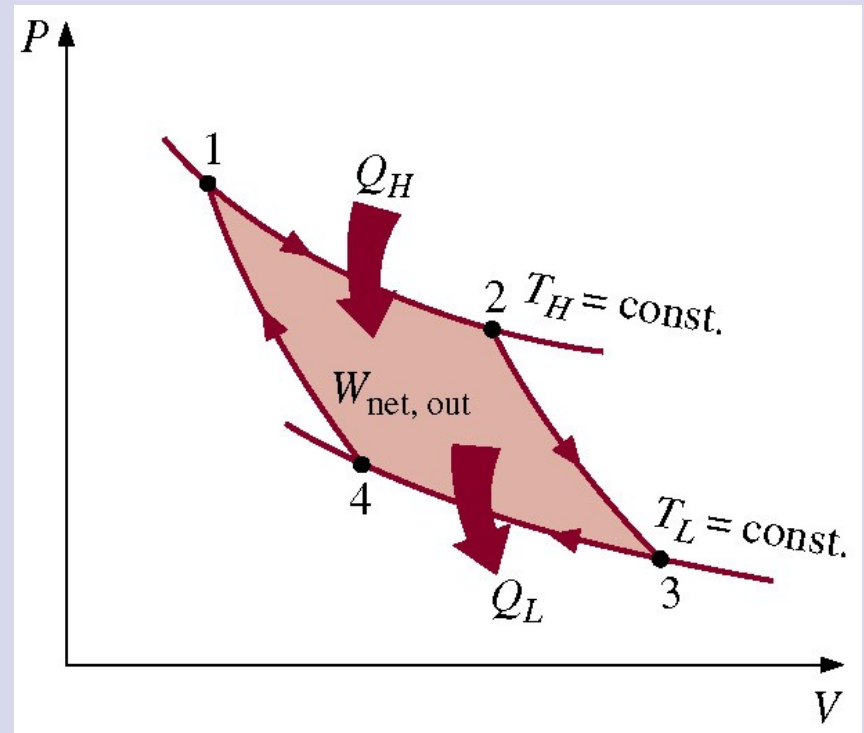
$$= \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

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

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

Since

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



The cyclic integral of Irreversible Heat Engine

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

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

We cannot use this
It is Irreversible

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

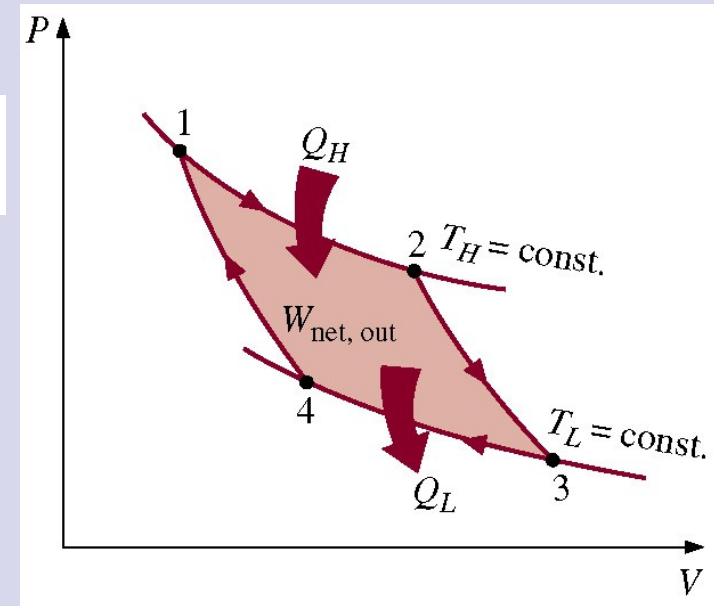
$$W_{irr} < W_{rev}$$

$$(Q_H - Q_L)_{irr} < (Q_H - Q_L)_{rev}$$

$$Q_H - Q_{L irr} < Q_H - Q_{L rev}$$

$$Q_{L irr} > Q_{L rev}$$

$$\frac{Q_H}{T_H} - \frac{Q_{L irr}}{T_L} < 0$$



The cyclic integral of Reversible Refrigeration

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

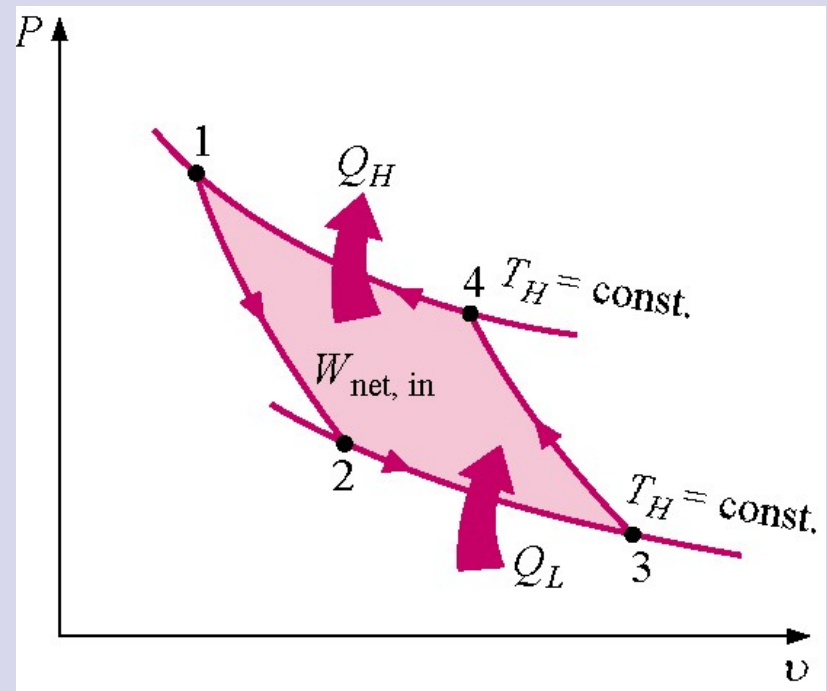
$$= \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

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

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

Since

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



The cyclic integral of Irreversible Refrigeration

$$\oint \frac{\delta Q}{T} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L}$$

We cannot use this
It is Irreversible

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

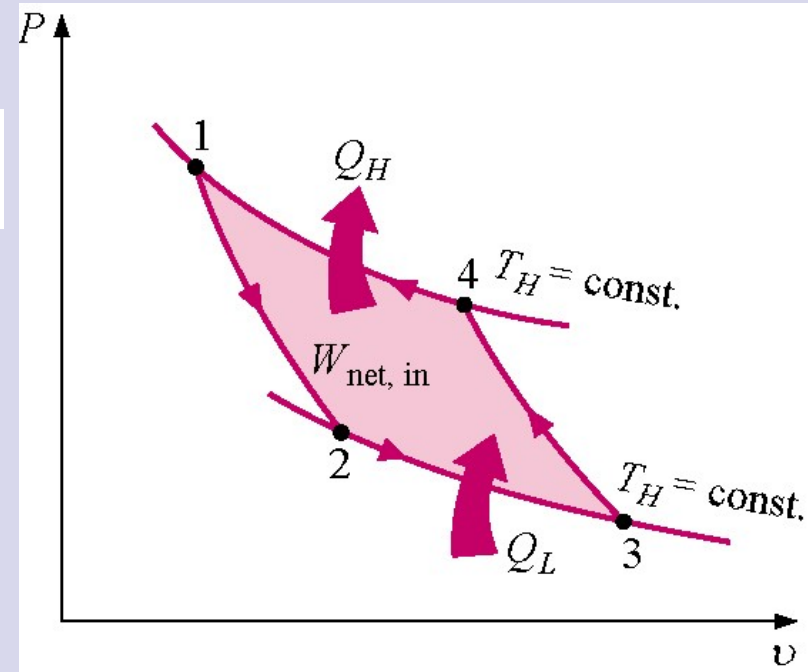
$$W_{irr} > W_{rev}$$

$$(Q_H - Q_L)_{irr} > (Q_H - Q_L)_{rev}$$

$$Q_{H\,irr} - Q_L > Q_{H\,rev} - Q_L$$

$$Q_{H\,irr} > Q_{H\,rev}$$

$$-\frac{Q_{H\,irr}}{T_H} + \frac{Q_L}{T_L} < 0$$



Derivation of Clausius Inequality

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

$\oint \frac{\delta Q}{T}$ Irreversible	Reversible	
$0 >$	$= 0$	Heat Engine
$0 >$	$= 0$	Refrigeration

The equality in the Clausius inequality holds for totally or just internally reversible cycles and the inequality for the irreversible ones.

- The Clausius inequality gives the basis for two important ideas
 - Entropy (S)
 - Entropy generation (S_g)
- These two terms gives quantitative evaluations for systems from second law perspective.

Derivation of Entropy (Reversible Process)

For reversible cycle A-B

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

For reversible cycle C-B

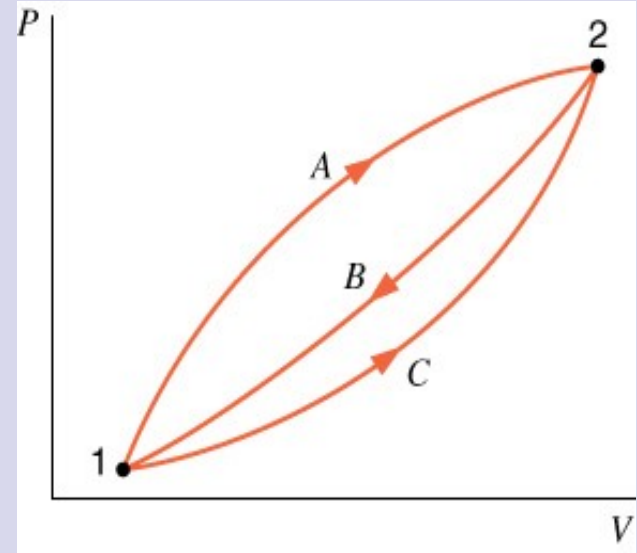
$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left(\frac{\delta Q}{T} \right)_C + \int_2^1 \left(\frac{\delta Q}{T} \right)_B = 0$$

Subtracting gives

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

Since paths A and C are arbitrary, it follows that the integral of $\delta Q/T$ has the same value for ANY reversible process between the two states.

$\therefore$ the quantity $\int \frac{\delta Q}{T}$ is independent of the path and dependent on the end states only



All paths are arbitrary

Derivation of Entropy (Reversible Process)

Recall	work & heat	are dependent on path	<u>Path functions</u>
	properties	$\begin{cases} \text{are independent of path} \\ \text{and depend on state only} \end{cases}$	<u>Point functions</u>

$\Rightarrow \int \frac{\delta Q}{T}$ is a thermodynamic property
we call it entropy (S)

Entropy (the unit)

S = entropy (kJ/K); s = specific entropy (kJ/kg K)

$$dS \equiv \left(\frac{\delta Q}{T} \right)_{rev} \quad \text{integrating} \quad S_2 - S_1 = \int \left(\frac{\delta Q}{T} \right)_{rev}$$

$S_2 - S_1$ depends on the end states only and not on the path, $\therefore$ it is same for any path reversible or irreversible

Derivation of Entropy (Irreversible Process)

Consider 2 cycles **AB** is reversible and **CB** is irreversible

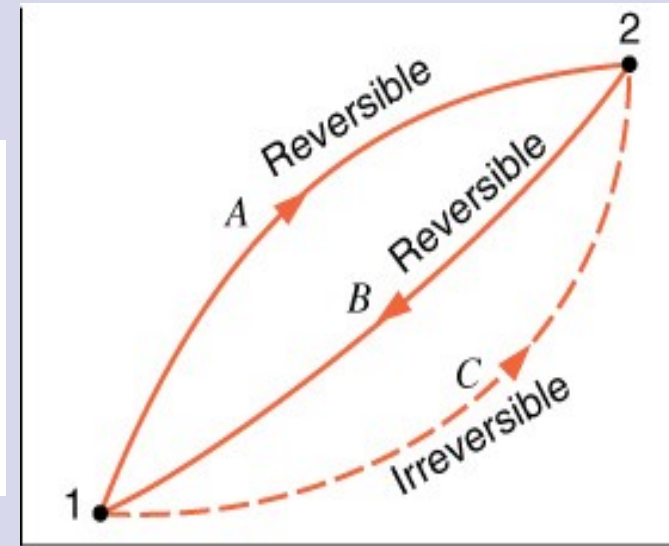
for cycle A-B (reversible)

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

for path C-B (irreversible)

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_C + \int_2^1 \left(\frac{\delta Q}{T} \right)_B < 0$$

$$\left\{ \begin{array}{l} \text{comparing gives} \\ \int_1^2 \left(\frac{\delta Q}{T} \right)_A > \int_1^2 \left(\frac{\delta Q}{T} \right)_C \end{array} \right.$$



$$\text{but } \int_1^2 \left(\frac{\delta Q}{T} \right)_A \stackrel{\text{reversible}}{=} \int_1^2 dS_A \stackrel{\text{it is a property}}{=} \int_1^2 dS_C$$

$$\therefore \int_1^2 dS_C > \int_1^2 \left(\frac{\delta Q}{T} \right)_C$$

$$\text{in general } \Rightarrow dS \geq \frac{\delta Q}{T}$$

$$\text{or } S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

equality for reversible
inequality for irreversible

Derivation of Entropy (Any Process)

$$dS \geq \frac{\delta Q}{T}$$

$$\text{or } S_2 - S_1 \geq \int \frac{\delta Q}{T}$$

equality for reversible
inequality for irreversible

This can be written out in a common form as an equality

$$dS \equiv \frac{\delta Q}{T} + \delta S_{gen}$$

or

$$S_2 - S_1 = \int \frac{\delta Q}{T} + S_{gen} \quad \left\{ \begin{array}{l} \text{for any process,} \\ \text{with } S_{gen} \geq 0 \end{array} \right.$$

2nd law of thermodynamics for a closed system

Entropy Balance Equation for a closed system

$$S_{gen} \equiv \text{entropy generation} \quad \left\{ \begin{array}{l} > 0 \text{ for irreversible process} \\ = 0 \text{ for a reversible process} \end{array} \right.$$

In any irreversible process always entropy is generated ($S_{gen} > 0$) due to irreversibilities occurring inside the system.

Example (6-1) Entropy change during isothermal process

A friction-less piston-cylinder device contains a liquid-vapor mixture of water at 300 K. During a constant pressure process, 750 kJ of heat is transferred to the water. As a result, part of the liquid in the cylinder vaporizes. Determine the entropy change of the water during this process.

Solution:

- This is simple problem.
- No irreversibilities occur within the system boundaries during the heat transfer process.
- Hence, the process is internally reversible process ($S_g = 0$).

$$\Delta S = \int \left(\frac{\delta Q}{T} \right)_{rev} = \frac{1}{T} \int (\delta Q)_{rev} = \frac{Q}{T}$$

$$\Delta S = \frac{Q}{T}$$

$$\Delta S = \frac{Q}{T_{sys}} = \frac{750 \text{ kJ}}{300 \text{ K}} = 2.5 \text{ kJ / K}$$

- We computed the entropy change for a system using the RHS of the equation.
- But we can not get easy form each time.
- So, we need to know how to evaluate the LHS which is path independent.

Entropy change for different substances ($\Delta S = S_2 - S_1$)

- We need to find how to compute the left hand side of the entropy balance for the following substances:
 1. Pure substance like water, R-134, Ammonia etc..
 2. Solids and liquids
 3. Ideal gas

ΔS for Pure Substances -1

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

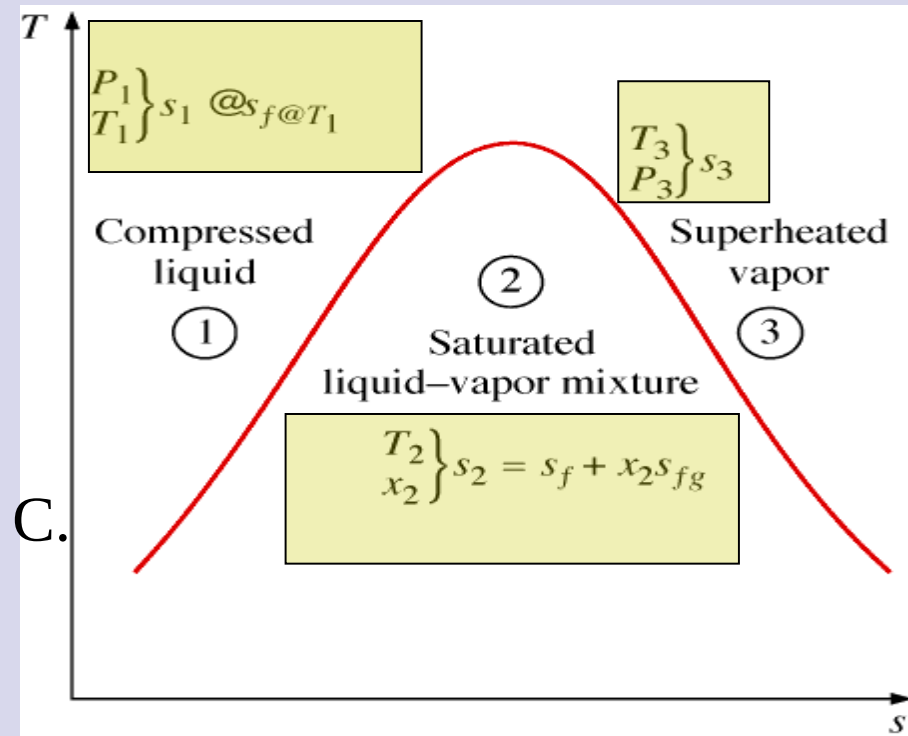
These values were tabulated after conducting a tedious integration.

These values are given relative to an arbitrary reference state.

For water its assigned zero at 0.01 C.
For R-134 it is assigned a zero at -40 C.

Entropy change for a closed system with mass m is given as expected:

$$\Delta S = m(s_2 - s_1)$$



The increase of entropy principle (closed system)

There is some entropy generated during an irreversible process such that

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

Entropy
change

Entropy transfer
with heat

Entropy generation
due to irreversibility

This is the entropy balance for a closed system.

The increase of entropy principle (closed system)

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

- The entropy change can be evaluated independently of the process details.
- However, the entropy generation depends on the process, and thus it is not a property of the system.
- The entropy generation is always a positive quantity or zero and this generation is due to the presence of irreversibilities.
- The direction of entropy transfer is the same as the direction of the heat transfer: a positive value means entropy is transferred into the system and a negative value means entropy is transferred out of the system.

The increase of entropy principle (closed system)

- For an isolated (or simply an **adiabatic** closed system), the heat transfer is zero, then

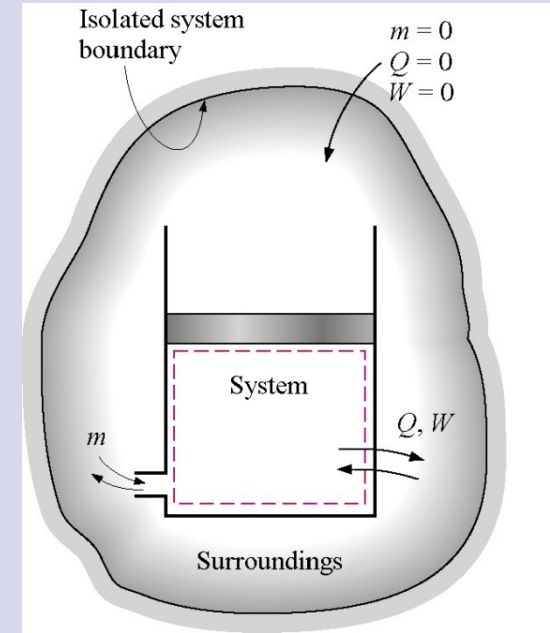
$$\Delta S = S_2 - S_1 = \cancel{\int \frac{\delta Q}{T}} + S_{\text{gen}} \Rightarrow \Delta S_{\text{adiabatic}} = S_{\text{gen}}$$

- This means that the entropy of an adiabatic system during a process always increases or, In the limiting case of a reversible process, remains constant.
- In other words, it never decreases.
- This is called ***Increase of entropy principle.***
- This principle is a quantitative measure of the second law

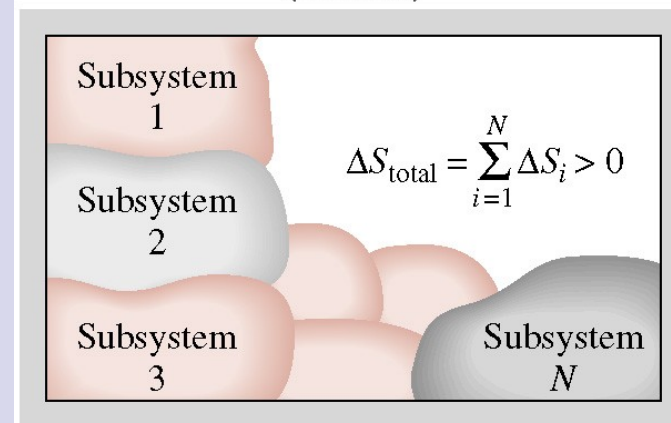
The increase of entropy principle

- Now suppose the system is not adiabatic.
- We can make it adiabatic by extending the surrounding until no heat, mass, or work are crossing the boundary of the surrounding.
- This way, the system and its surroundings can be viewed again as an isolated system.
- The entropy change of an isolated system is the sum of the entropy changes of its components (the system and its surroundings), and is never less than zero.
- Now, let us apply the entropy balance for an isolated system:

$$S_{gen} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$



(Isolated)



Summary of the increase of entropy principle

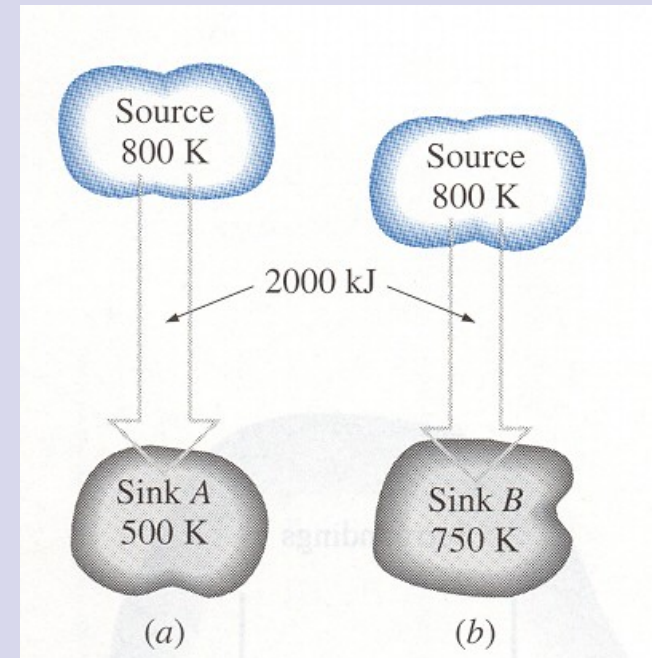
$$S_{gen} \begin{cases} > 0 & \text{irreversible process} \\ = 0 & \text{reversible process} \\ < 0 & \text{impossible process} \end{cases}$$

Let us now have an example on this concept.

Example (6-2): entropy generation during heat transfer processes

A heat source at 800 K losses 2000 kJ of heat to a sink at (a) 500 K and (b) 750 K. Determine which heat transfer process is more irreversible.

- Solution:
- Both cases involve heat transfer via a finite temperature difference and thus are irreversible.
- Each reservoir undergoes an internally reversible isothermal process.



Take the two reservoirs as your system. Thus they form an adiabatic system and thus

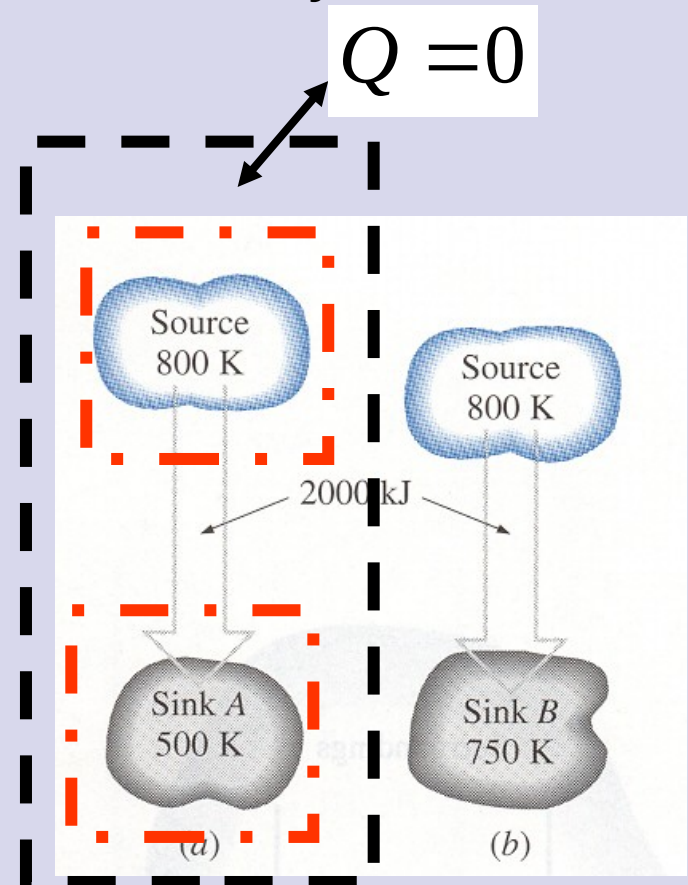
$$\Delta S_{total} = \frac{Q}{T} + S_{gen} = 0, \text{ (adiabatic)}$$

$$\Delta S_{total} = 0 + S_{gen} = \Delta S_{sys} + \Delta S_{surr}$$

Now consider each system alone

$$\Delta S_{source} = \frac{Q}{T} + S_{gen} = 0, \text{ Int. reversible}$$

$$\Delta S_{sink} = \frac{Q}{T} + S_{gen} = 0, \text{ Int. reversible}$$



$$\Delta S_{source} = \frac{-2000}{800} = -2.5 \text{ kJ/K}, \quad \Delta S_{sink} = \frac{2000}{500} = +4.0 \text{ kJ/K}$$

$$\therefore \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = -2.5 + 4.0 = +1.5 = S_{gen}$$

Let us repeat the same with case b.

$$\Delta S_{total} = \frac{Q}{T} + S_{gen} = 0, \text{ (adiabatic)}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 0 + S_{gen}$$

Now consider each system alone

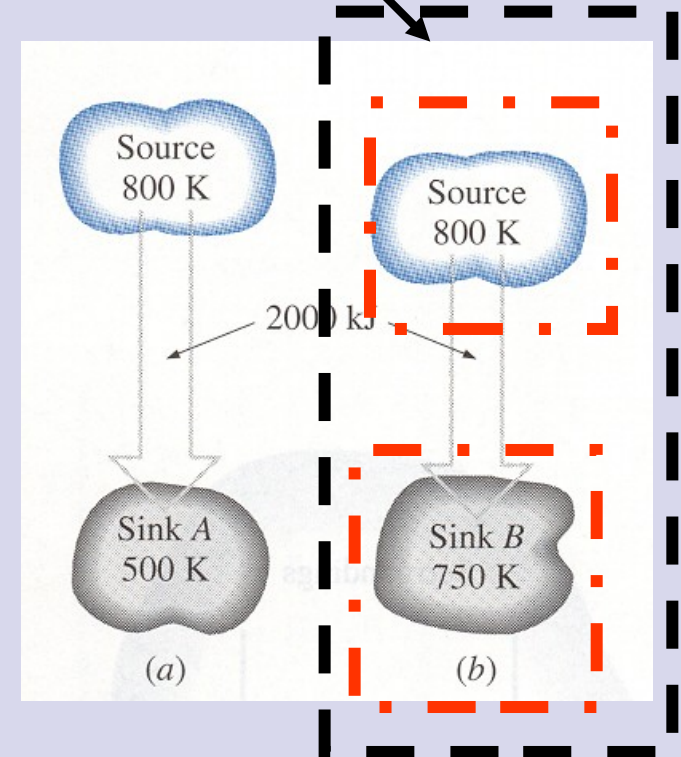
$$\Delta S_{source} = \frac{-2000}{800} = -2.5 \text{ kJ / K}$$

$$\Delta S_{sink} = \frac{2000}{750} = +2.7 \text{ kJ / K}$$

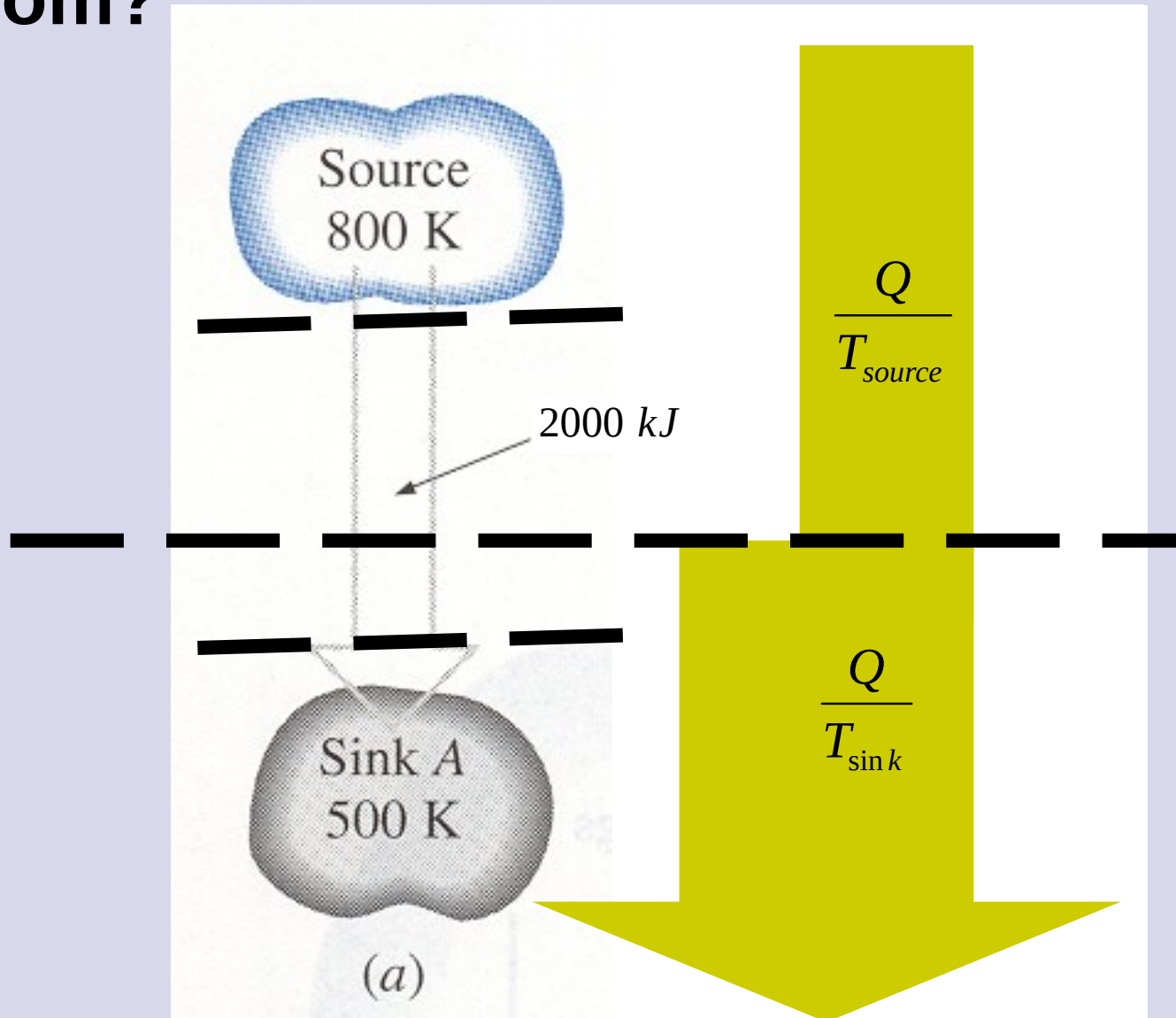
$$\therefore \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = -2.5 + 2.7 = +0.2 = S_{gen}$$

Hence the case b involves less irreversibility.

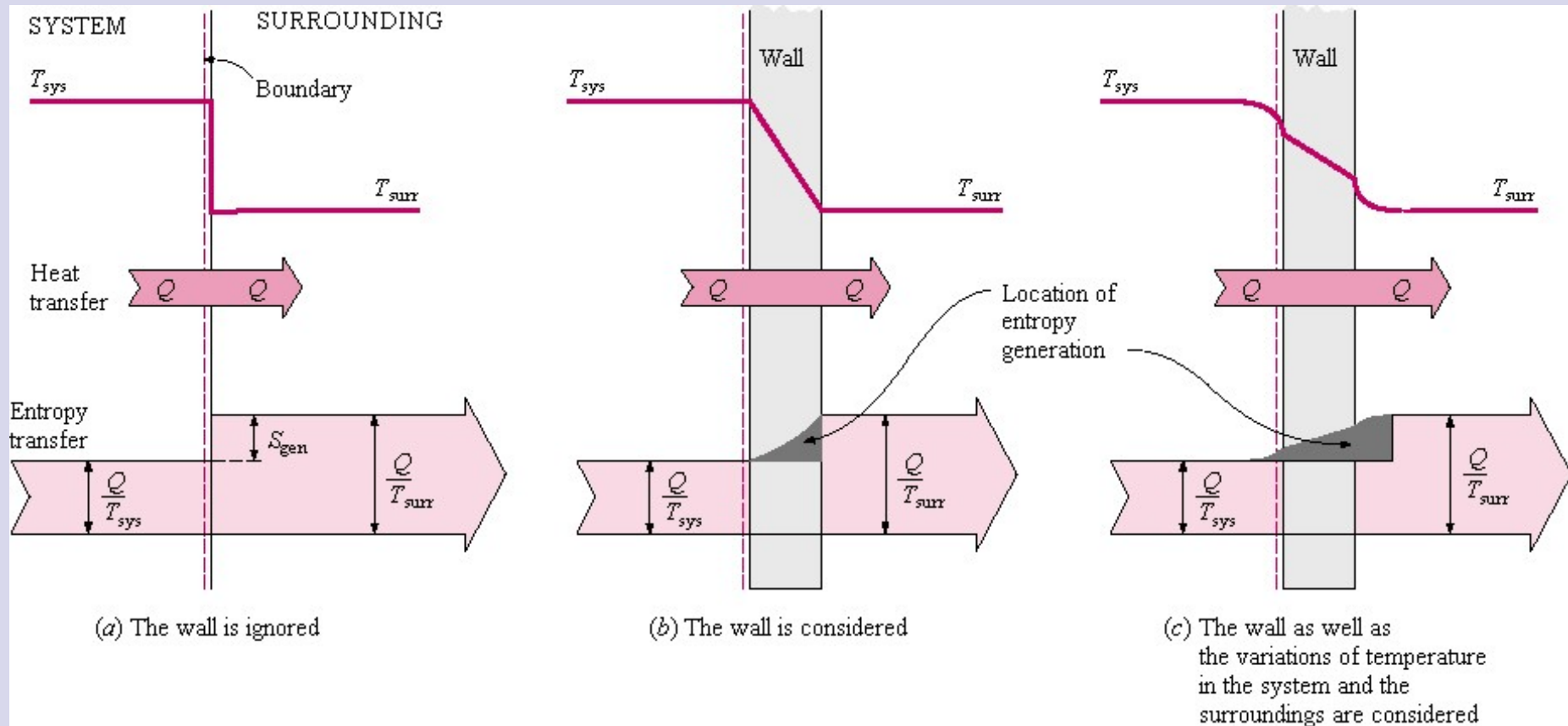
$$Q = 0$$



Where does the irreversibility arise from?

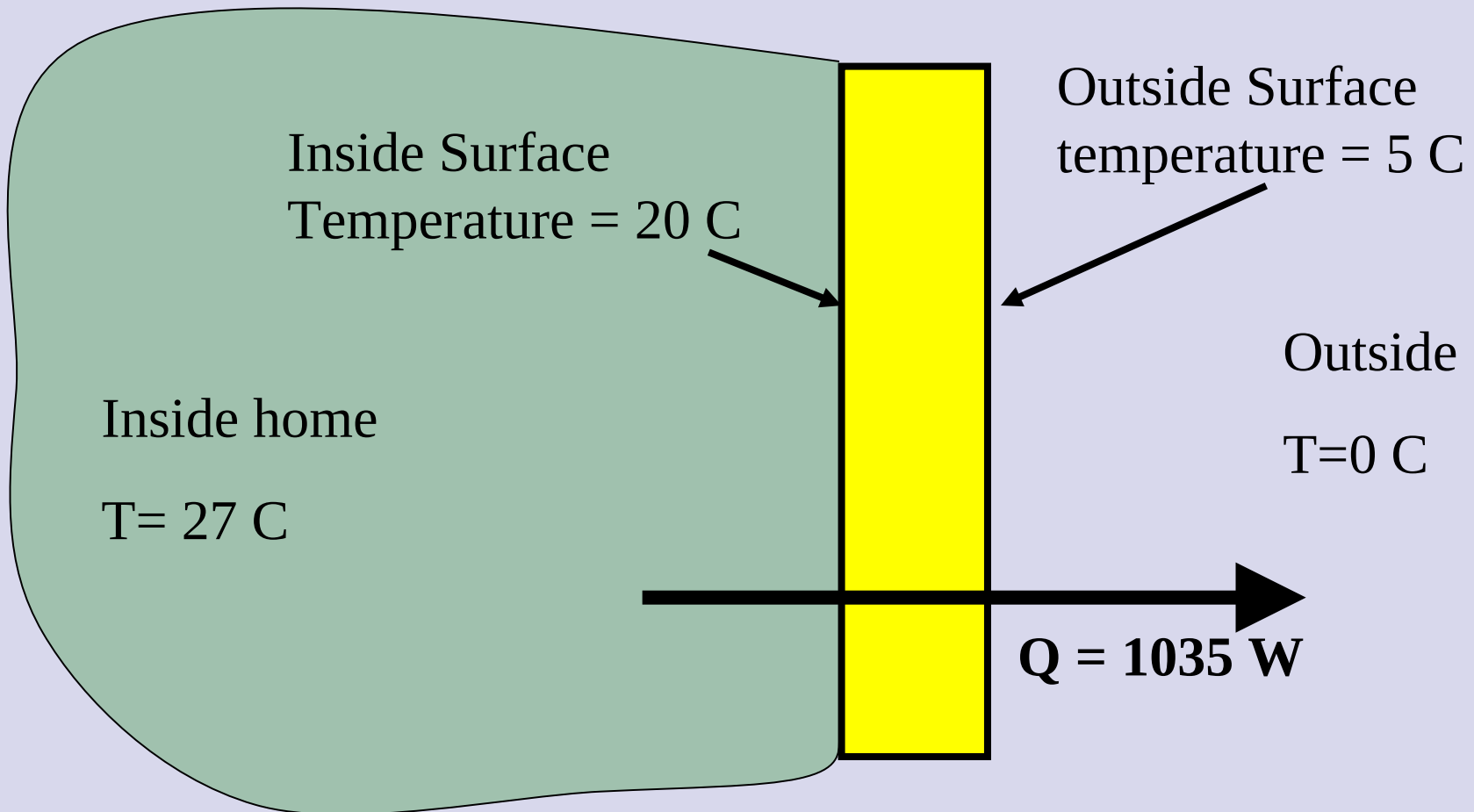


?Where is entropy generated



Example (6-17): Entropy Generation in a Wall

Steady heat transfer in a wall. The temperatures are shown in the figure. The rate of heat transfer through the wall is 1035 W.



A) Determine the rate of entropy generation in the wall

This is a steady state problem.

$$\frac{\dot{Q}_k}{T_k} + \dot{m}_i s_i - \dot{m}_e s_e + \dot{S}_{gen} = 0$$

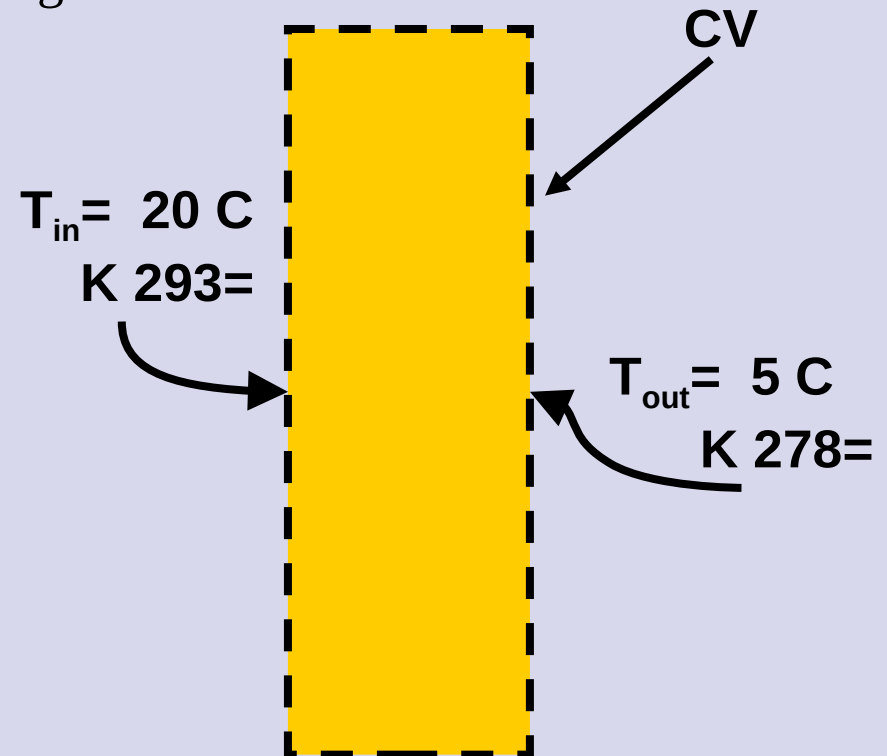
$$\frac{\dot{Q}_{in}}{T_{in}} - \frac{\dot{Q}_{out}}{T_{out}} + \dot{S}_{gen} = 0$$

$$\frac{1035 \text{ W}}{293 \text{ K}} - \frac{1035 \text{ W}}{278 \text{ K}} + \dot{S}_{gen} = 0$$

$$\dot{S}_{gen} = 0.191 \text{ W/K}$$

We have to set the CV correctly.

For part a of the question, the CV boundary will be as shown in the figure below.



B) Determine the rate of entropy generation for the process

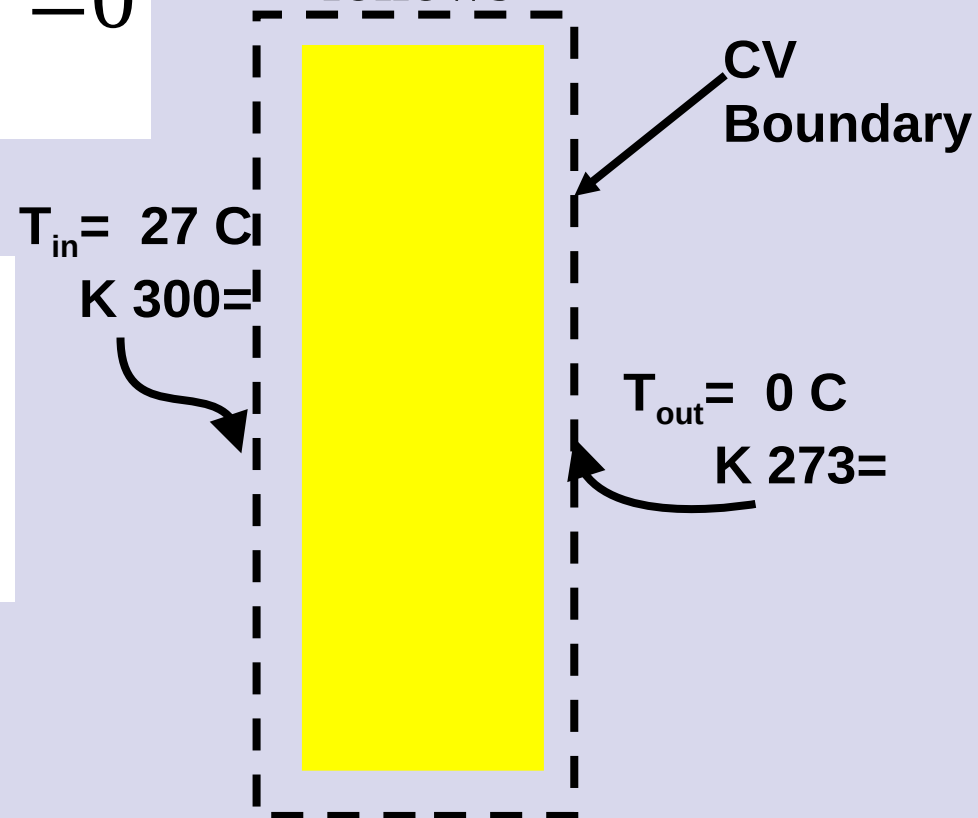
$$\frac{\dot{Q}_k}{T_k} + \cancel{\dot{m}_i s_i} - \cancel{\dot{m}_e s_e} + \dot{S}_{gen} = 0$$

$$\frac{\dot{Q}_{in}}{T_{in}} - \frac{\dot{Q}_{out}}{T_{out}} + \dot{S}_{gen} = 0$$

$$\frac{1035 \text{ W}}{300 \text{ K}} - \frac{1035 \text{ W}}{273 \text{ K}} + \dot{S}_{gen} = 0$$

$$\dot{S}_{gen} = 0.341 \text{ W/K}$$

We will extend the CV boundary as follows



Special case: S_{gen} for closed system with constant temperature surroundings T_{surr}

$$S_{gen} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{sys} = S_2 - S_1 = m(s_2 - s_1)$$

for closed system

$$\Delta S_{surr} = \frac{Q_{surr}}{T_{surr}} = - \frac{Q_{sys}}{T_{surr}}$$

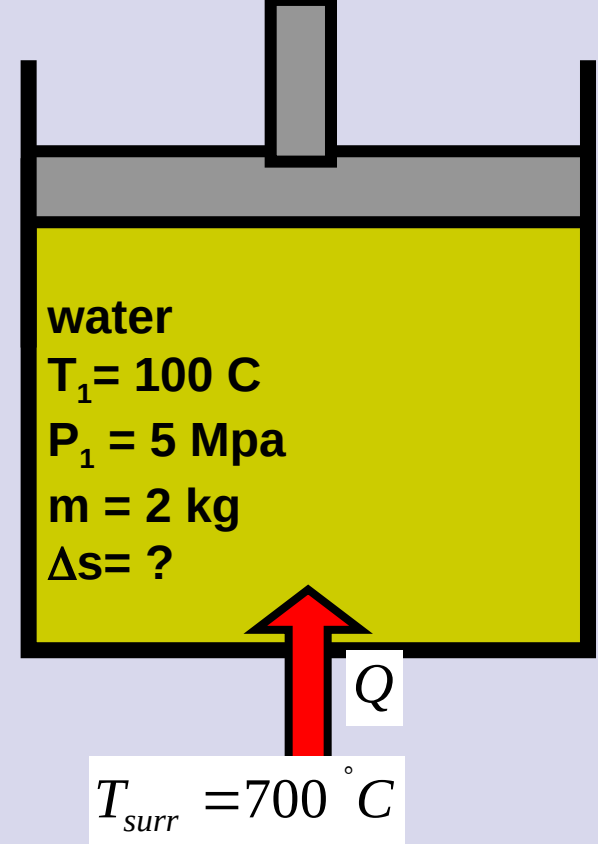
$$S_{gen} = m(s_2 - s_1) - \frac{Q_{sys}}{T_{surr}} \geq 0$$

system surroundings

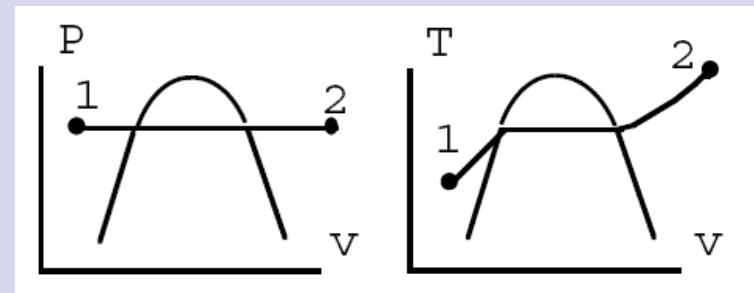
Example:

A piston/cylinder contains 2 kg of water at 5 MPa, 100°C. Heat is added from a reservoir at 700°C to the water until it reaches 700°C.

Find the work, heat transfer, and total entropy production for the system and surroundings.



- Solution
- This is a constant pressure process.
- Hence the work is , $W = mP(v_2 - v_1)$
- To get the heat,
- $Q - W = m(u_2 - u_1) \Rightarrow Q = m(h_2 - h_1)$



To get the entropy change for the system, $\Delta s = m(s_2 - s_1)$

To get the total entropy production for the system and the surrounding, we apply the entropy balance equation for the extended system (system + the immediate surrounding).

$$S_{gen} = m(s_2 - s_1) - \frac{Q_{sys}}{T_{surr}}$$

system *surroundings*

So let us begin our solution. State 1 is fixed.
Go to the tables and get the following

$$v_1 = 0.00104$$

$$u_1 = 417.52$$

$$h_1 = 422.72,$$

$$s_1 = 1.303$$

State 2 is fixed also since the pressure is constant ($P_2=P_1$).

Go to the tables and get the following

$$v_2 = 0.08849 \quad u_2 = 3457.6$$

$$h_2 = 3900.1 \quad s_2 = 7.5122,$$

$${}_1Q_2 = 2(3900.1 - 422.72) = \mathbf{6954.76 \text{ kJ}}$$

$${}_1W_2 = {}_1Q_2 - m(u_2 - u_1) = \mathbf{874.6 \text{ kJ}}$$

$$m(s_2 - s_1) = {}_1Q_2/T_{\text{res}} + {}_1S_2_{\text{gen}}$$

$${}_1S_2_{\text{gen}} = m(s_2 - s_1) - {}_1Q_2/T_{\text{res}}$$

$$= 2(7.5122 - 1.303) - 6954/973 = \mathbf{5.27 \text{ kJ/K}}$$

Some Remarks about Entropy

Processes can occur in certain direction only, a direction that complies with the increase of entropy.

$$S_{gen} \geq 0$$

Entropy is a non- conserve property. Entropy is conserved during the idealized reversible process only and increasing during all actual processes.

The greater the extent of the irreversibilities, the greater the entropy generation. Therefore, it can be used as a quantitative measure of irreversibilities.

Property diagrams involving entropy

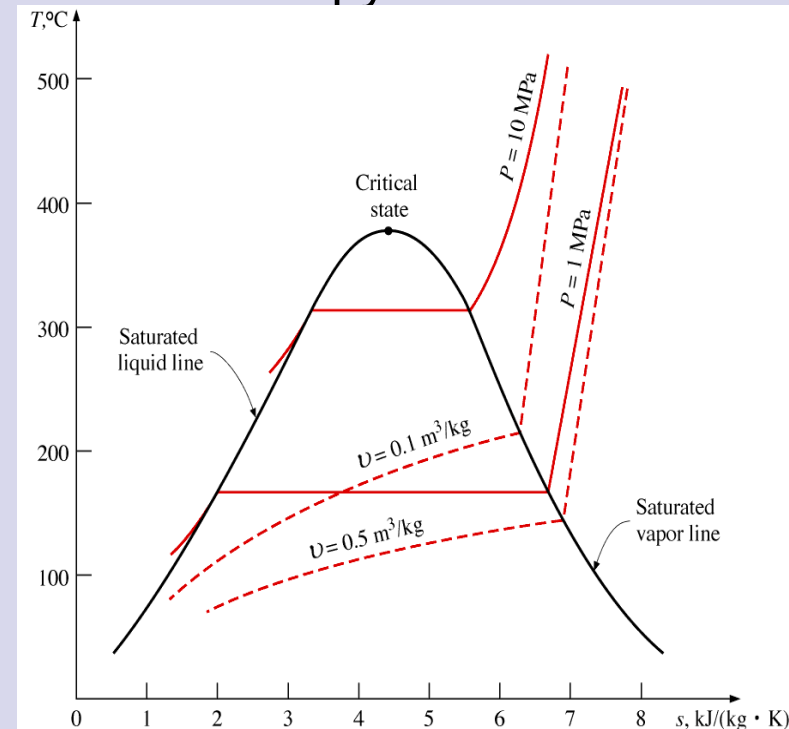
In the second-law analysis, it is very helpful to plot the processes on T-s and h-s diagrams for which one of the coordinates is entropy.

- Recall the definition of entropy

$$dS = \frac{\delta Q_{\text{int,rev}}}{T}$$

$$\delta Q_{\text{int,rev}} = TdS$$

- Property diagrams serves as great visual aids in the thermodynamic analysis of process.
- We have used P-v and T-v diagrams extensively in conjunction with the first law of thermodynamics.



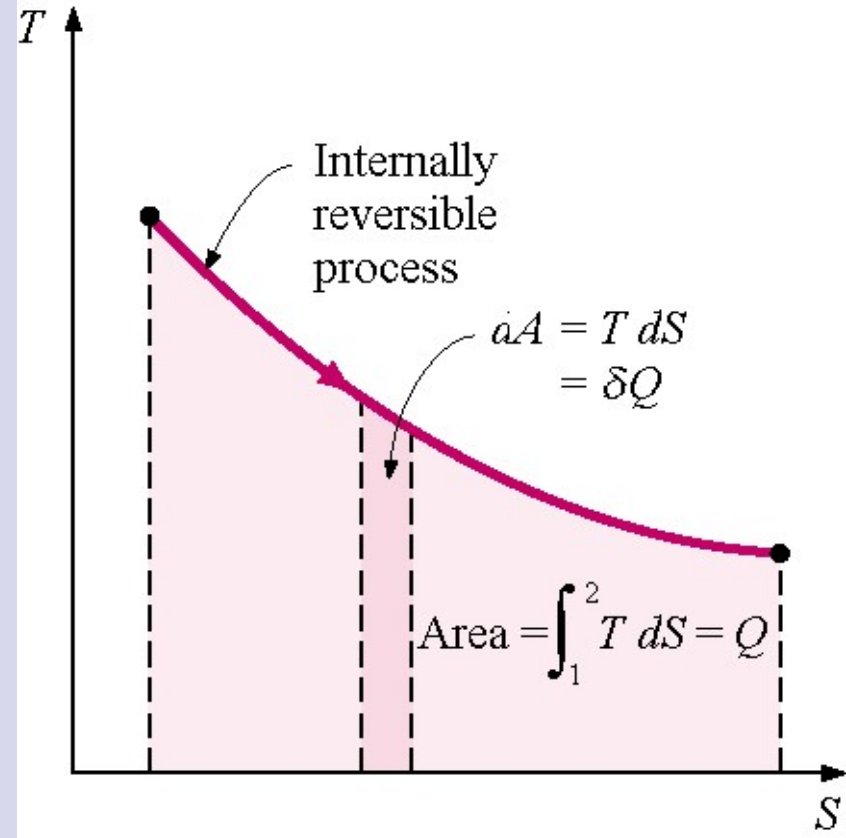
$$\delta W = PdV$$

Thus

$$Q_{\text{int,rev}} = \int T dS$$

This area has no meaning
for irreversible processes!

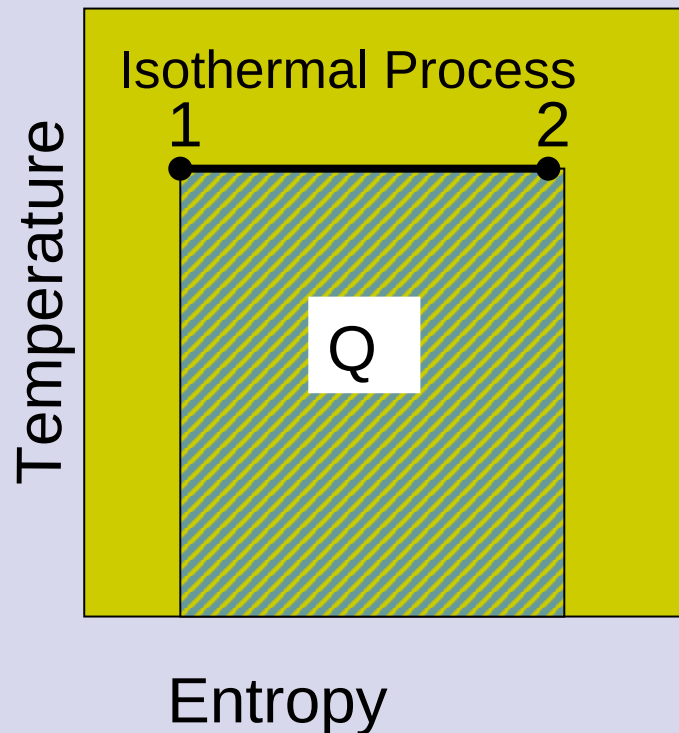
It can be done only for a reversible
process for which you know the
relationship between T and s during a
process. Let us see some of them.



Isothermal internally reversible .process

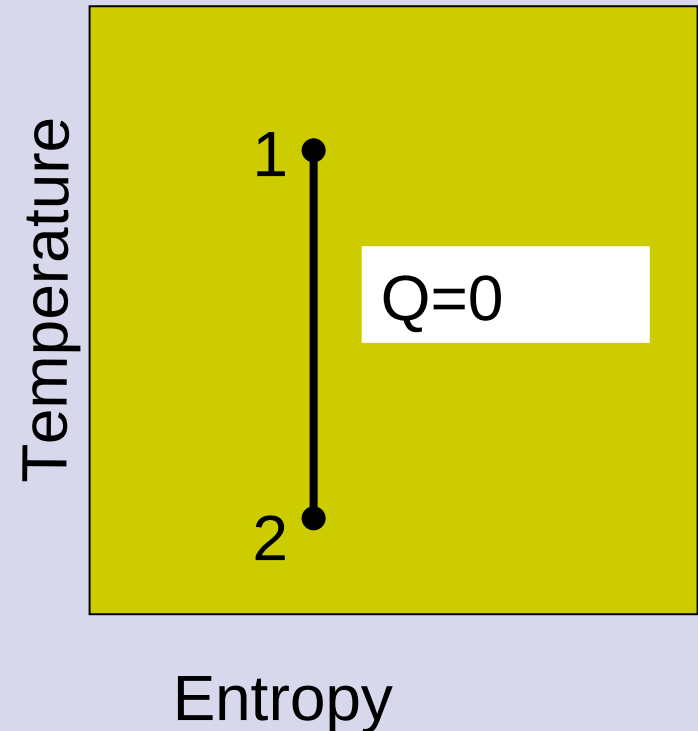
$$Q_{\text{int,rev}} = T_0 \int^2 dS$$

$$= T_0 \Delta S = T_0 m \Delta s$$



Adiabatic internally reversible process

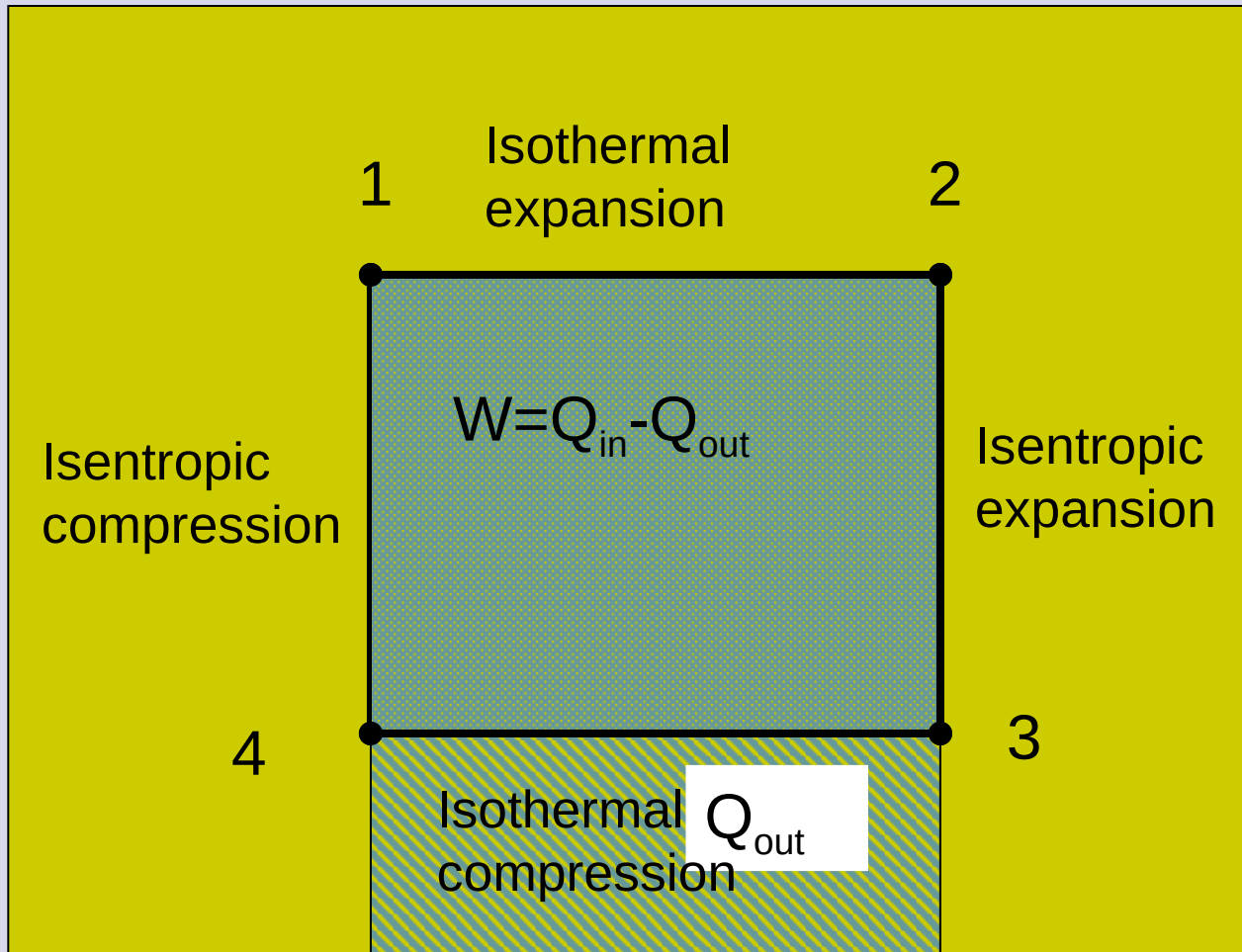
- In this process $Q = 0$, and therefore the area under the process path must be zero.
- This process on a T-s diagram is easily recognized as a vertical-line.



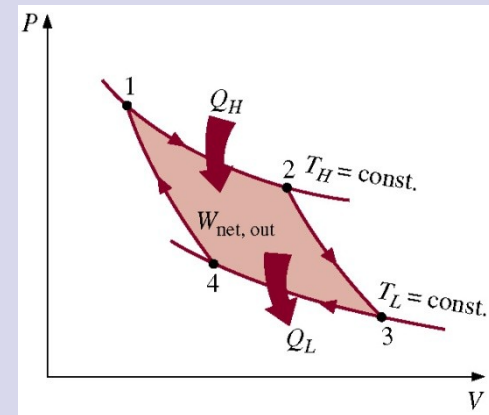
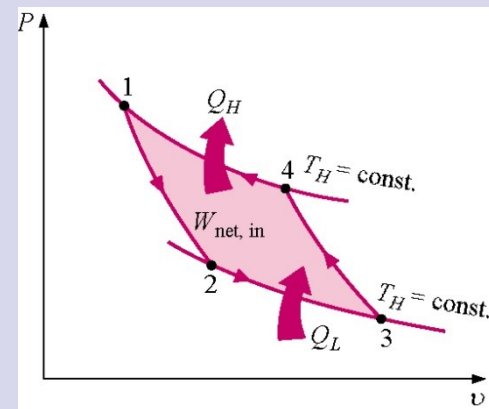
Isentropic Process

T-s Diagram for the Carnot Cycle

Temperature



Entropy



Another important diagram is the *h-s* Diagram

- This diagram is important in the analysis of steady flow devices such as turbines.
- In analyzing the steady flow of steam through an adiabatic turbine, for example,
- The vertical distance between the inlet and the exit states (Δh) is a measure of the work output of the turbine,
- The horizontal distance (Δs) is a measure of the irreversibilities associated with the process.

