

# **Session 5**

## **The second law: Spontaneity and reversibility. Entropy generation.**

# Entropy and the second law in classical thermodynamics

# Introduction - Second law of thermodynamics

## First law

- Expresses the conservation of energy for thermodynamical systems
- Comes from first principles
- It is obeyed separately by any individual interaction (and therefore also globally)

## Second law

- Describes spontaneous processes and establishes a limit to the ability of extracting useful work from a system
- Comes from probabilistic considerations: it does not make sense for individual interactions
- It might be locally (or temporarily) violated due to fluctuations
- It is strictly obeyed only in the thermodynamic limit (i.e. large systems)

## Reminder: heat reservoirs

*A heat reservoir (or thermal reservoir) is a system whose temperature remains constant in spite of heat transfer to or from it.*

They are called *heat sources* or *heat sinks* depending on the direction of heat transfer.

Examples:

- very large masses such as the atmosphere, an ocean or a lake, where local temperature gradients are quickly counteracted.
- a combustor that is continuously supplied fuel and generates heat maintaining a constant temperature

## Reminder: P-V diagrams

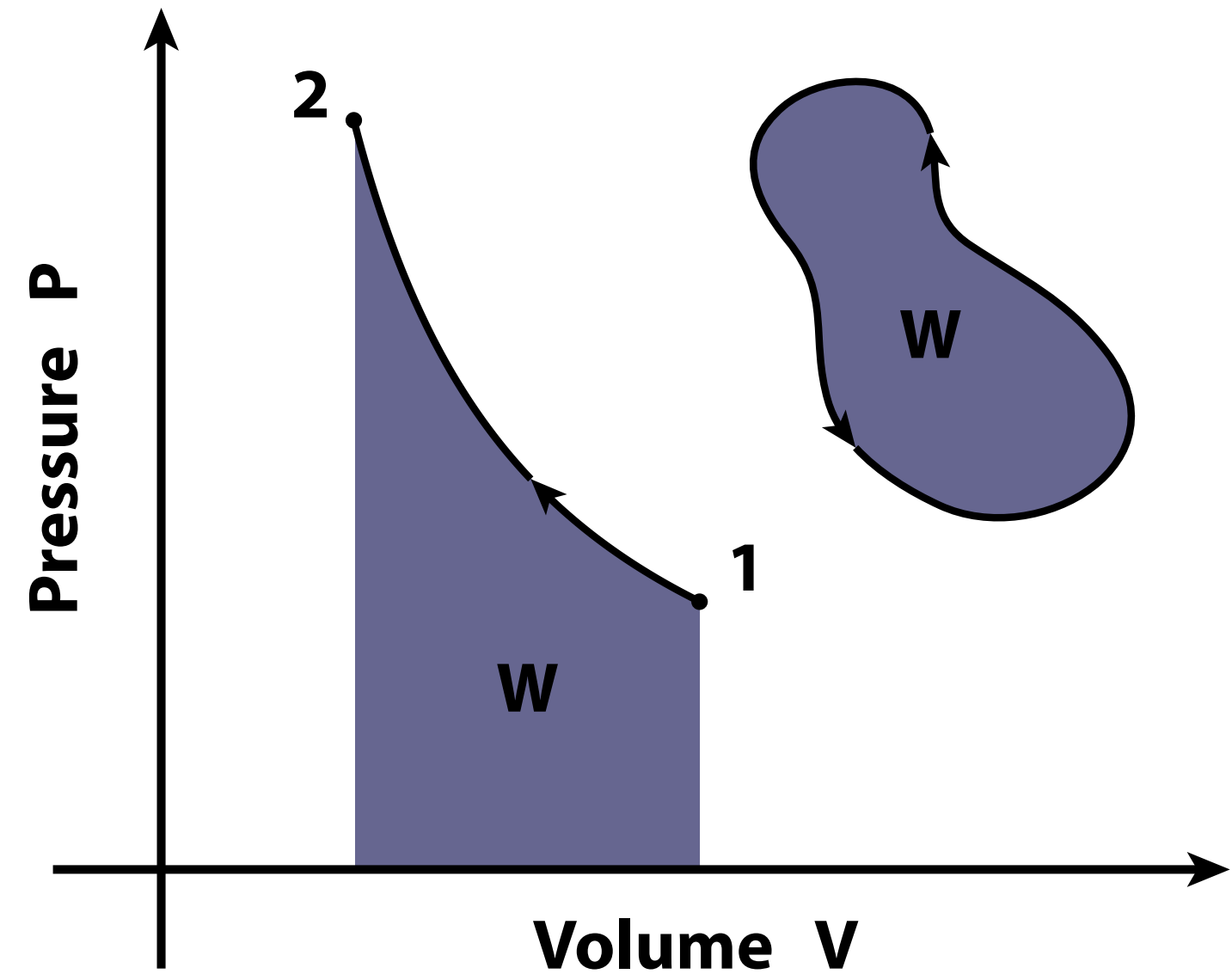
- They describe simple, pure compressible substances
- The temperature is determined by the equation of state.
- E.g. for ideal gases:

$$PV = NR_u T$$

- The energy transferred to the system in form of work is associated to its volume changes:

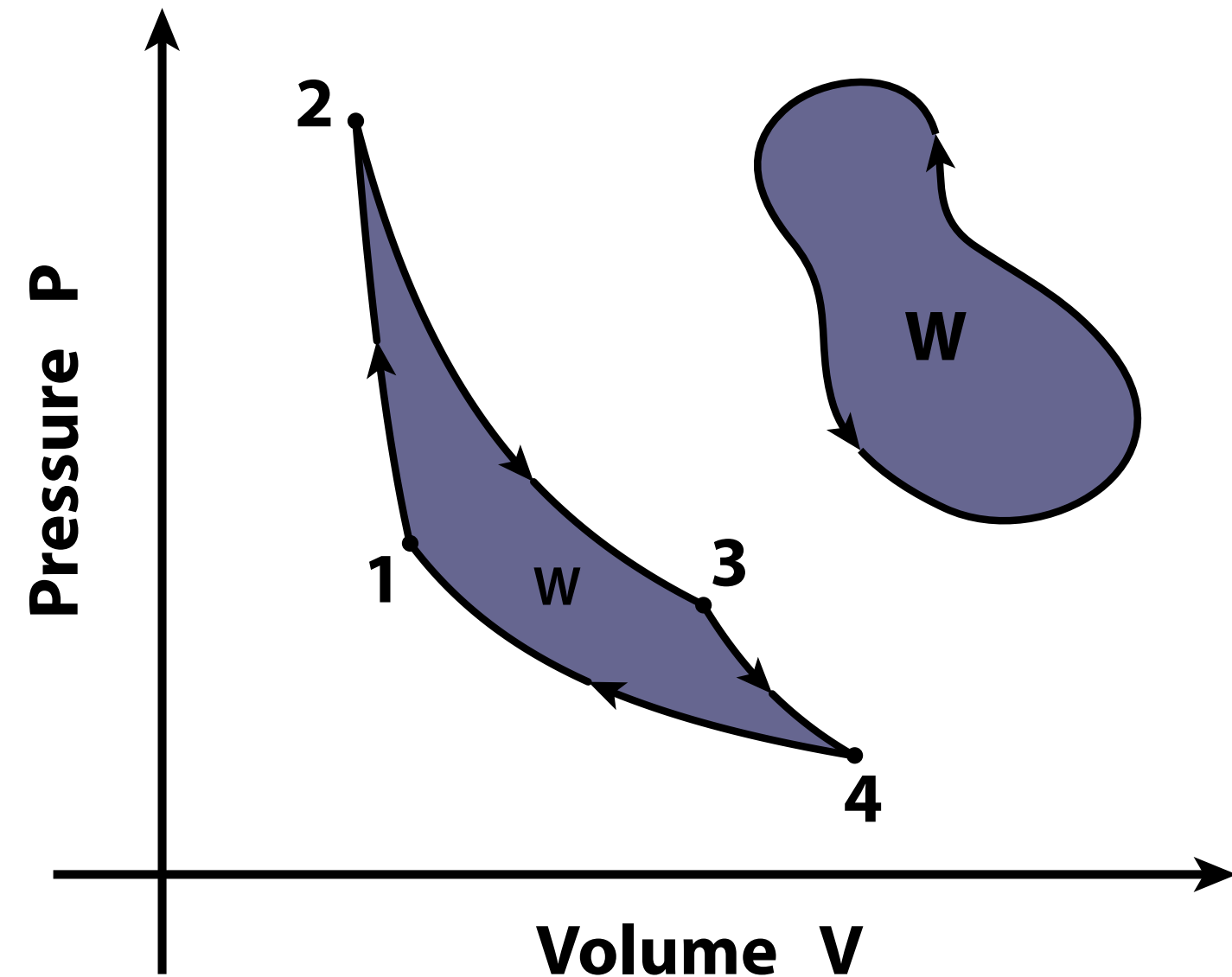
$$\delta W = -P dV$$

(mind the sign)

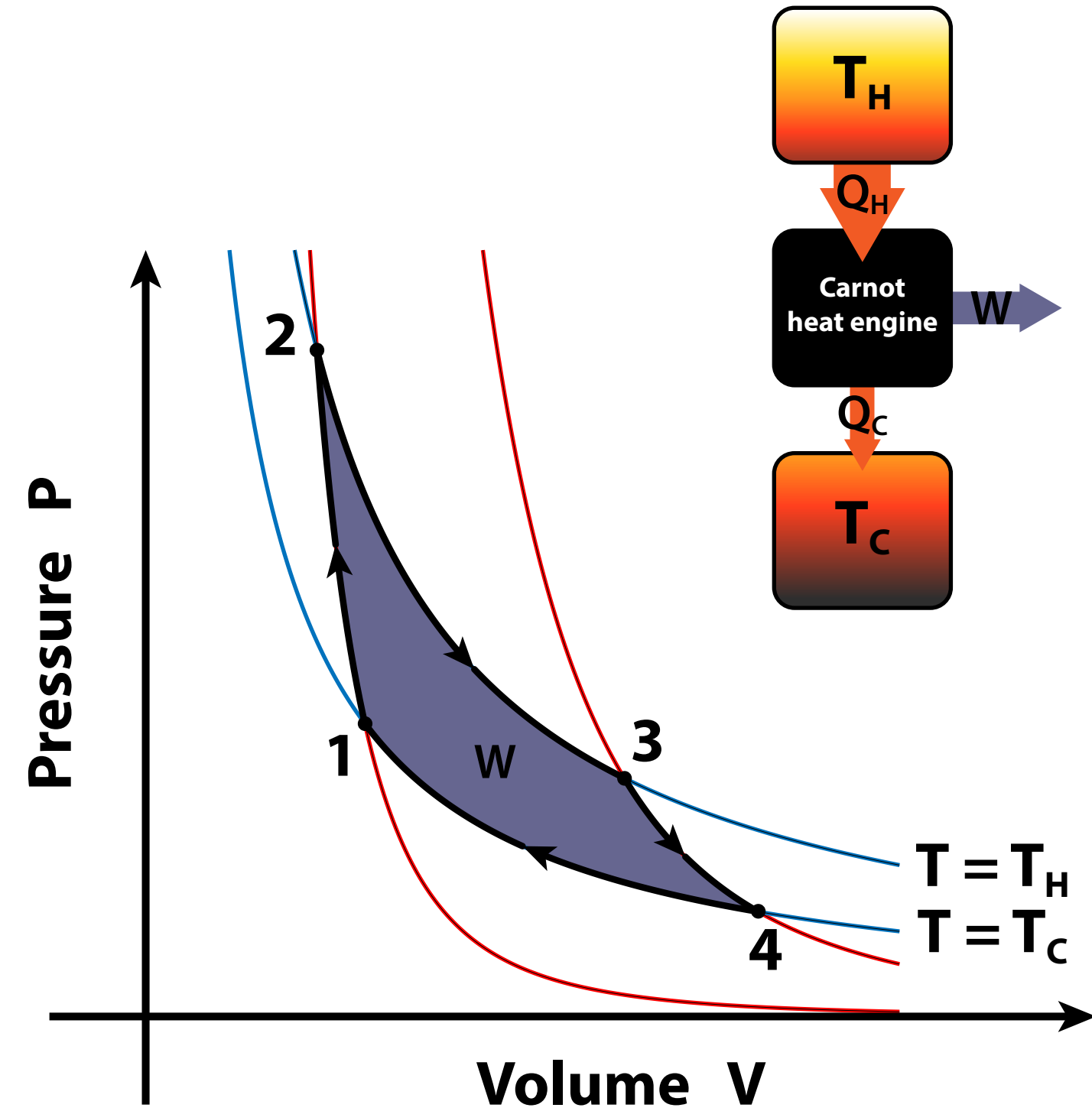
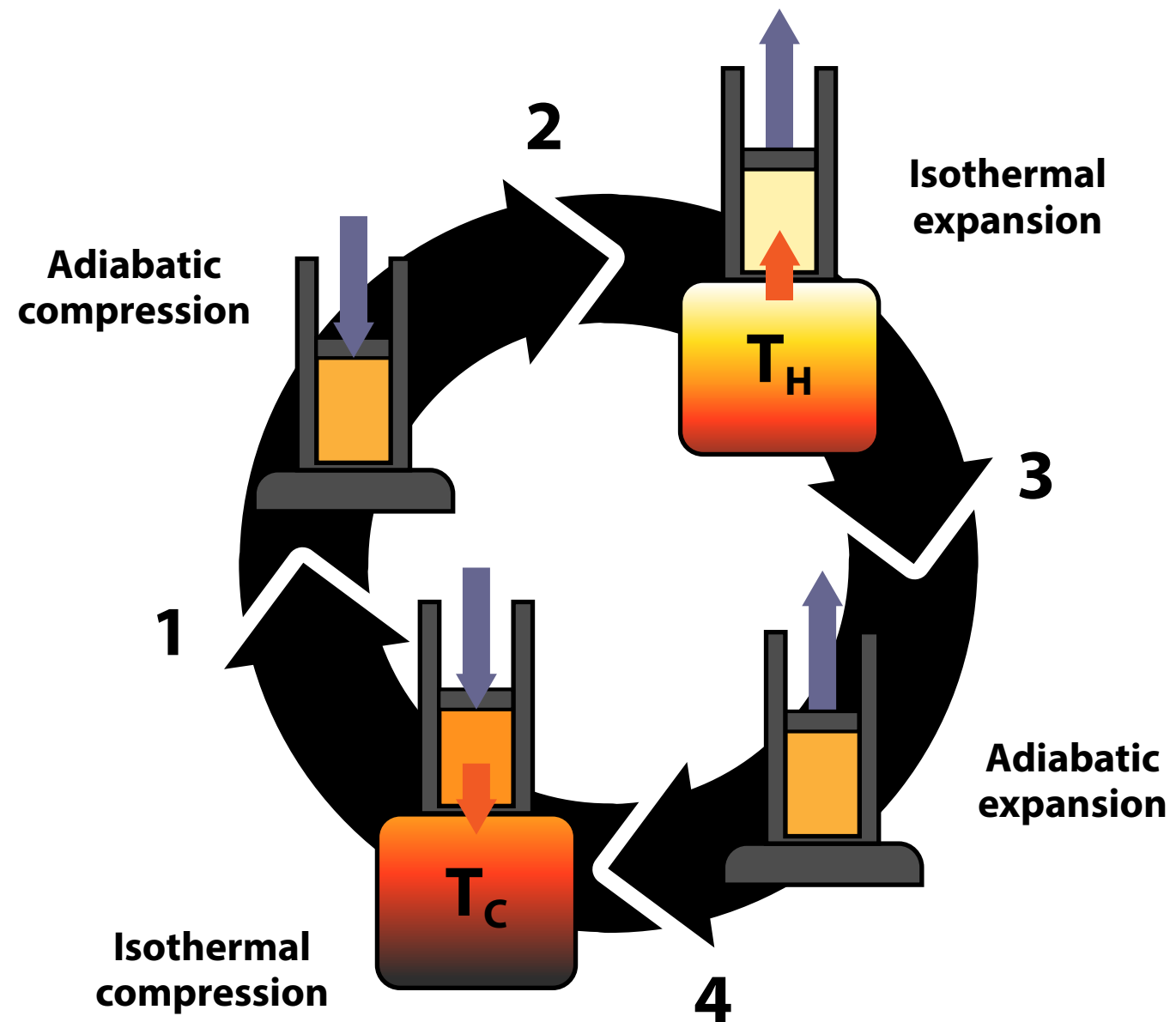


## Reminder: cyclic processes

- Any process for which the initial state of the system and the final state are the same.
- Therefore, after completing the process, the same transformation can be applied again with the same result. Hence the name "cycle".
- Can be composed of a sequence of processes. After the sequence is completed it can be applied again.



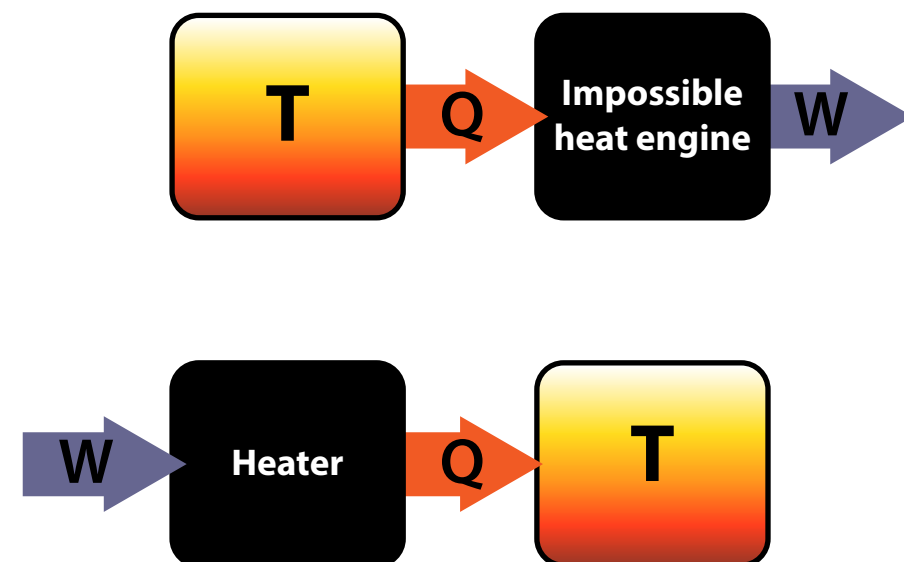
# The Carnot cycle: ideal heat engine



# Second law - classical statements

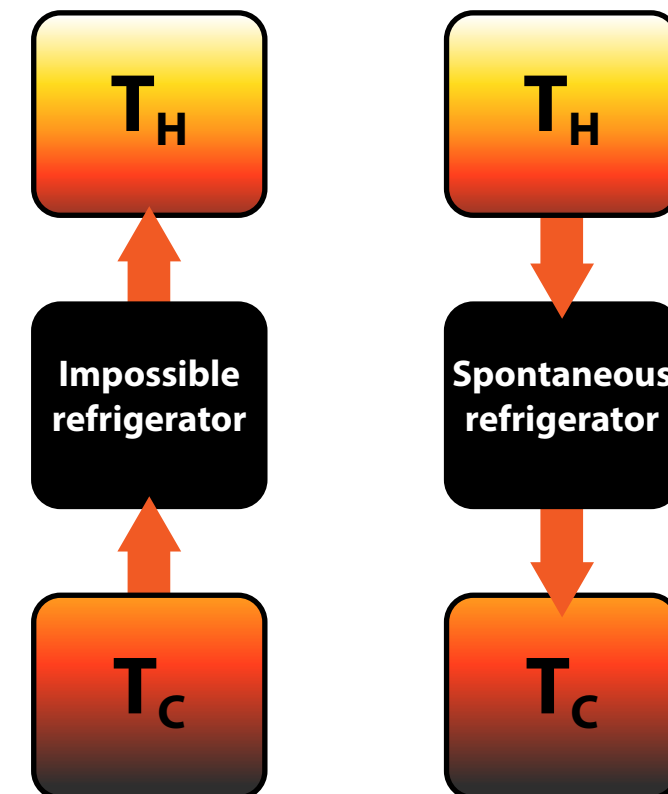
## Kelvin's statement

*A transformation whose only final result is to transform into work heat extracted from a thermal reservoir is impossible.*



## Clausius' statement

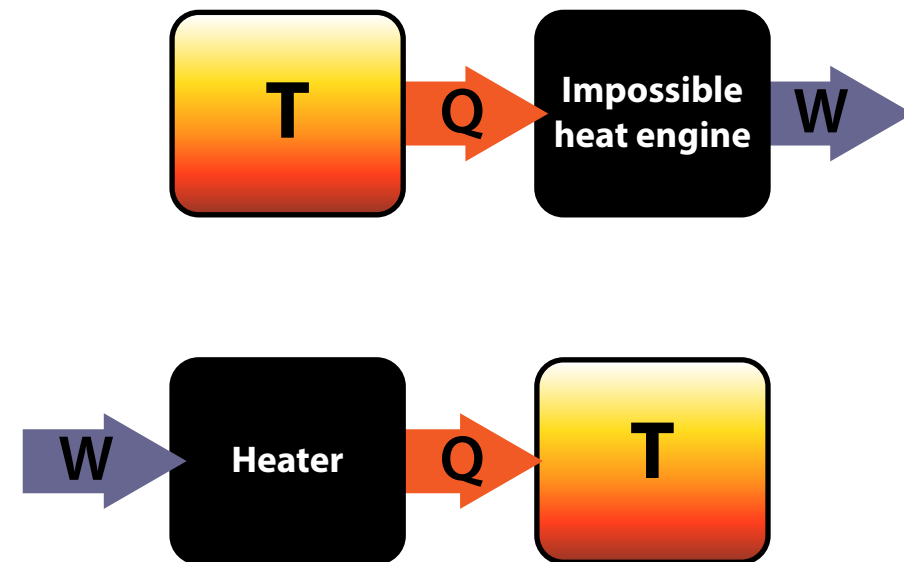
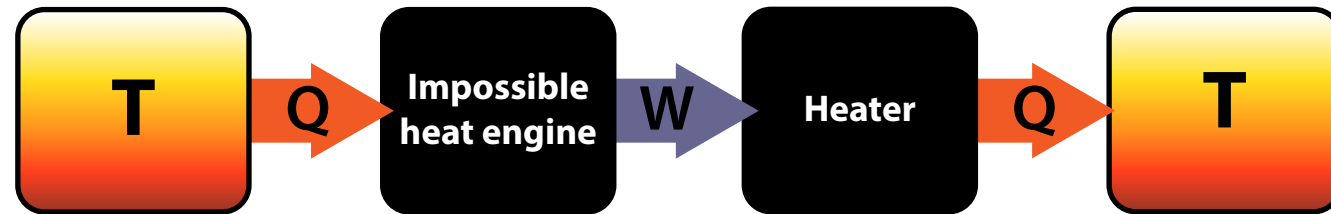
*A transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible.*





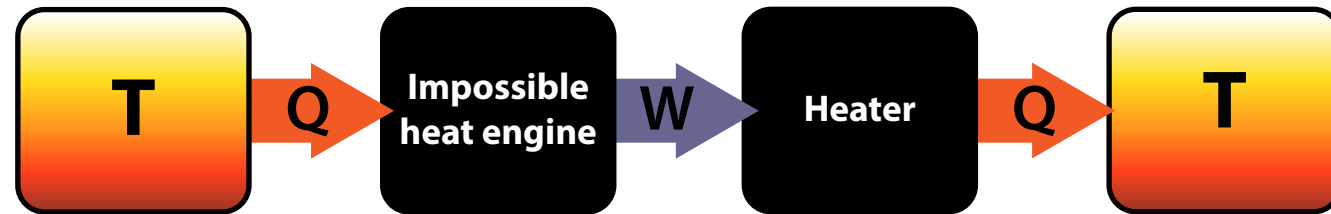
# Second law - classical statements

Combined machine:

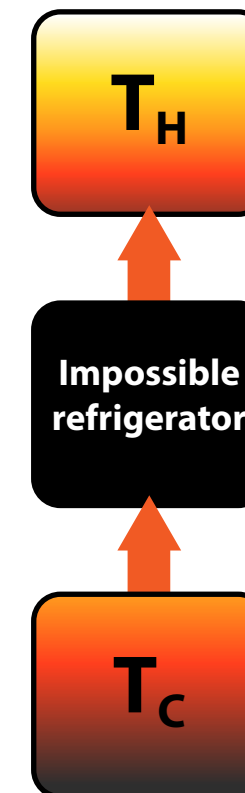
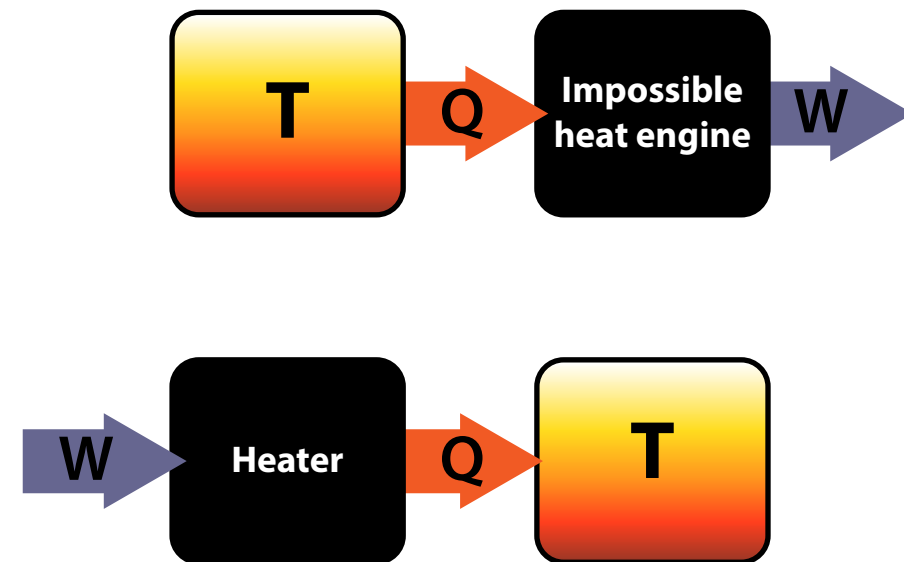


# Second law - classical statements

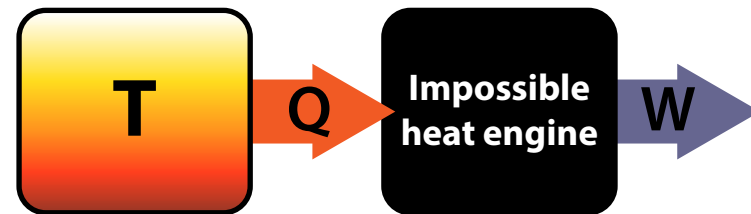
Combined machine:



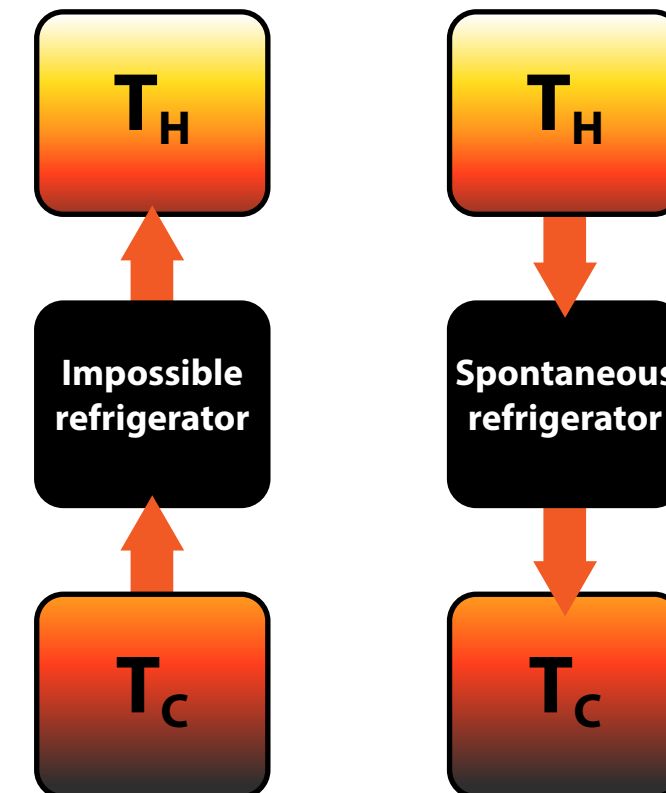
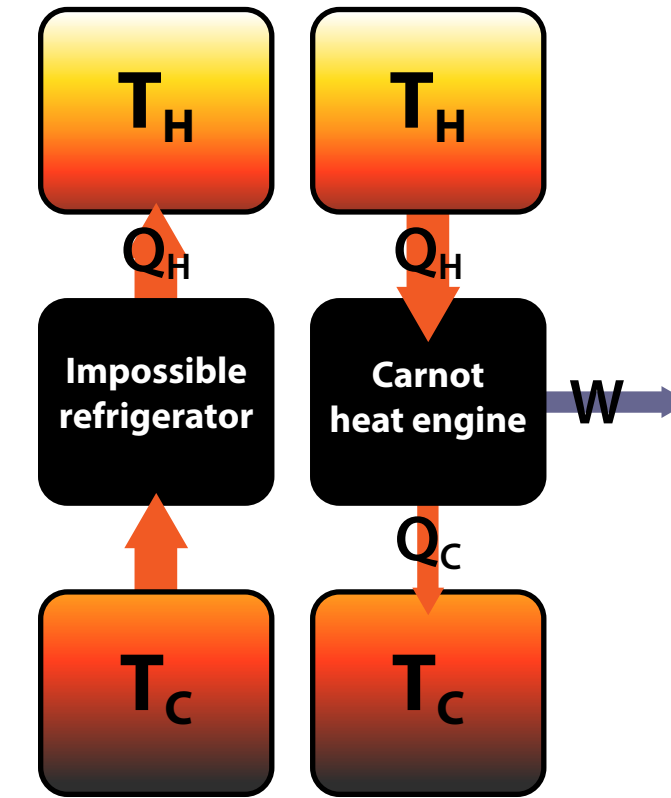
is  
equal  
to



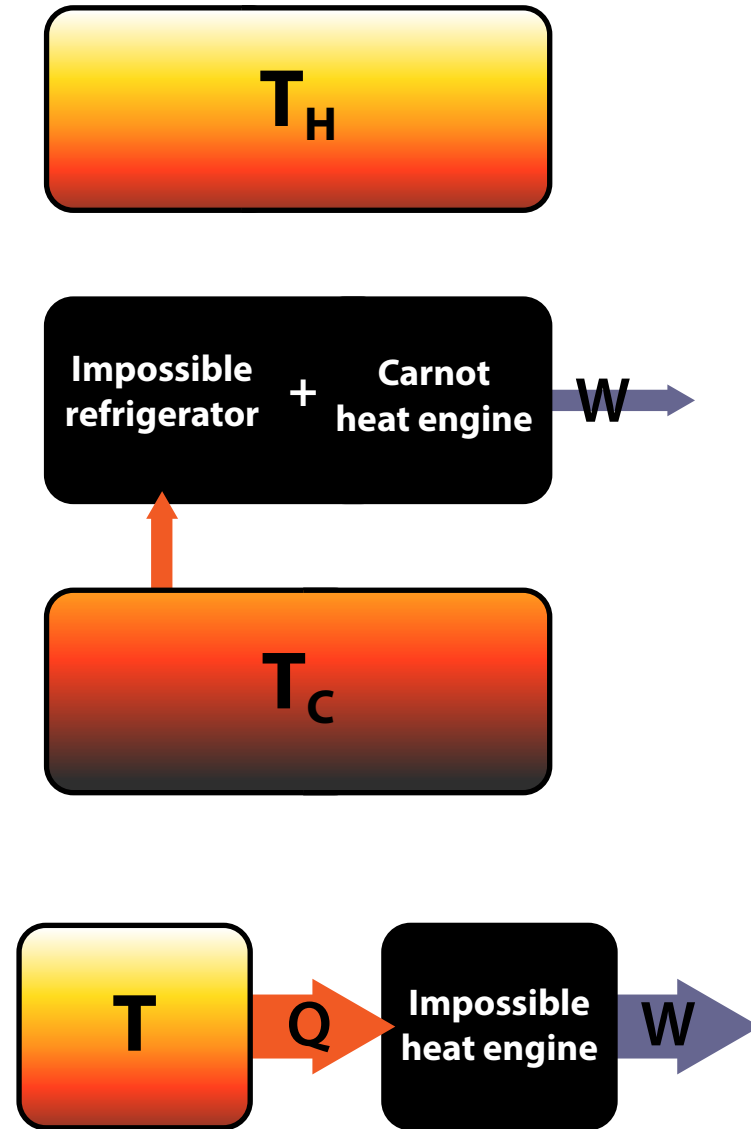
# Second law - classical statements



Combined machine:

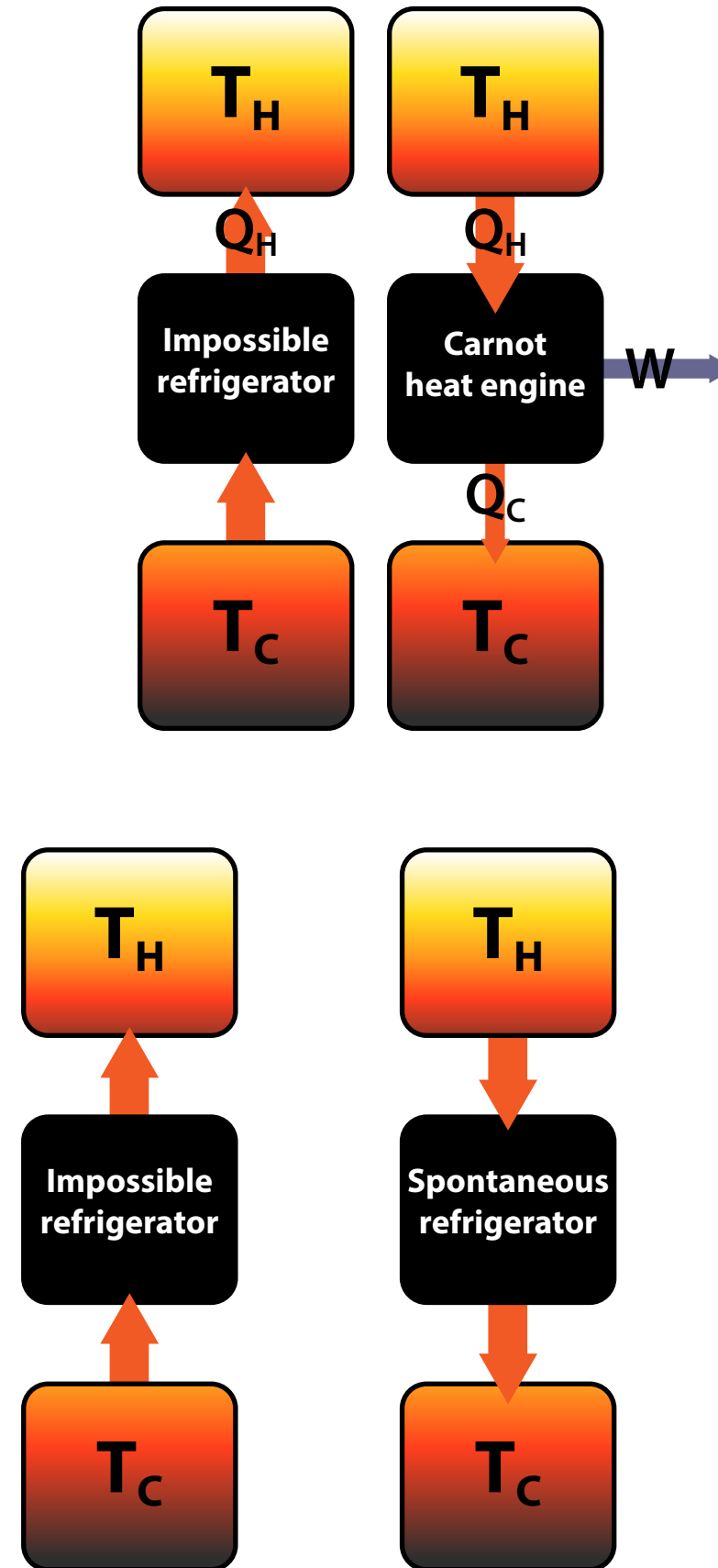


# Second law - classical statements



is  
equal  
to

Combined machine:



# Entropy - classical thermodynamics

## For reversible processes

Infinitesimal entropy variation:

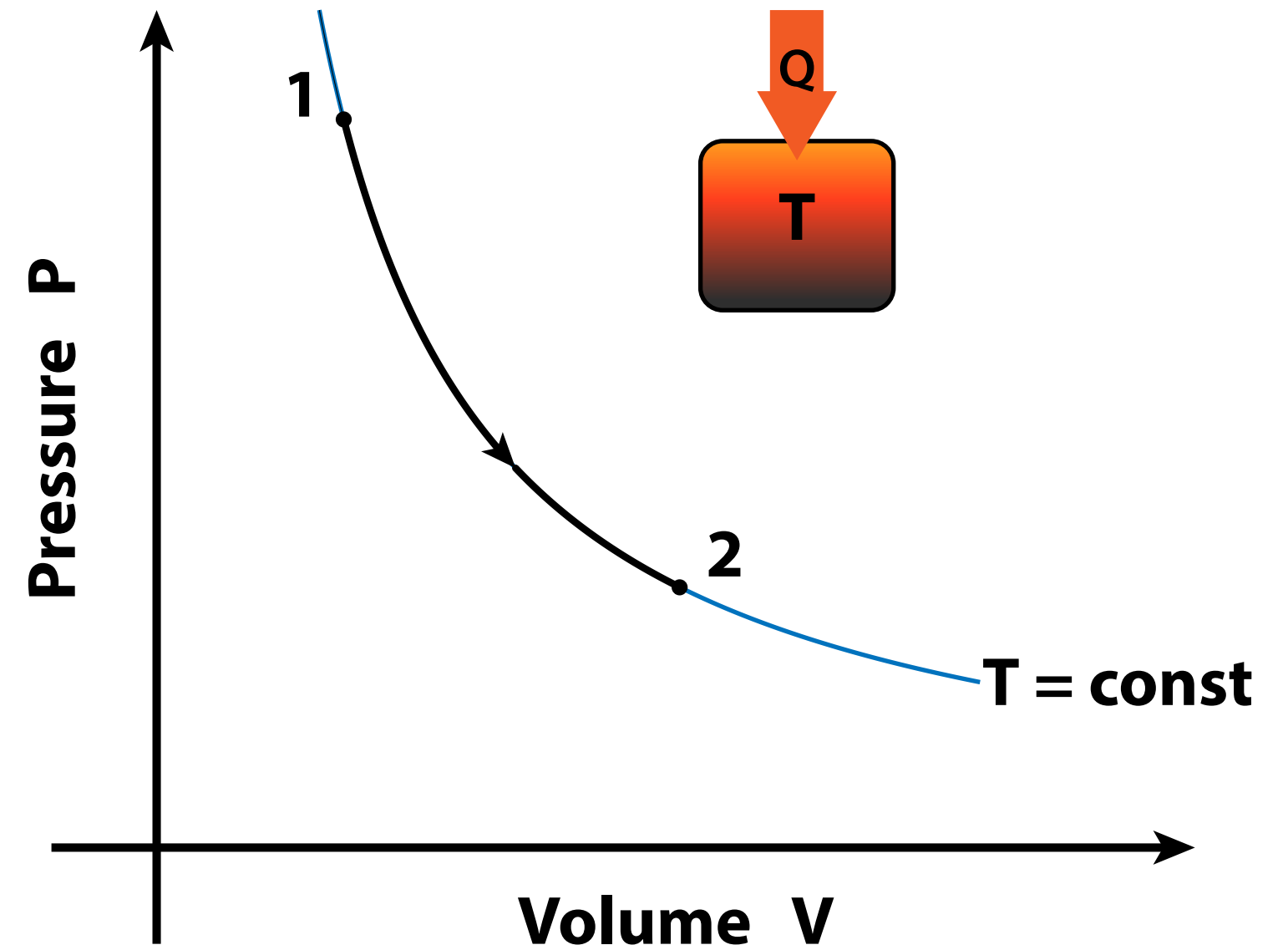
$$dS = \frac{\delta Q}{T}$$

Variation during finite process:

$$\Delta S = \int_1^2 \frac{\delta Q}{T}$$

At constant temperature  
(for isothermal processes or  
for thermal reservoirs)

$$\Delta S = \frac{1}{T} \int_1^2 \delta Q = \frac{Q}{T}$$



# Exact and inexact differentials

## For reversible processes

Entropy variation is path independent

$$\left( \int_1^2 dS \right)_I = \left( \int_1^2 dS \right)_{II}$$

(e.g.) Heat exchange is path dependent

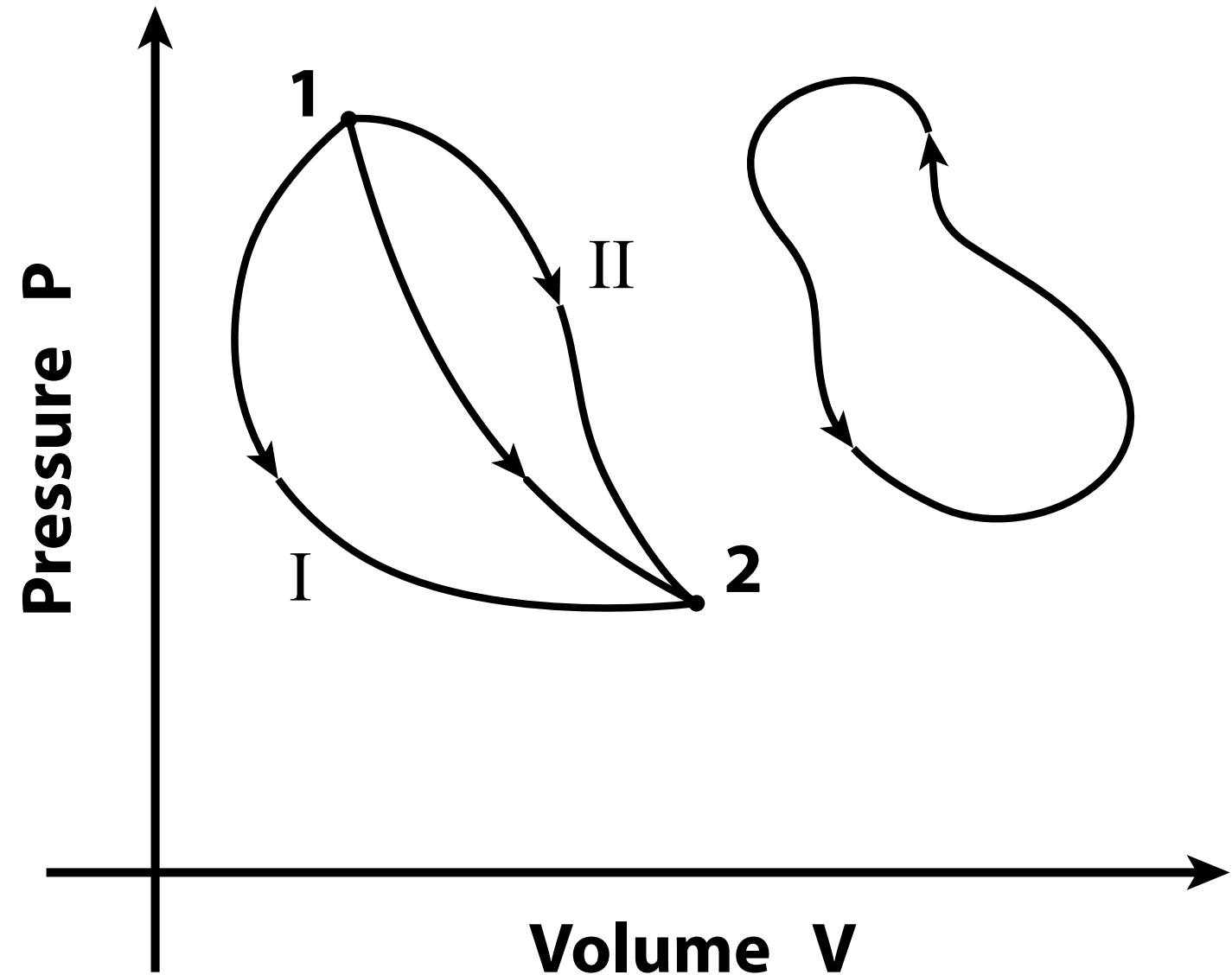
$$\left( \int_1^2 \delta Q \right)_I \neq \left( \int_1^2 \delta Q \right)_{II}$$

Entropy variation for cyclic process

$$\oint dS = 0$$

Entropy is a state function:

$$\int_1^2 dS = S(2) - S(1)$$



# Entropy generation

## Heat exchange between two thermal reservoirs

Entropy decrease of the hotter system

$$\Delta S_A = \frac{Q}{T + \Delta T}$$

Entropy increase of the colder system

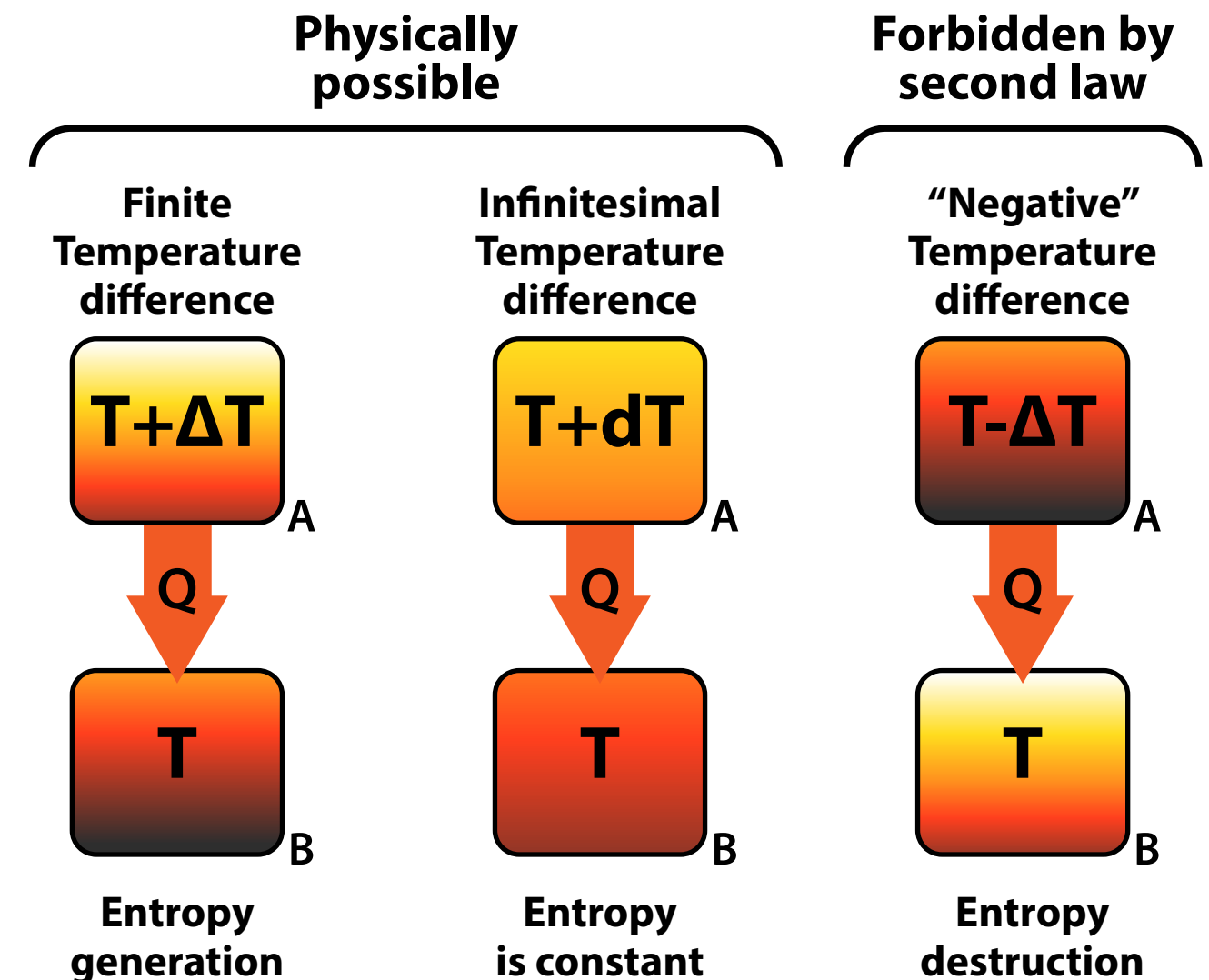
$$\Delta S_B = \frac{Q}{T} > \Delta S_A$$

Entropy *generation*: finite T difference

$$S_{\text{gen}} = \Delta S_B - \Delta S_A$$

Entropy is *constant*: infinitesimal T difference

Entropy *destruction*: violates second law  
(hotter system would have to receive heat)



# Entropy and the second law of thermodynamics

For a reversible process:

$$\int_1^2 \frac{\delta Q}{T} = S(2) - S(1)$$

In general:

$$\int_1^2 \frac{\delta Q}{T} \leq S(2) - S(1)$$

For an isolated system  $\delta Q = 0$

$$S(2) \geq S(1)$$

For an isolated system

$dS > 0$  evolving towards equilibrium

$dS = 0$  at equilibrium

$dS < 0$  forbidden by second law

*For any transformation occurring in an isolated system, the entropy of the final state can never be less than that of the initial state.*

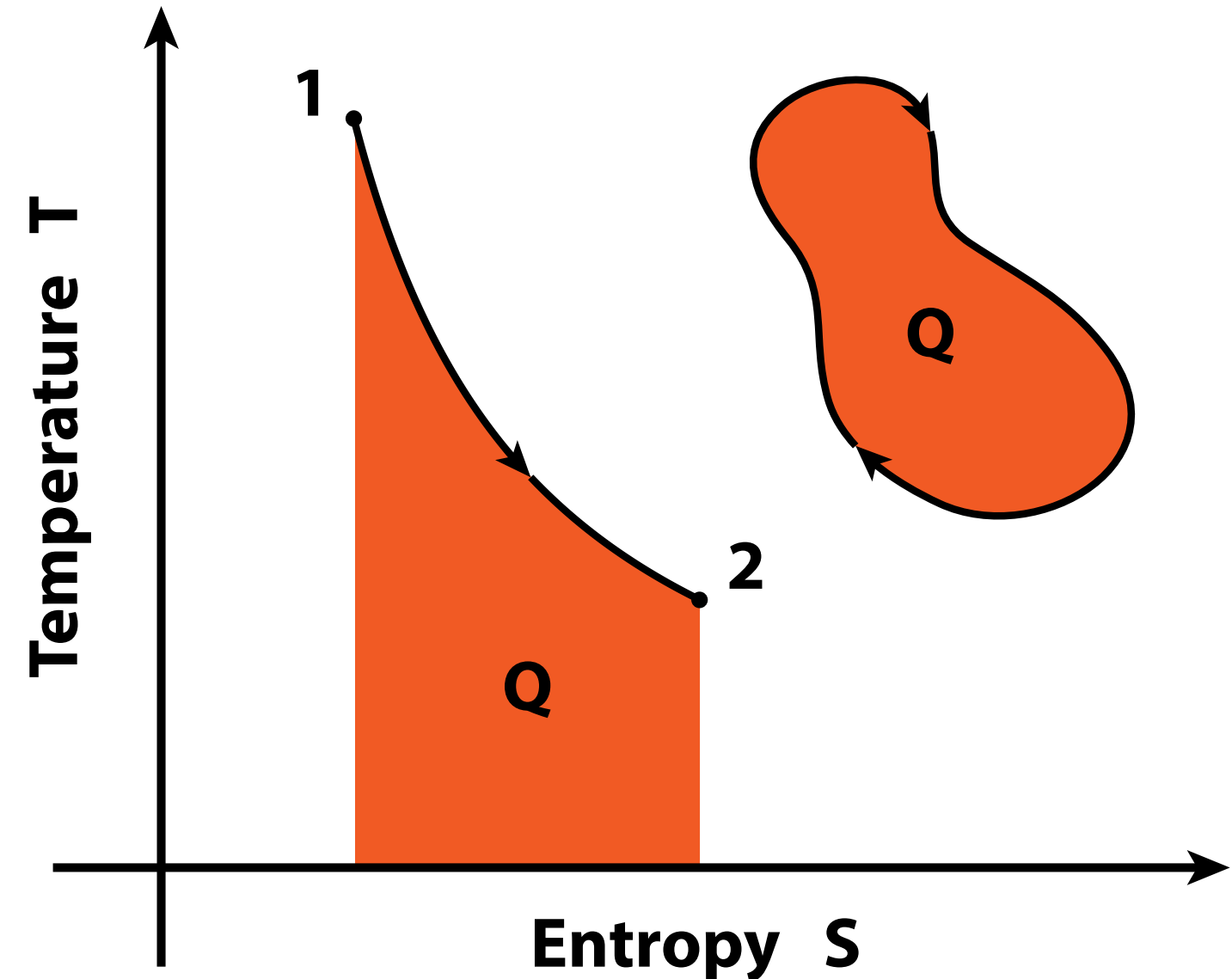
*The state of maximum entropy is the most stable state for an isolated system.*



# T-S Diagrams

- As we will see, for a simple, pure compressible substance, two independent variables (such as  $T$  and  $S$ ) completely determine the state of the system at equilibrium.
- The other state variables are determined by the equation of state.
- For reversible processes, the energy transferred to the system in form of heat is associated to its entropy changes:

$$\delta Q = +T dS$$



# Specific entropy

Entropy variation is the ratio:

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

The heat exchange is additive (energy is an extensive property)

The temperature is an intensive property.

Therefore entropy is additive: it is an *extensive property*.

For a composite system, as long as:

- the energy of the system is the sum of the energies of its parts
- the work performed by the system during a transformation  
is the sum of the work performed by all the parts

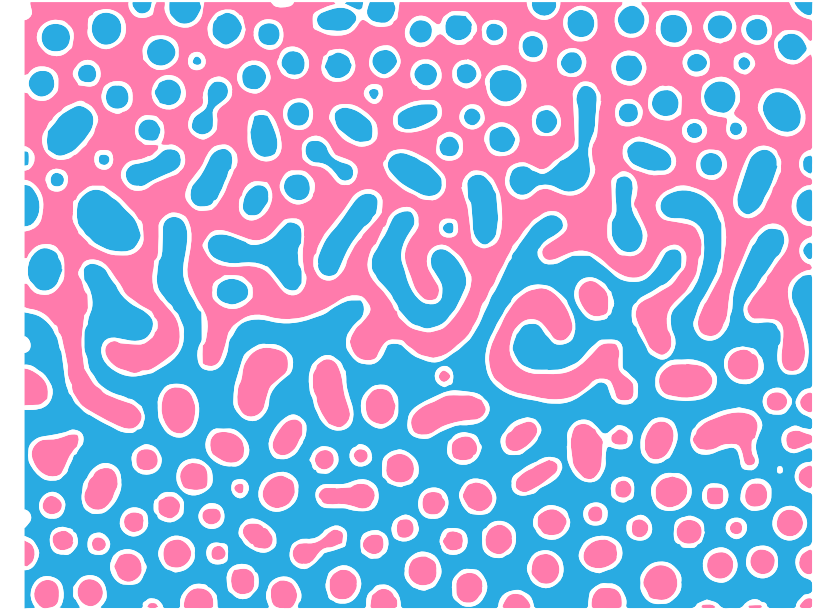
then *the entropy of the composite system is the sum of the entropies of all its parts*.

The *specific entropy* is an intensive property defined as:  $s = \frac{S}{m}$

# Specific entropy

Counterexample:

the energy of a system composed of two substances is the sum of the energies of the two substances only if we can neglect the surface energy at the interface between them (e.g. surface tension)



For a composite system, as long as:

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then *the entropy of the composite system is the sum of the entropies of all its parts*.

The *specific entropy* is an intensive property defined as:  $s = \frac{S}{m}$

# The state postulate

Entropy is a state function.

The state of a given amount (i.e. given mass  $m$  or number of moles) of a pure, simple compressible substance is completely described by two state variables (e.g. internal energy  $U$  and volume  $V$ ):

$$S = S(U, V, m)$$

The *specific entropy*  $s = S/m$  can be written as function of the specific internal energy  $u = U/m$  and the specific volume  $v = V/m$

$$s = s(u, v)$$

# Entropy, temperature and pressure

We consider a fixed amount of pure, simple compressible substance.  
The first law of thermodynamics for an infinitesimal process is:

$$dU = \delta Q + \delta W$$

Where:

$dU$  is the variation of internal energy of the system

$\delta Q = +T dS$  is the energy transferred to the system in the form of heat

$\delta W = -P dV$  is the energy transferred to the system in the form of work

Since the amount is fixed, the mass  $m$  is constant.

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If the process is isochoric (const  $V$ ):  $\delta W = 0$

$$dU = \delta Q = T dS$$

therefore:

$$T = \left( \frac{\partial U}{\partial S} \right)_{m,V} \quad \text{or:} \quad \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{m,V} = \left( \frac{\partial s}{\partial u} \right)_v$$

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If the internal energy is constant:  $dU = 0$

$$\delta Q = -\delta W \implies T dS = P dV \quad \text{therefore:} \quad P = T \left( \frac{\partial S}{\partial V} \right)_{m,U} \quad \text{or:} \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{m,U} = \left( \frac{\partial s}{\partial v} \right)_u$$

# Gibbs Equation - the fundamental thermodynamic relation

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The first law can thus be written as:

$$dU = T dS - P dV$$

Or in term of specific quantities:

$$du = T ds - P dv$$



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or:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

or:

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

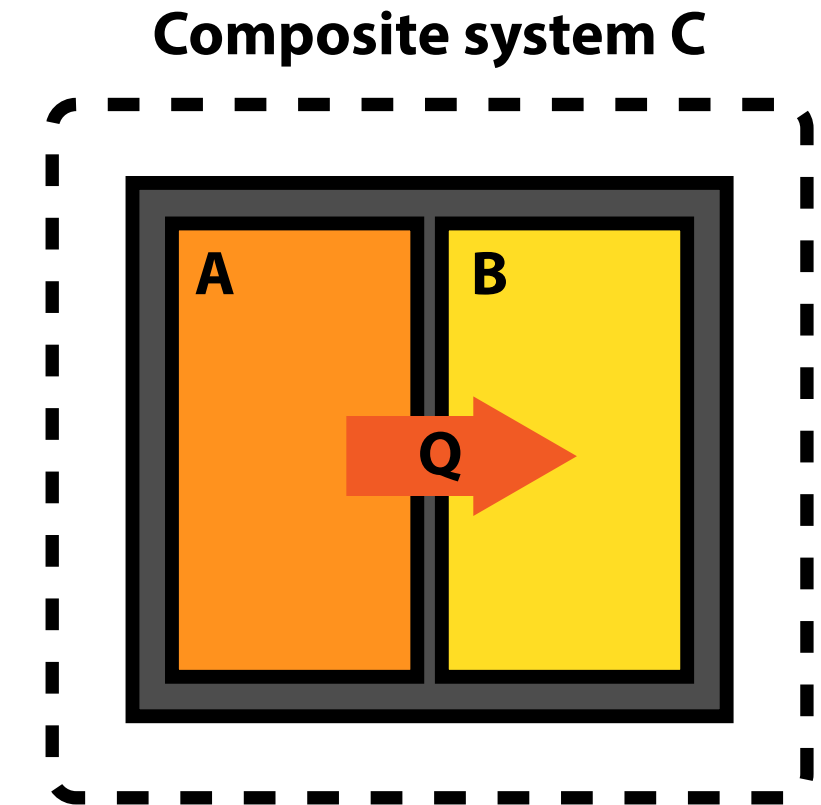
**Gibbs  
equation**

# Thermal equilibrium and temperature

Two chambers A and B of pure substances are connected so that:

- they cannot exchange mass (masses fixed).
- they can exchange energy in form of heat.
- they cannot exchange work (volumes fixed)

Initially, they are not in thermal equilibrium:  $T_A \neq T_B$ .



The composite system C is isolated:  $dU_C = dU_A + dU_B = 0$

Its entropy is:

$$S_C = S_A(U_A, V_A, m_A) + S_B(U_B, V_B, m_B)$$

$$dS_C = \left( \frac{\partial S_A}{\partial U_A} \right)_{m_A, V_A} dU_A + \left( \frac{\partial S_B}{\partial U_B} \right)_{m_B, V_B} dU_B \quad \text{using} \quad \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{m, V}$$

$$dS_C = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A = \left( \frac{1}{T_B} - \frac{1}{T_A} \right) dU_B$$

If  $T_A \neq T_B$ , then  $dS_C > 0$

If  $T_A = T_B$ , then  $dS_C = 0$

# Mechanical equilibrium and pressure

Two chambers A and B of pure substances are connected so that:

- they cannot exchange mass (masses fixed).
- they can exchange energy in form of heat.
- they can exchange energy in form of work.

Initially, they are not in thermal equilibrium:  $T_A \neq T_B$ .  
they are not in mechanical equilibrium:  $P_A \neq P_B$ .

Following a similar procedure, and using  $\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{m,U}$  and  $dV_A + dV_B = 0$

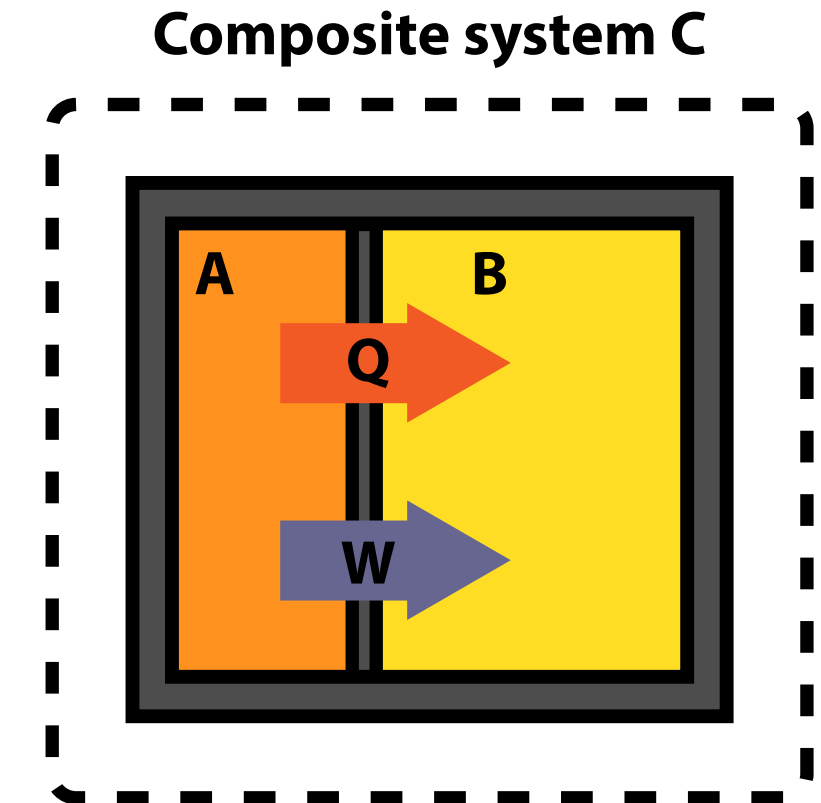
$$dS_C = \left( \frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left( \frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV_A$$

Assuming thermal equilibrium ( $T_A = T_B = T$ ):

$$dS_C = \frac{1}{T} (P_A - P_B) dV_A = \frac{1}{T} (P_B - P_A) dV_B$$

If  $P_A \neq P_B$ , then  $dS_C > 0$

If  $P_A = P_B$ , then  $dS_C = 0$

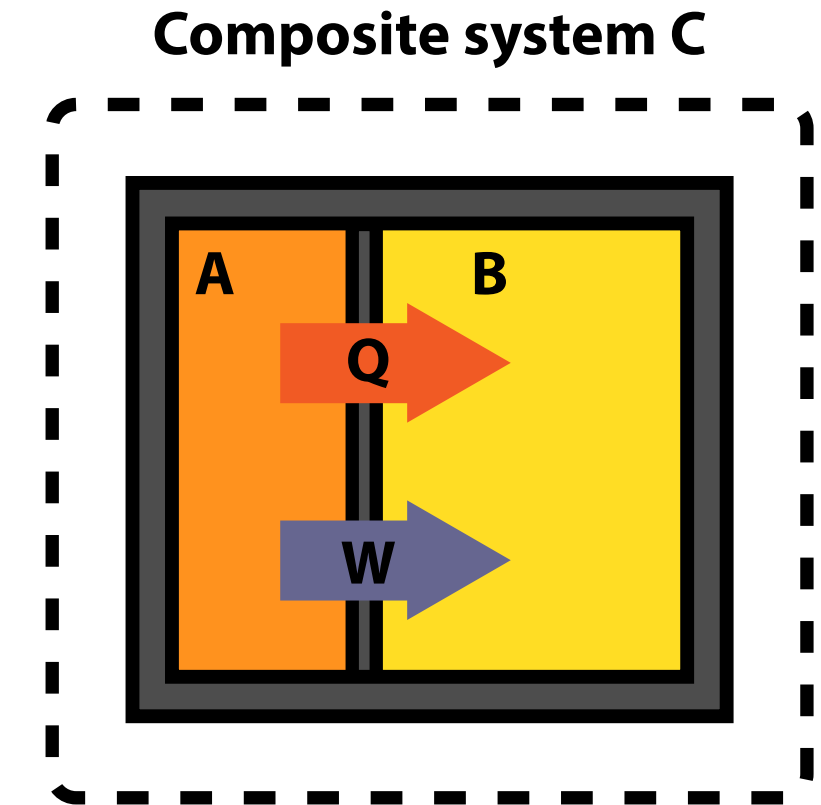


# Entropy variation

The previous results can be generalized:

*Whenever pressure gradients or temperature gradients are present within an isolated system, it will evolve towards the equilibrium thus reducing the gradients until pressure and temperature are uniform.*

*During this spontaneous process, the entropy increases until it reaches its maximum value corresponding to the equilibrium state.*



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Now we will see how to calculate entropy variation in some cases.