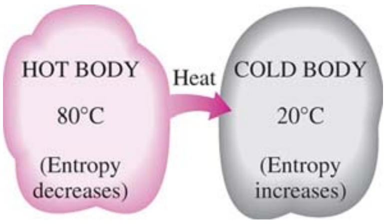
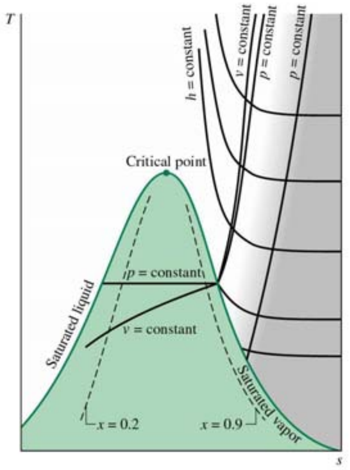
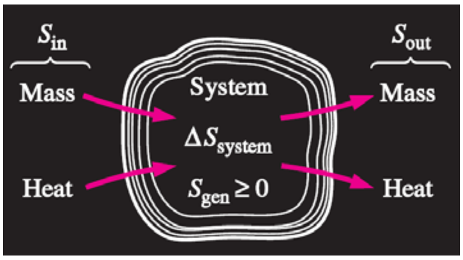


Thermodynamics I

Entropy

Dr.-Eng. Zayed Al-Hamamre



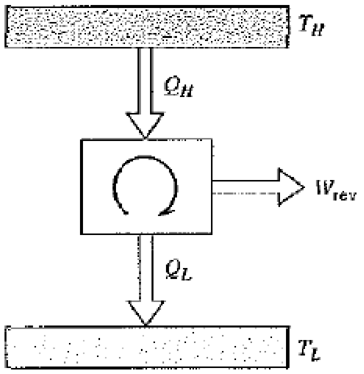


Content

- Developing the Clausius Inequality
- The cyclic integral
- Entropy
- The Entropy Change in Reversible Processes
- Entropy Generation
- The Increase of Entropy Principle
- The Entropy Change of a Control Mass (closed System) During an Irreversible processes
- Entropy of Pure Substances
- Entropy of Solid and Liquids
- Entropy change in Processes Involving Ideal Gas
- Entropy as Rate Equation

The Inequality of Clausius

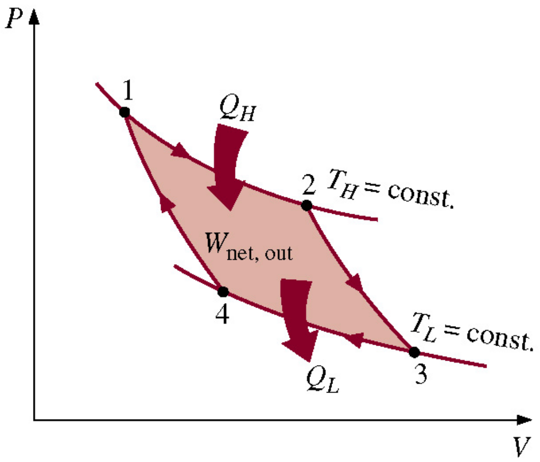
$$\oint \frac{\delta Q}{T} \leq 0$$



- 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 cyclic integral

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



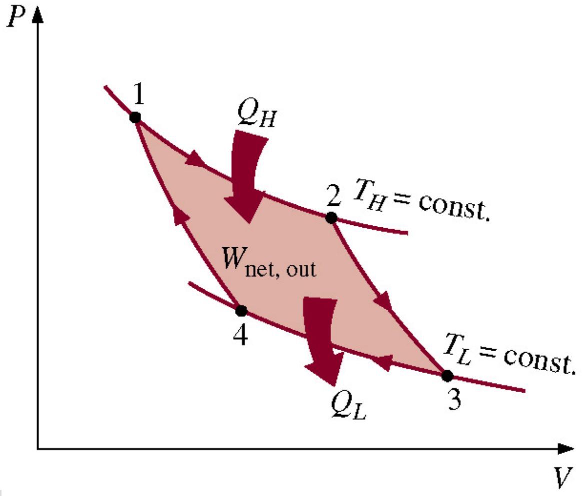
$$\oint \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T}$$

The cyclic integral

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

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

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



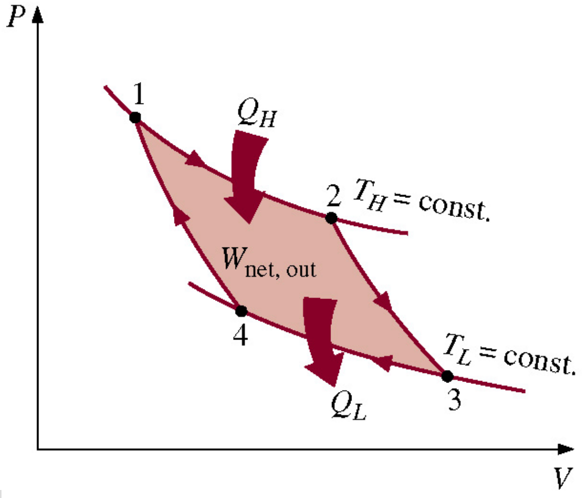
The cyclic integral of Reversible Heat Engine

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

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

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

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

It is Irreversible

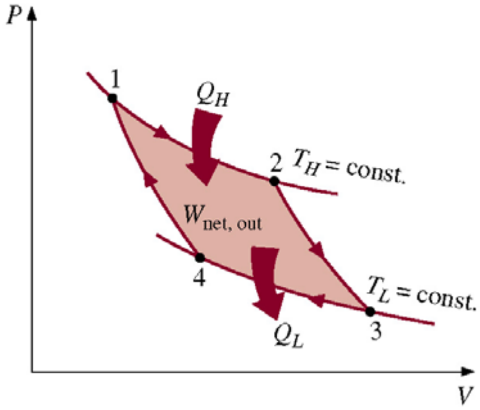
$$W_{irr} < W_{rev}$$

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

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

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

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



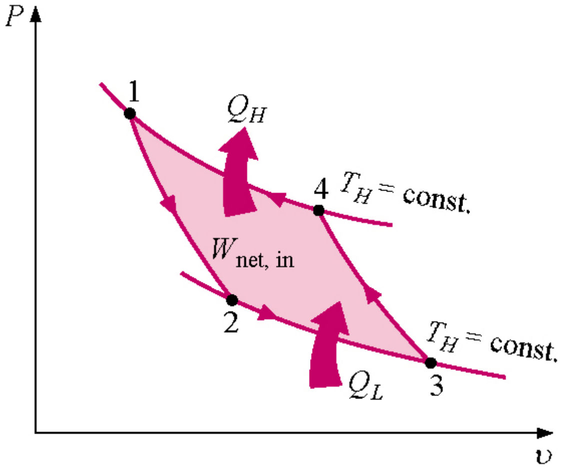
The cyclic integral of Reversible Refrigeration

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

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

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

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

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

It is Irreversible

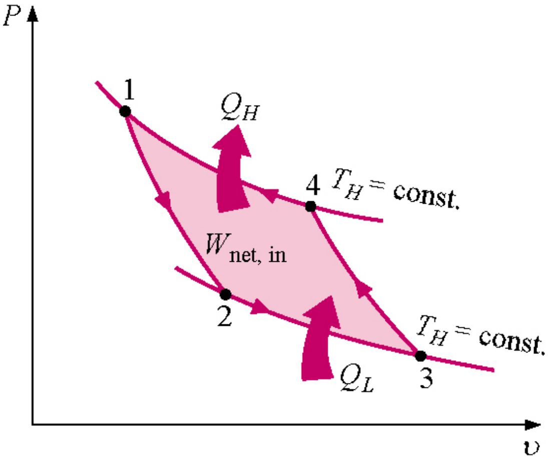
$$W_{irr} > W_{rev}$$

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

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

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

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



Derivation of Clausius Inequality

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

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

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

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

Derivation of Entropy (Reversible Process)

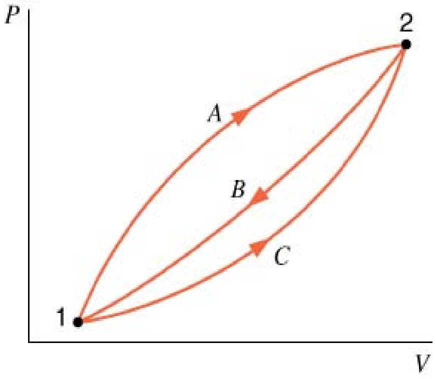
For reversible cycle A-B

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

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



All paths are arbitrary

Since paths A and C are arbitrary, it follows that the integral of δQ/T has the same value for ANY reversible process between the two sates.

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

---

Derivation of Entropy (Reversible Process)

Recall
- work & heat — are dependent on path — Path functions
- properties — are independent of path and depend on state only — Point functions

$$\Rightarrow \int \frac{\delta Q}{T}$$ is a thermodynamic property

we call it entropy (S)

- The **change** in the entropy of a substance in going from one state to another is the same for all processes, both reversible and irreversible

Entropy (the unit)

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

$$dS \equiv \left(\frac{\delta Q}{T}\right)_{rev}$$ integrating $$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev}$$

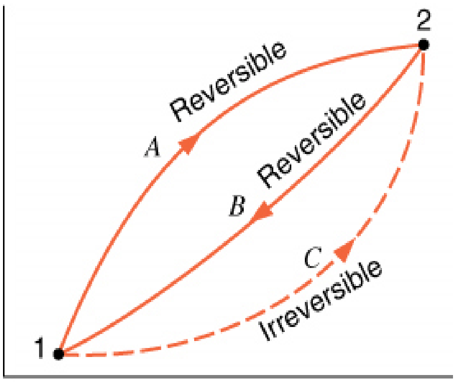
$$\Rightarrow \boxed{dQ_{rev} = T\,dS'}$$

$S_2 - S_1$ 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)

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

comparing gives

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

$$\text{but } \int_1^2 \left(\frac{\delta Q}{T}\right)_A \underbrace{=\!=}_{\text{reversible}} \int_1^2 dS_A \underbrace{=\!=}_{\text{it is a property}} \int_1^2 dS_C \qquad \therefore \int_1^2 dS_C > \int_1^2 \left(\frac{\delta Q}{T}\right)_C$$

$$\text{in general} \Rightarrow dS \geq \frac{\delta Q}{T} \qquad \text{or } S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

equality for reversible
inequality for irreversible

Derivation of Entropy (Any Process)

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

equality for reversible
inequality for irreversible

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

$$dS \equiv \frac{\delta Q}{T} + \delta S_{gen} \qquad \text{or} \qquad \boxed{S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}} \quad \left\{ \begin{array}{l} \text{for any process,} \\ \text{with } S_{gen} \geq 0 \end{array} \right.$$

2nd law of thermodynamics for a closed system

Entropy Balance Equation for a closed system

$$S_{gen} \equiv \text{ entropy generation} \begin{cases} > 0 & \text{for irreversible process} \\ = 0 & \text{for a reversible process} \end{cases}$$

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

Example

- Heat is transferred in two places, the boiler and the condenser

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T}\right)_{\text{boiler}} + \int \left(\frac{\delta Q}{T}\right)_{\text{condenser}}$$

- Since the temperature remains constant in both the boiler and condenser

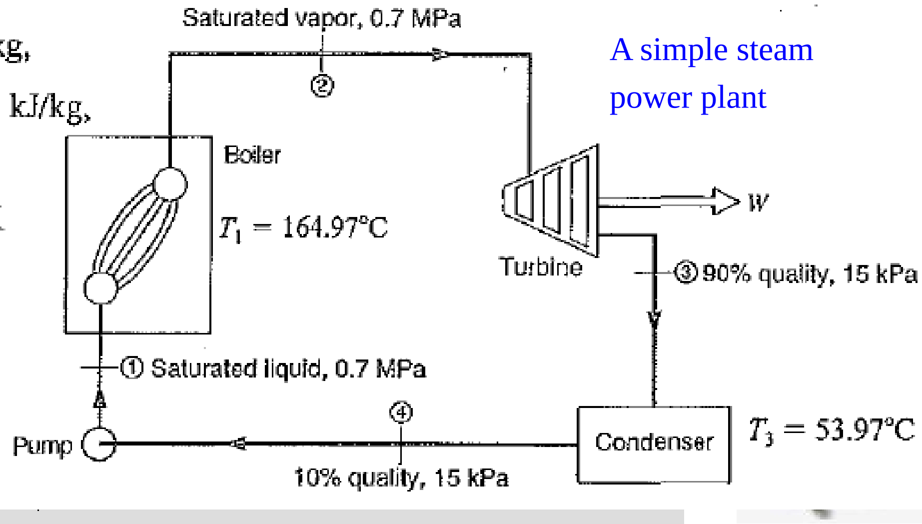
$$\oint \frac{\delta Q}{T} = \frac{1}{T_1}\int_1^2 \delta Q + \frac{1}{T_3}\int_3^4 \delta Q = \frac{{}_1Q_2}{T_1} + \frac{{}_3Q_4}{T_3}$$

${}_1q_2 = h_2 - h_1 = 2066.3$ kJ/kg,

${}_3q_4 = h_4 - h_3 = -1898.4$ kJ/kg,

$\oint \frac{\delta Q}{T} = -1.087$ kJ/kg-K

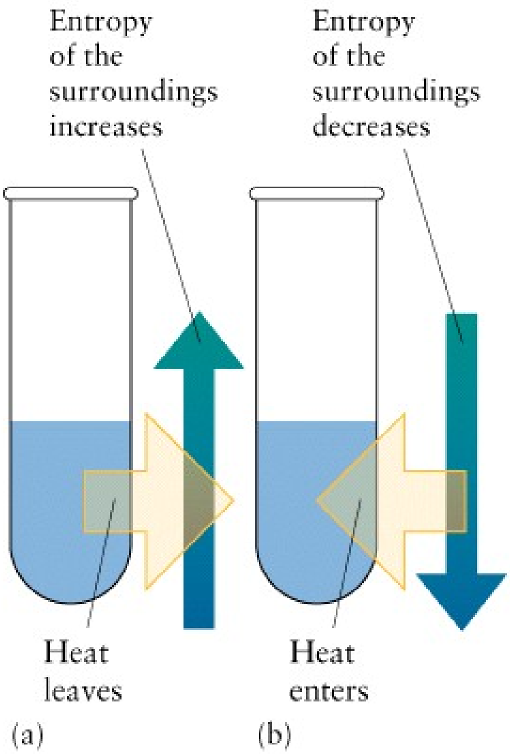
Satisfies the inequality of Clausius

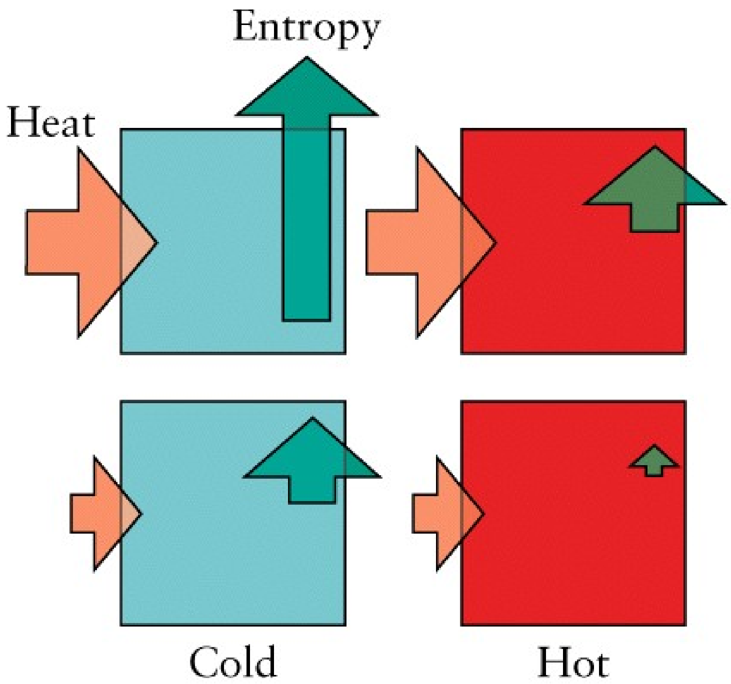


A simple steam power plant

Entropy change for system and surrounding

- When the heat transfer into the surroundings and increases their entropy. But if the heat transfer to the system the entropy of the surroundings decreases.
- The blue-green arrows indicate the direction of entropy change in the surroundings.





- The entropy change due to heat transfer depends on both the amount of heat transferred and the temperature of the system. A lot of heat transferred to a cold system (upper left) results in a large increase in the entropy of the system. A small quantity of heat transferred to a hot system (lower right) results in a small increase in entropy of the system.

- ➢ You take more entropy after you drink a cup of hot tea than a cup of iced tea.
- ➢ You take more entropy when you’re in fever than when you’re normal after you drink a cup of tea.

Example Entropy change during isothermal

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 ($S_g = 0$).**

Example Cont.

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

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

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

- **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.**

Example

Cylinder/piston setup contains I L of saturate liquid refrigerant R-12 at 20°C. The piston now slowly expands, maintaining constant temperature to a final pressure of 400 kPa in a reversible process. Calculate the required work and heat transfer to accomplish this process.

Example Cont.

The increase of entropy principle (closed system)

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

- 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.

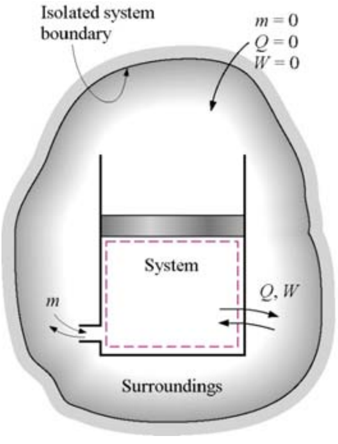
The increase of entropy principle (closed system)

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

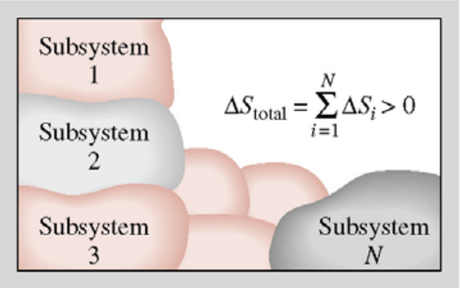
$$\Delta S = S_2 - S_1 = \int_1^2 \cancel{\frac{\delta Q}{T}} + S_{gen} \quad \Rightarrow \quad \Delta S_{adiabatic} = S_{gen}$$

- 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



(Isolated)



$$\Delta S_{total} = \sum_{i=1}^{N} \Delta S_i > 0$$

- 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:

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

Summary of the increase of entropy principle

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

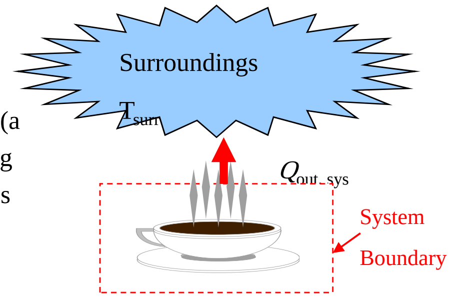
Important Remarks

- Processes can occur in a certain direction only , not in any direction. A process must proceed in the direction that complies with the increase of entropy principle. A process that violates this principle is impossible.
- Entropy is a non-conserved property. Entropy is conserved during the idealized reversible process only and increases during all actual processes.
- The performance of engineering systems is degraded by the presence of irreversibilities, and the entropy generation is is a measure of the magnitude of the irreversibilities present during a process.

Entropy generation during heat transfer

- The principle of increase of entropy for a closed system exchanging heat with its surroundings at a constant temperature T_{surr} is found by using the equation for the entropy generated for an isolated system.

A general closed system (a cup of coffee) exchanging heat with its surroundings



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

$$\Delta S_{sys} = (S_2 - S_1)_{sys}$$

$$\sum \Delta S_{surr} = \frac{Q_{net,\,surr}}{T_{surr}}$$

Entropy generation during heat transfer

$$S_{gen} = \Delta S_{total} = m(s_2 - s_1)_{sys} + \frac{Q_{net,\,surr}}{T_{surr}} \geq 0$$

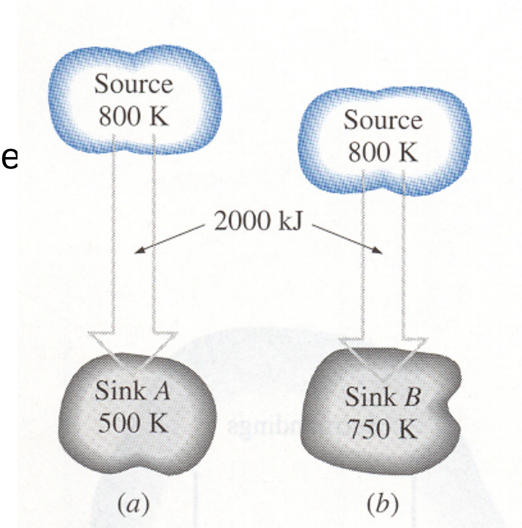
where

$$Q_{net,\,surr} = -Q_{net,\,sys} = -(0 - Q_{out,\,sys}) = Q_{out,\,sys}$$

Example: 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

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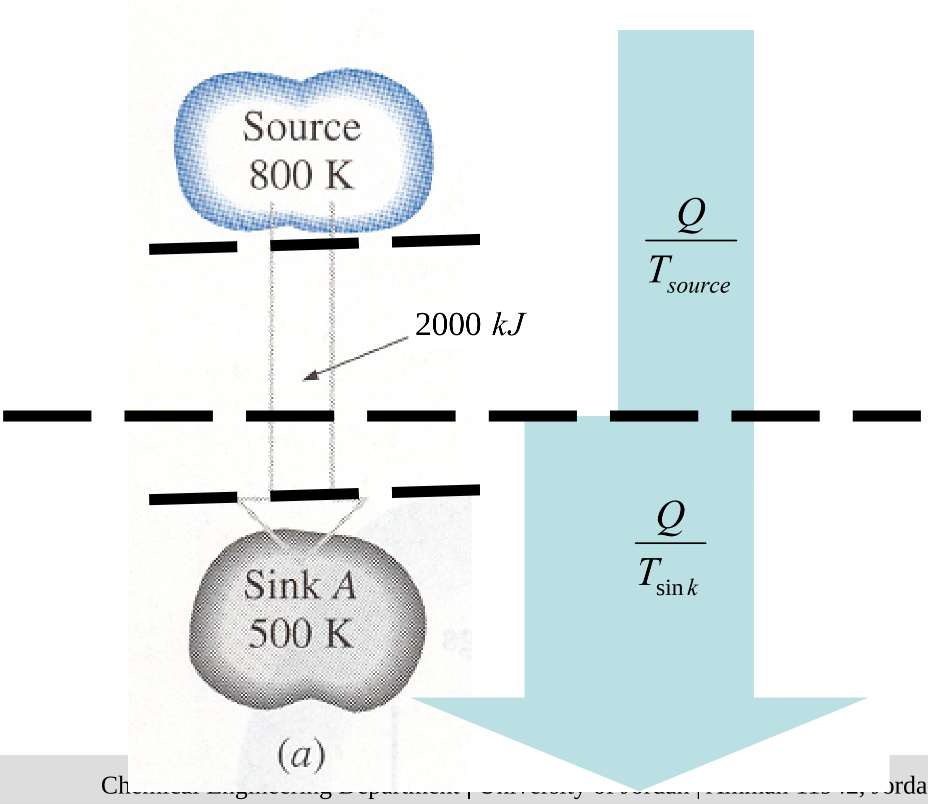
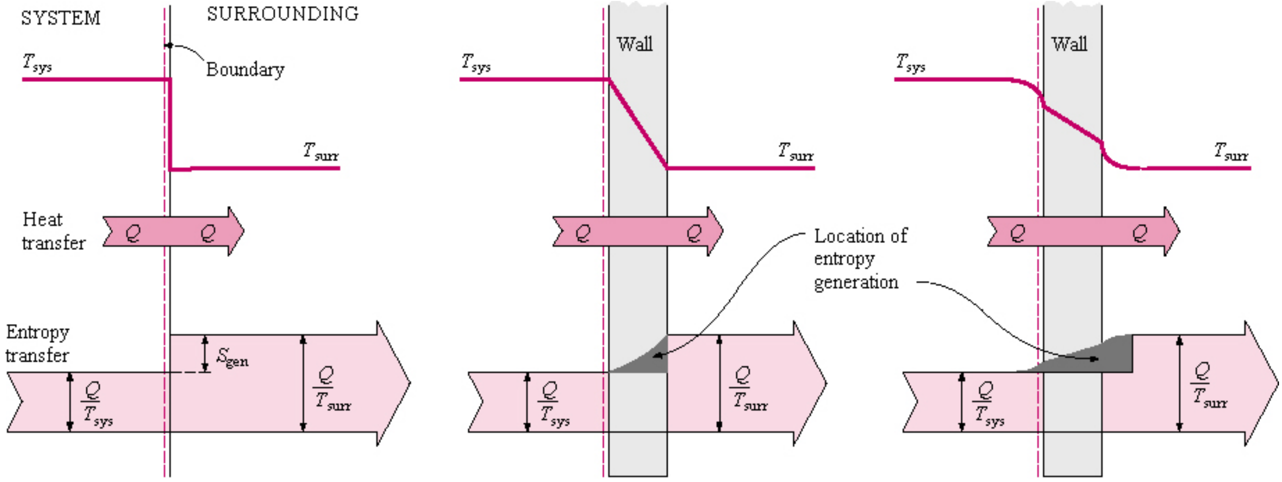
Example: Cont.

Example: Cont.

Where does the irreversibility arise from?



Where is entropy generated?



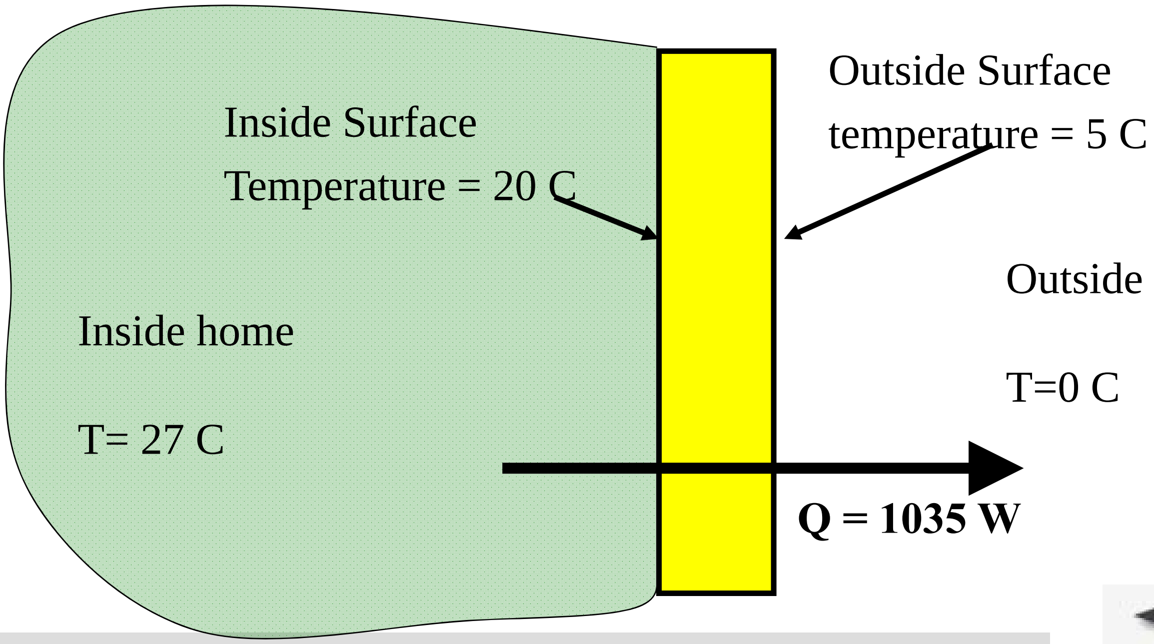
(*a*) The wall is ignored

(*b*) The wall is considered

(*c*) The wall as well as the variations of temperature in the system and the surroundings are considered

Example: 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.**



Inside Surface
Temperature = 20 C

Outside Surface
temperature = 5 C

Inside home

T= 27 C

Outside

T=0 C

Q = 1035 W

A) Determine the rate of entropy generation in the wall

B) Determine the rate of entropy generation for the process

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

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

$$\Delta S_{sys} = S_2 - S_1 = \underbrace{m\left(s_2 - s_1\right)}_{\text{for closed system}}$$

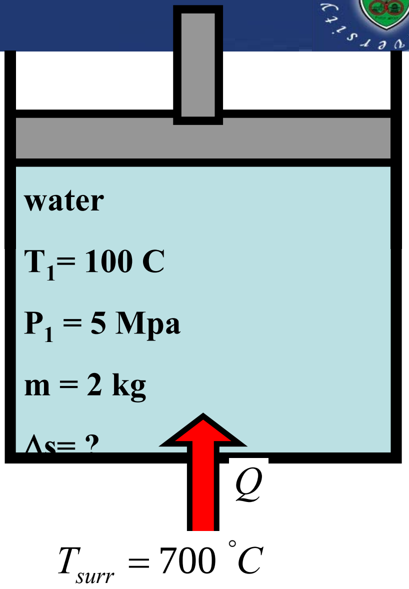
$$\Delta S_{surr} = Q_{surr}/T_{surr} = -Q_{sys}/T_{surr}$$

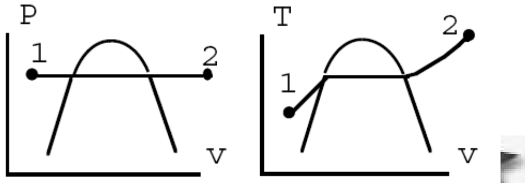
$$\boxed{S_{gen} = \underbrace{m(s_2 - s_1)}_{system} - \underbrace{Q_{sys}/T_{surr}}_{surroundings} \geq 0}$$

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.





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).

$$S_{gen} = \underbrace{m\left(s_2 - s_1\right)}_{system} - \underbrace{Q_{sys}/T_{surr}}_{surroundings}$$

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 (P2=P1).

Go to the tables and get the following

$v_2 = 0.08849$ $u_2 = 3457.6$

$h_2 = 3900.1$ $s_2 = 7.5122,$

Some Remarks about Entropy

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

$$\boxed{S_{gen} \geq 0}$$

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

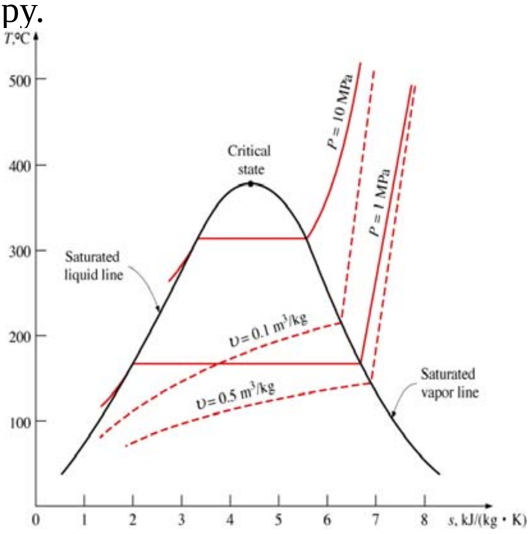
In the second-law analysis, it is very helpful to plot the processes on T-s and h-s diagrams for which one of the coordinates is entropy.

- Recall the definition of entropy

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

- Property diagrams serves as great visual aids in the thermodynamic analysis of process.

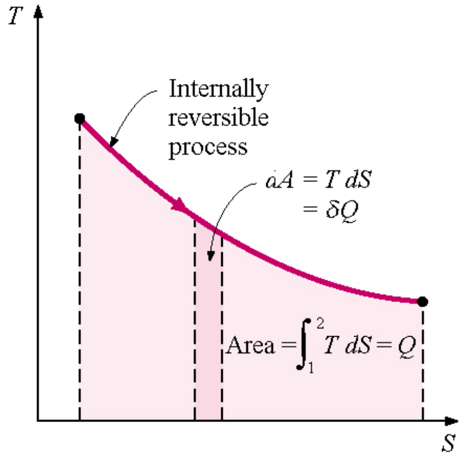
- We have used P-v and T-v diagrams extensively in conjunction with the first law of thermodynamics.



$$\delta W = PdV$$

Property diagrams involving entropy

$$Q_{\text{int},rev} = \int_1^2 TdS$$

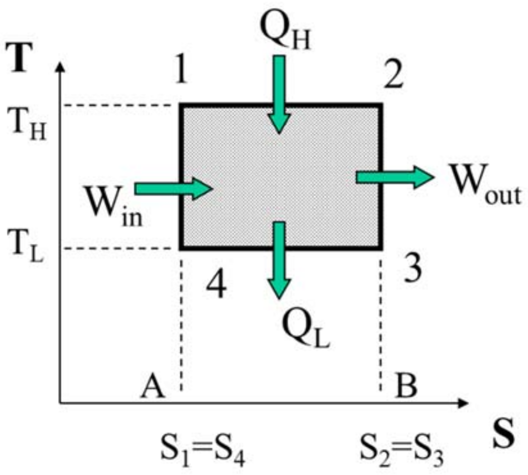


This area has no meaning for irreversible processes!

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.

Example

- Show the Carnot cycle on a T-S diagram and identify the heat transfer at both the high and low temperatures, and the work output from the cycle.



1-2, reversible isothermal heat transfer

$Q_H = \int TdS = T_H(S_2-S_1)$ area 1-2-B-A

2-3, reversible, adiabatic expansion

isentropic process, S=constant ($S_2=S_3$)

3-4, reversible isothermal heat transfer

$Q_L = \int TdS = T_L(S_4-S_3)$, area 3-4-A-B

4-1, reversible, adiabatic compression

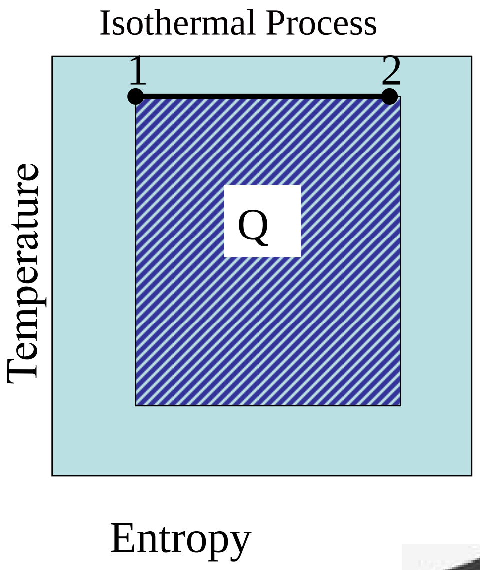
isentropic process, $S_1=S_4$

Net work $W_{net} = Q_H - Q_L$, the area enclosed by 1-2-3-4, the shaded area

Isothermal internally reversible process.

$$Q_{\text{int},rev} = T_0\int_1^2 dS = T_0\Delta S = T_0 m\,\Delta s$$

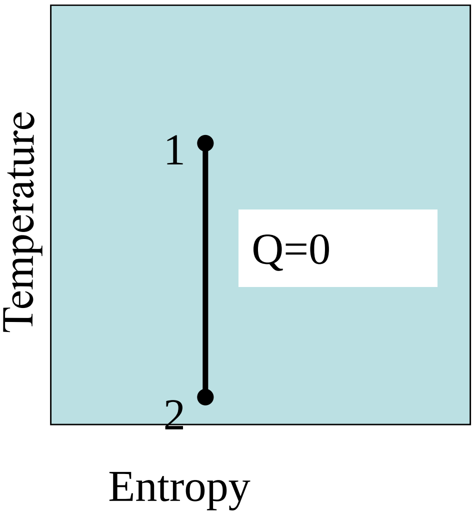
$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q_{net}}{T} = \frac{Q_{net}}{T_o}$$

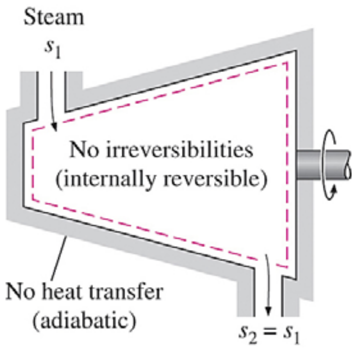


Adiabatic internally reversible process

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.

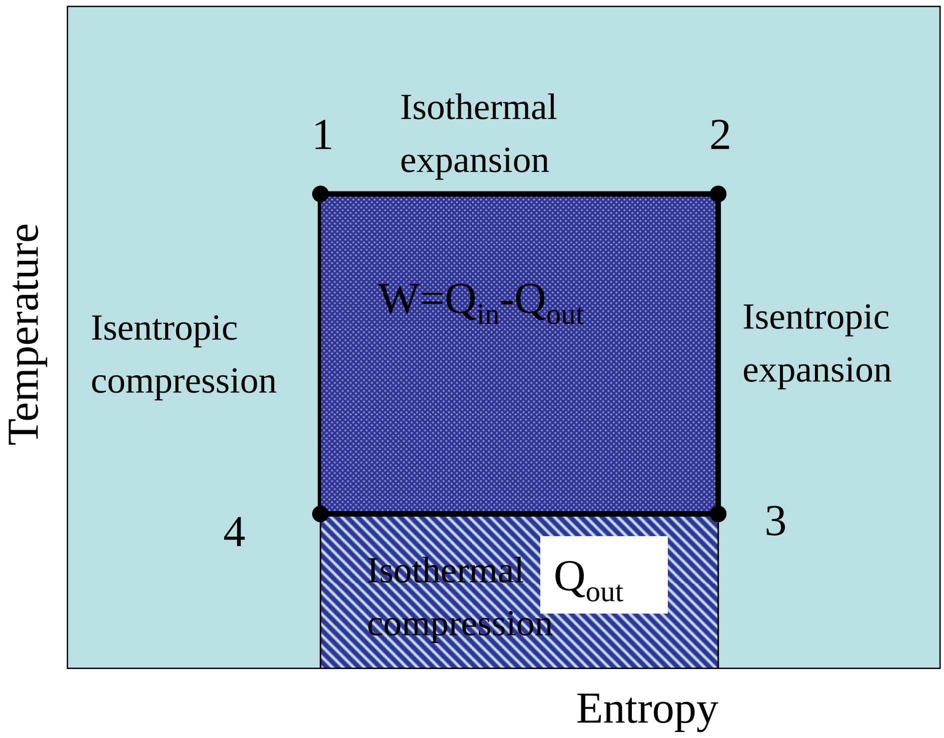


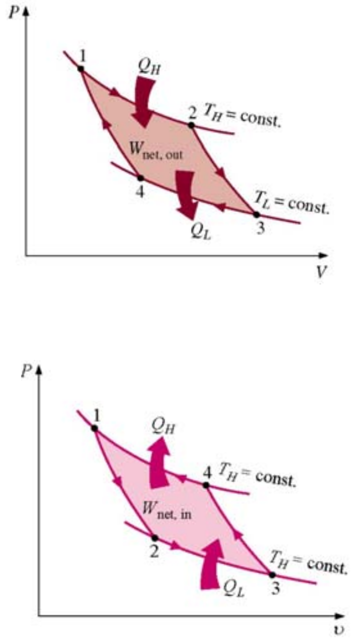


The isentropic process appears as a *vertical* line segment on a *T-s* diagram.

$$\Delta s = 0 \quad \text{or} \quad s_2 = s_1$$

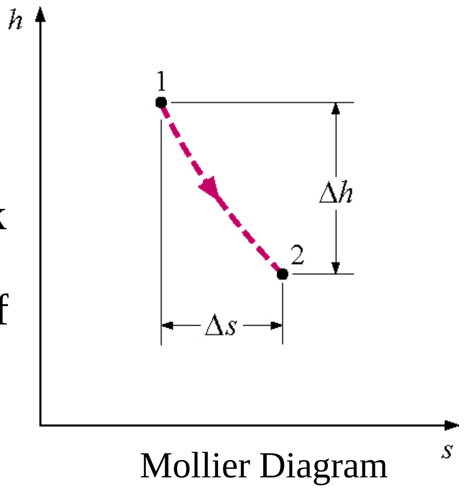
T-s Diagram for the Carnot Cycle





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.



Mollier Diagram

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**

Thermodynamic Relations: TdS Equations

- ➢ From the third law of thermodynamics, which is based on observations of low-temperature chemical reactions, it is concluded that the entropy of all pure substances (in the appropriate structural form) can be assigned the absolute value of zero at the absolute zero of temperature.
- ➢ When there is no change of composition, as would occur in a chemical reaction, it is quite adequate to give values of entropy relative to some arbitrarily selected reference state, such as was done earlier when tabulating values of internal energy and enthalpy.
- ➢ In each case, whatever reference value is chosen, it will cancel out when the change of property is calculated between any two states.

Thermodynamic Relations: TdS Equations

- For a simple compressible substance in the absence of motion or gravitational effects.

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

- For a reversible process of a simple compressible substance

$$\delta Q = T\,dS \qquad \text{and} \qquad \delta W = P\,dV$$

the first-law equation $\quad T\,dS = dU + P\,dV$

$$H = U + PV \quad \Rightarrow \quad dH = dU + P\,dV + V\,dP$$

$$\Rightarrow \quad T\,dS = dH - V\,dP$$

$$\Rightarrow \quad T\,ds = du + P\,dv \qquad ds = \frac{du}{T} + \frac{P\,dv}{T}$$

$$T\,ds = dh - v\,dP \qquad ds = \frac{dh}{T} - \frac{v\,dP}{T}$$

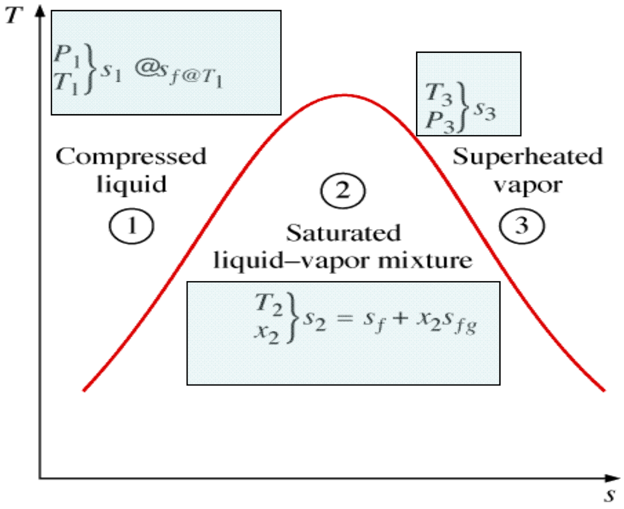
$$ds = \frac{du}{T} + \frac{P}{T}dv = \frac{dh}{T} - \frac{v}{T}dP$$

Gibbs equations.

ΔS for Pure Substances

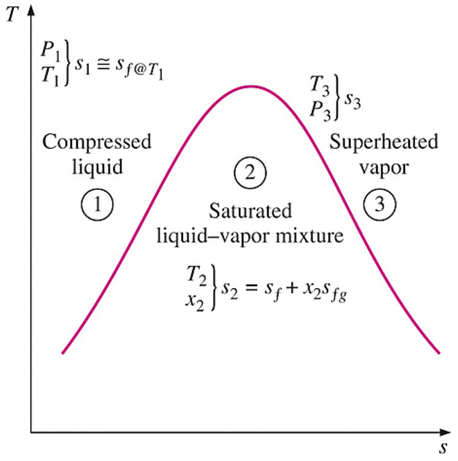
- The entropy of a pure substance is determined from the tables, just as for any other property
- These values were tabulated after conducting a tedious integration.
- These values are given relative to an arbitrary reference state.
- For water its assigned zero at 0.01 C.
- For R-134 it is assigned a zero at -40 C.
- Entropy change for a closed system with mass m is given as expected:

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

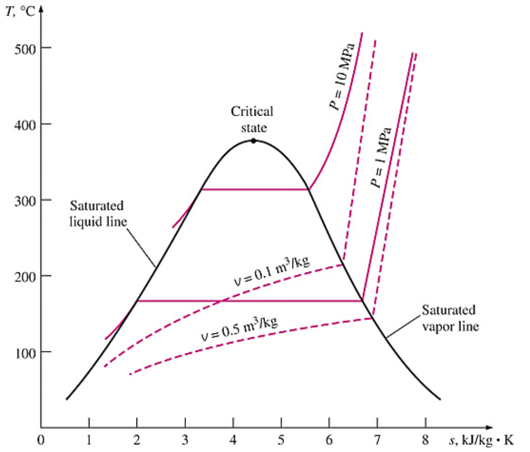


Entropy Change of Pure Substances

- Entropy is an extensive property of a system.
- Thus the value of entropy of a system is fixed once the state of the system is fixed.



The entropy of a pure substance is determined from the tables (like other properties).



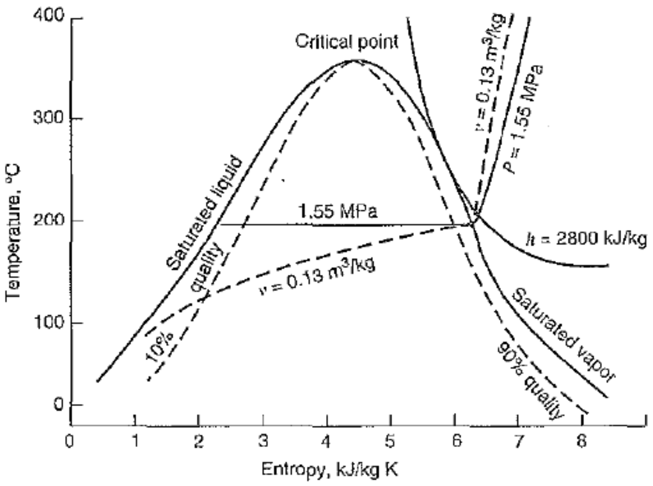
Schematic of the *T-s* diagram for water.

Entropy change

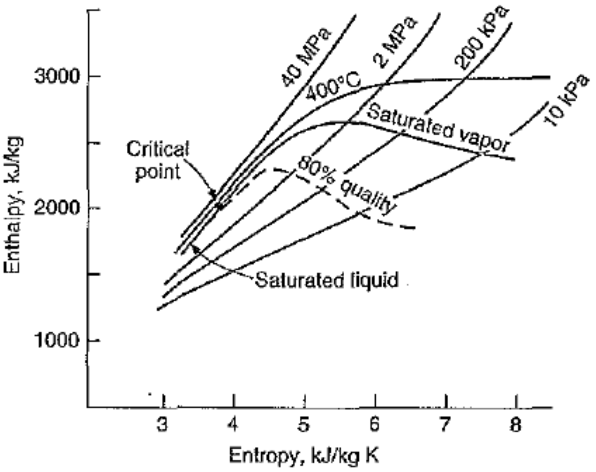
$$\Delta S = m\Delta s = m(s_2 - s_1) \qquad \text{(kJ/K)}$$

Entropy Change of Pure Substances

- The thermodynamic properties of a substance are often shown on a temperature entropy diagram and on an enthalpy--entropy diagram (Mollier diagram)



T-S diagram for steam



h-S diagram for steam

Example

Consider steam is undergoing a phase transition from liquid to vapor at a constant temperature of 20°C. Determine the entropy change $s_{fg}=s_g-s_f$ using the Gibbsian equations and compare the value to that read directly from the thermodynamic table.

$$ds = \frac{du}{T} + \frac{P}{T}dv, \text{ change from liquid to vapor}$$

$$s_{fg} = s_g - s_f = \frac{1}{T}(u_g - u_f) + \frac{P}{T}(v_g - v_f)$$

From table A-4:

$T=20°C$, $P = 2.338$ kPa, $v_f = 0.001002(m^3/kg)$, $v_g=57.79(m3/kg)$, $u_f=83.9(kJ/kg)$, $u_g=2402.9(kJ/kg)$

Substituting into the Tds relation:

$$s_{fg}= \underbrace{(1/293)}_{\mathbf{1/T}}\underbrace{(2402.9\text{-}83.9)}_{\mathbf{u_g - u_f}} + \underbrace{(2.338/293)}_{\mathbf{P/T}}\underbrace{(57.79\text{-}0.001002)}_{\mathbf{v_g - v_f}} = 8.375(\text{kJ/kg K})$$

Compares favorably with the tabulated value $s_{fg}=8.3715(\text{kJ/kg K})$

Entropy Change of Liquids and Solids

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

Since $dv \cong 0$ for liquids and solids

$$ds = \frac{du}{T} = \frac{c\,dT}{T}$$

since $c_p = c_v = c$ and $du = c\,dT$

Liquids and solids can be approximated as *incompressible substances* since their specific volumes remain nearly constant during a process.

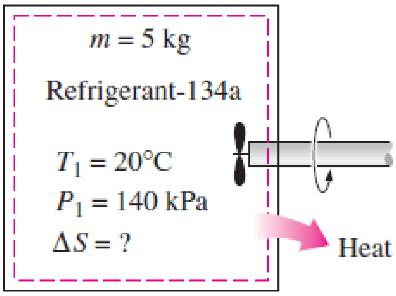
Liquids, solids: $$s_2 - s_1 = \int_1^2 c(T)\frac{dT}{T} \cong c_{\text{avg}} \ln\frac{T_2}{T_1} \qquad (\text{kJ/kg}\cdot\text{K})$$

For and isentropic process of an incompressible substance

Isentropic: $$s_2 - s_1 = c_{\text{avg}} \ln\frac{T_2}{T_1} = 0 \quad \rightarrow \quad T_2 = T_1$$

Example

A rigid tank contains 5 kg of refrigerant-134a initially at 20°C and 140 kPa. The refrigerant is now cooled while being stirred until its pressure drops to 100 kPa. Determine the entropy change



Example Cont.

Example

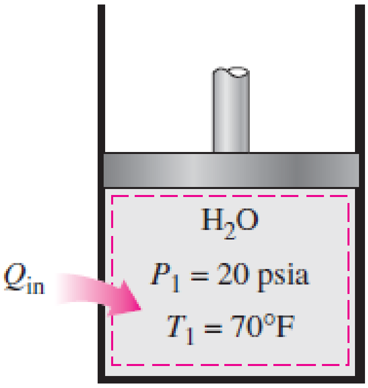
A 50-kg block of iron casting at 500 K is thrown into a large lake that is at a temperature of 285 K. The iron block eventually reaches thermal equilibrium with the lake water. Assuming an average specific heat of 0.45 kJ/kg · K for the iron, determine (*a*) the entropy change of the iron block, (*b*) the entropy change of the lake water, and (*c*) the entropy generated during this process.

Example Cont.

Example Cont.

Example

A piston–cylinder device initially contains 3 lbm of liquid water at 20 psia and 70°F. The water is now heated at constant pressure by the addition of 3450 Btu of heat. Determine the entropy change of the water during this process.



Example Cont.

Entropy Change of Ideal Gas

From the first *T ds* relation

$$ds = \frac{du}{T} + \frac{P\,dv}{T} \qquad du = c_v\,dT \qquad P = RT/v$$

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

$$s_2 - s_1 = \int_1^2 c_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1}$$

From the second *T ds* relation

$$ds = \frac{dh}{T} - \frac{v\,dP}{T}$$

$$dh = c_p\,dT \qquad v = RT/P$$

$$s_2 - s_1 = \int_1^2 c_p(T)\,\frac{dT}{T} - R\ln\frac{P_2}{P_1}$$

$$Pv = RT$$
$$du = C_v\,dT$$
$$dh = C_p\,dT$$

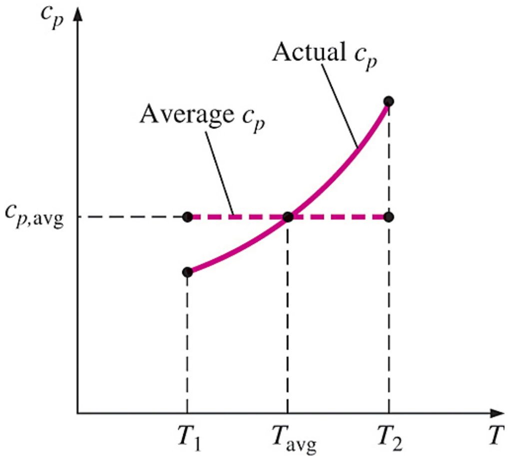
A broadcast from channel IG.

Constant Specific Heats (Approximate Analysis)

$$s_2 - s_1 = \int_1^2 c_v(T)\frac{dT}{T} + R\ln\frac{v_2}{v_1} \longrightarrow s_2 - s_1 = c_{v,\mathrm{avg}}\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$

$$s_2 - s_1 = \int_1^2 c_p(T)\frac{dT}{T} - R\ln\frac{P_2}{P_1} \longrightarrow s_2 - s_1 = c_{p,\mathrm{avg}}\ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

$$(\mathrm{kJ/kg\cdot K})$$



Entropy change of an ideal gas on a unit–mole basis

$$\bar{s}_2 - \bar{s}_1 = \bar{c}_{v,\mathrm{avg}}\ln\frac{T_2}{T_1} + R_u\ln\frac{v_2}{v_1} \qquad (\mathrm{kJ/kmol\cdot K})$$

$$\bar{s}_2 - \bar{s}_1 = \bar{c}_{p,\mathrm{avg}}\ln\frac{T_2}{T_1} - R_u\ln\frac{P_2}{P_1} \qquad (\mathrm{kJ/kmol\cdot K})$$

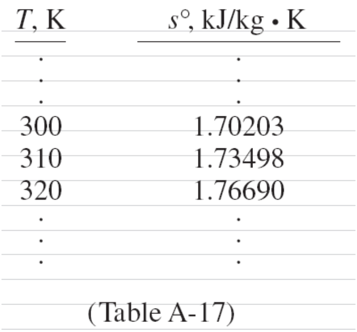
Under the constant-specific-heat assumption, the specific heat is assumed to be constant at some average value.

Variable Specific Heats (Exact Analysis)

We choose absolute zero as the reference temperature and define a function $s°$ as

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

$$\int_1^2 c_p(T)\frac{dT}{T} = s_2^\circ - s_1^\circ$$



T, K	s°, kJ/kg · K
.	.
.	.
.	.
300	1.70203
310	1.73498
320	1.76690
.	.
.	.
.	.

(Table A-17)

The entropy of an ideal gas depends on both T and P. The function s represents only the temperature-dependent part of entropy.

On a unit–mass basis

$$s_2 - s_1 = s_2^\circ - s_1^\circ - R\ln\frac{P_2}{P_1} \qquad (\mathrm{kJ/kg\cdot K})$$

where s_2° is the value of s° at T_2 and s_1° is the value at T_1

On a unit–mole basis

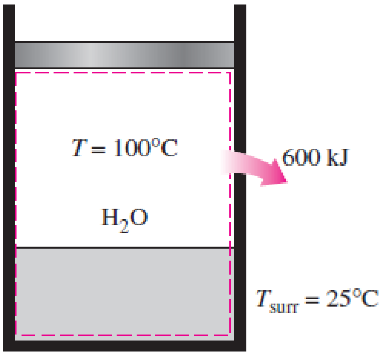
$$\bar{s}_2 - \bar{s}_1 = \bar{s}_2^\circ - \bar{s}_1^\circ - R_u\ln\frac{P_2}{P_1} \qquad (\mathrm{kJ/kmol\cdot K})$$

Example

Air is compressed from an initial state of 100 kPa and 17°C to a final state of 600 kPa and 57°C. Determine the entropy change of air during this compression process by using (*a*) property values from the air table and (*b*) average specific heats.

Example

A frictionless piston–cylinder device contains a saturated liquid–vapor mixture of water at 100C. During a constant-pressure process, 600 kJ of heat is transferred to the surrounding air at 25C. As a result, part of the water vapor contained in the cylinder condenses. Determine (*a*) the entropy change of the water and (*b*) the total entropy generation during this heat transfer process.



Example Cont.

Isentropic Processes for Ideal Gases

If a process is isentropic (that is adiabatic and reversible), ds = 0, $s_1 = s_2$,

then it can be shown that:

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1}, \text{ and } \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

$$\text{and } \frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^{k}, \text{ where } k = \frac{c_p}{c_v}$$

The above are referred to as the: ***first, second and third***, respectively, ***isentropic relations for Ideal Gases*** (assuming constant specific heats).

They can also be written as:

$\boxed{\begin{array}{l} \mathbf{T}\,v^{k-1} = \textbf{constant} \\ \mathbf{TP}^{(1-k)/k} = \textbf{constant} \\ \mathbf{P}\,v^{k} = \textbf{constant} \end{array}}$

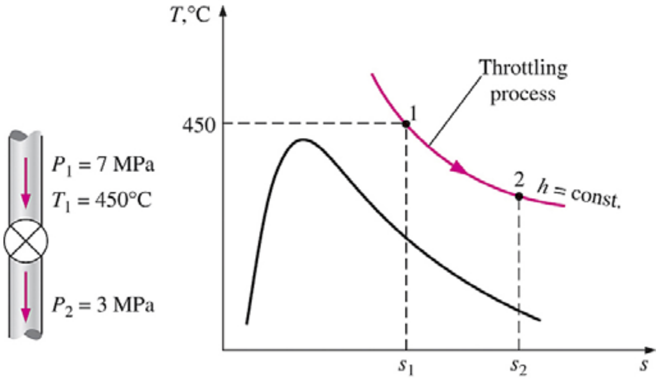
First isentropic relation

Second isentropic relation

Third isentropic relation

Example

Entropy balance for a throttling process



Example Cont.

Some Aspects of the 2nd Law

- Predicting The Direction Of Processes
- Establishing Conditions For Equilibrium
- Best Theoretical Performance Of Devices
- Factors Influencing Best Performance Of Devices

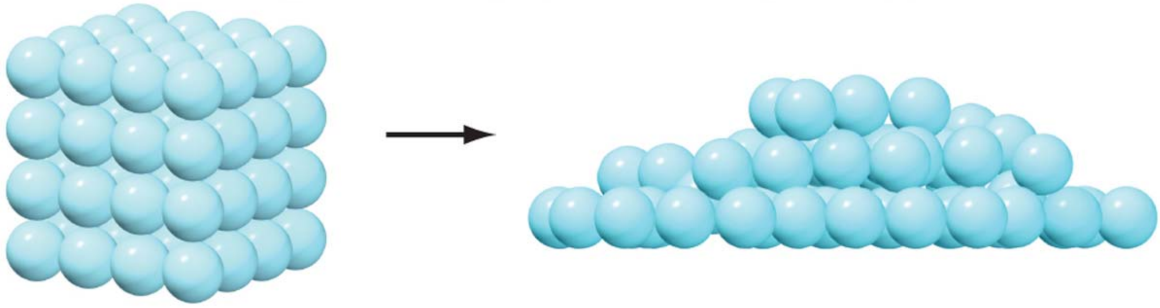
Familiar Spontaneous and Nonspontaneous Processes

Spontaneous	**Nonspontaneous**
Ice melting at room temperature	Water freezing at room temperature
Sodium metal reacting violently with water to produce sodium hydroxide and hydrogen gas [⏮ Section 7.7]	Sodium hydroxide reacting with hydrogen gas to produce sodium metal and water
A ball rolling downhill	A ball rolling uphill
The rusting of iron at room temperature	The conversion of rust back to iron metal at room temperature
Water freezing at −10°C	Ice melting at −10°C

- **Spontaneous**: process that ***does*** occur under a specific set of conditions
- **Nonspontaneous**: process that ***does not*** occur under a specific set of conditions

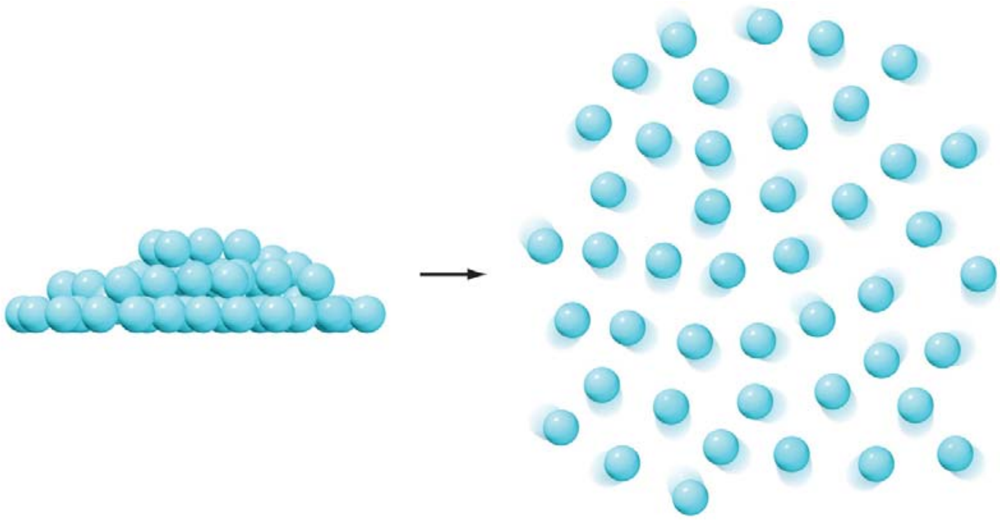
Entropy Changes in a System Qualitative

- $S_{\text{solid}} < S_{\text{liquid}}$



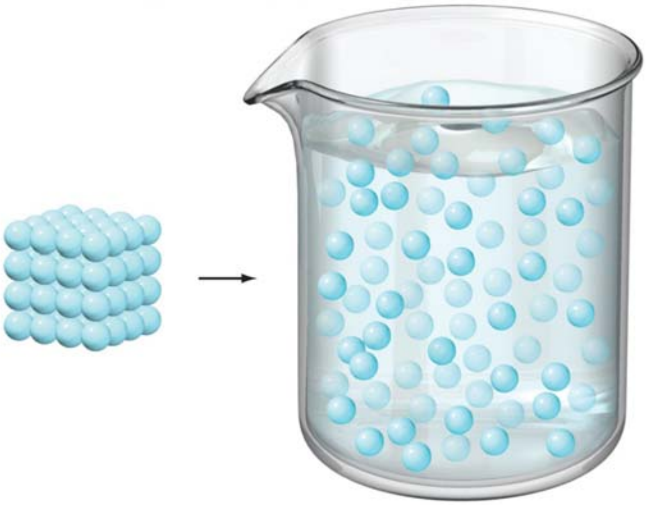
Entropy Changes in a System Qualitative

- $S_{\text{liquid}} < S_{\text{vapor}}$



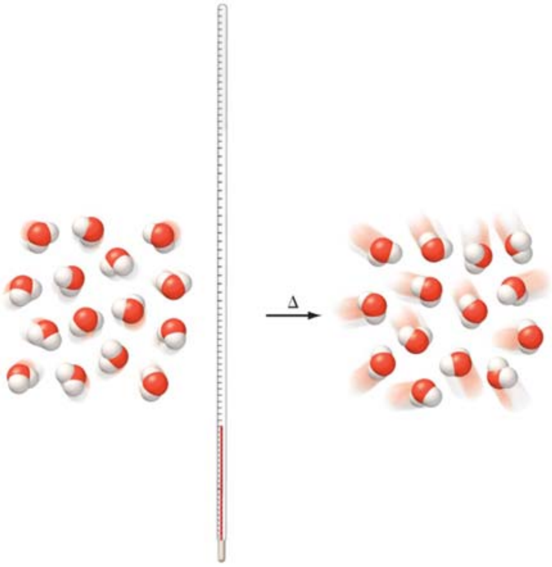
Entropy Changes in a System Qualitative

- $S_{pure} < S_{aqueous}$



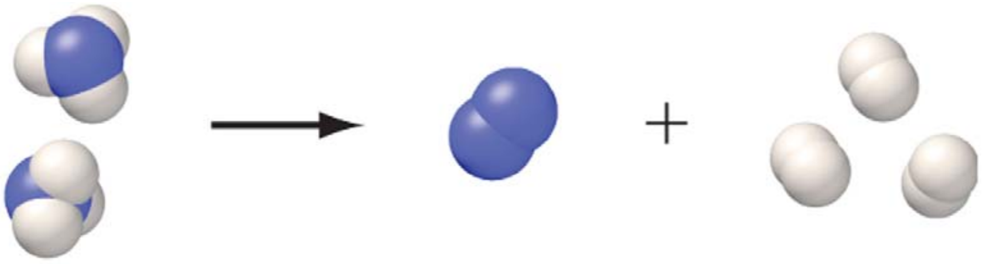
Entropy Changes in a System Qualitative

$S_{\text{lower temp}} < S_{\text{higher temp}}$



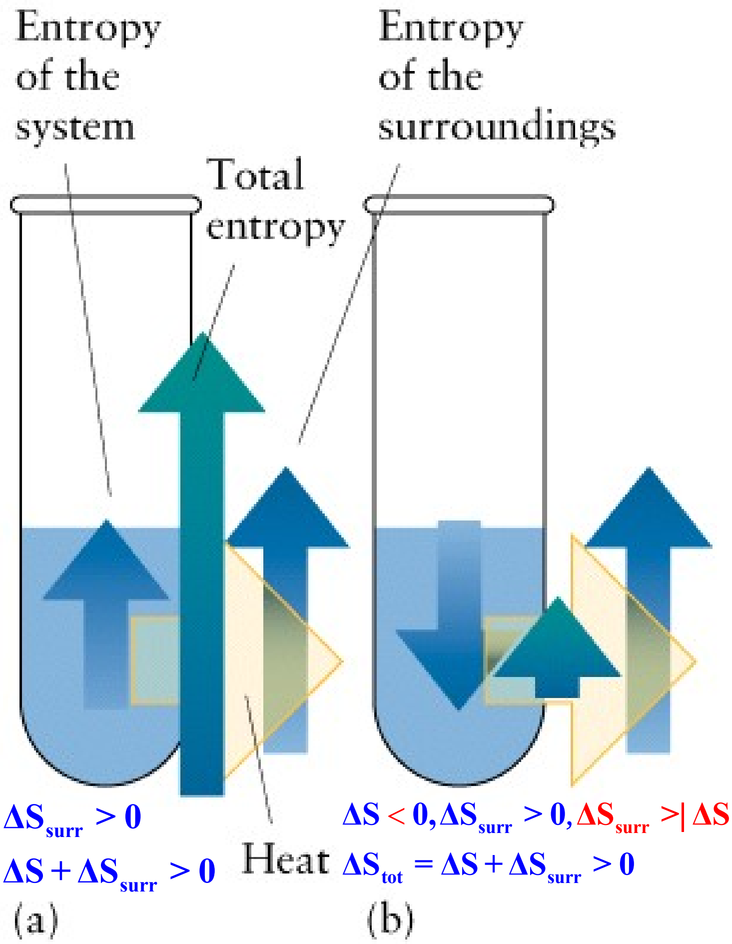
Entropy Changes in a System Qualitative

- $S_{\text{fewer moles}} < S_{\text{more moles}}$



$$2NH_3 \longrightarrow N_2 + 3H_2$$

In an exothermic reaction, (a) the overall entropy change is certainly positive when the entropy of the system increases. (b) The overall entropy change is positive even when the entropy of the system decreases, provided that the entropy increase in the surroundings is greater. The reaction is spontaneous in both cases.

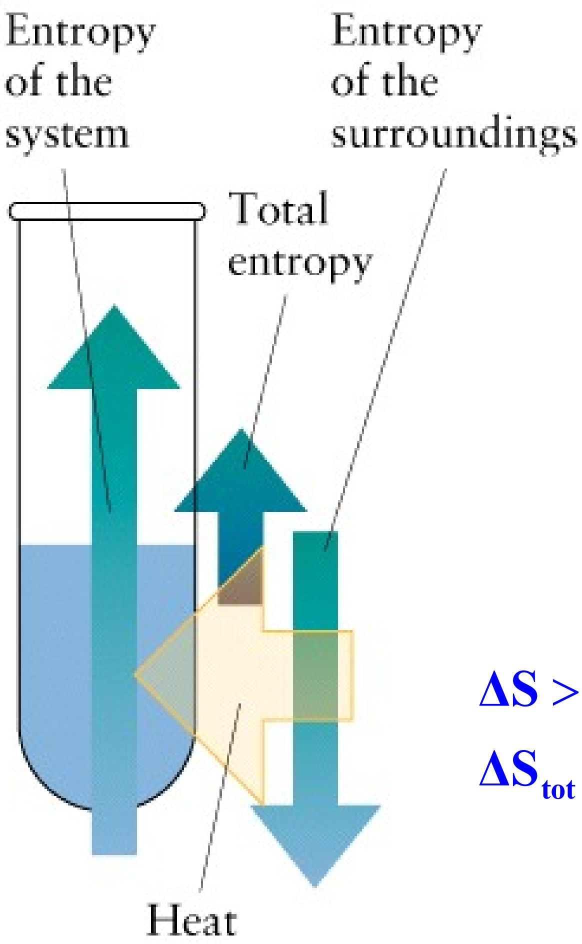


$\Delta S > 0, \Delta S_{surr} > 0$

$\Delta S_{tot} = \Delta S + \Delta S_{surr} > 0$

$\Delta S < 0, \Delta S_{surr} > 0, \Delta S_{surr} > |\Delta S|,$

$\Delta S_{tot} = \Delta S + \Delta S_{surr} > 0$



An endothermic reaction is spontaneous only when the entropy of the system increases enough to overcome the decrease in entropy of the surroundings, as it does here.

$$\Delta S > 0, \Delta S_{surr} < 0, |\Delta S_{surr}| < \Delta S,$$

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} > 0$$

Entropy Changes

If the entropy change for a system is known to be –187.5 J/K·mol and the enthalpy change for a system is known to be –35.8 kJ/mol, is the reaction spontaneous?

Example

For a reaction in which ΔH = 125 kJ/mol and ΔS = 325 J/K·mol, determine the temperature in Celsius above which the reaction is spontaneous.