

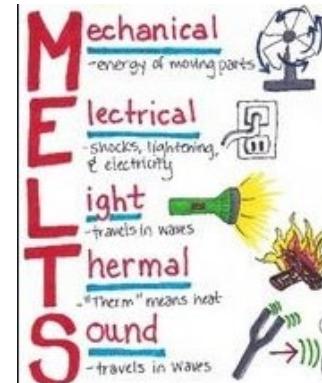
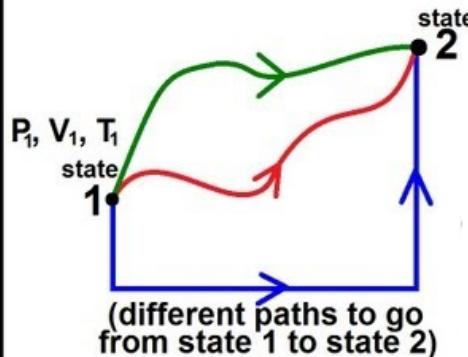
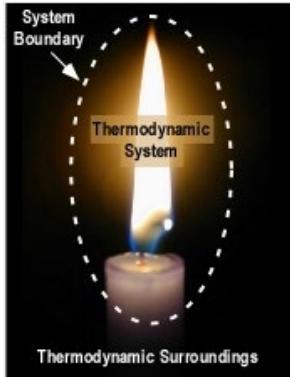
# Class 5: The second law of thermodynamics and entropy

Supernova explosion  
(lower right corner)  
near the Crab Nebula.  
These are highly  
irreversible processes  
resulting in chaos and  
an increase of entropy  
(NASA photo)

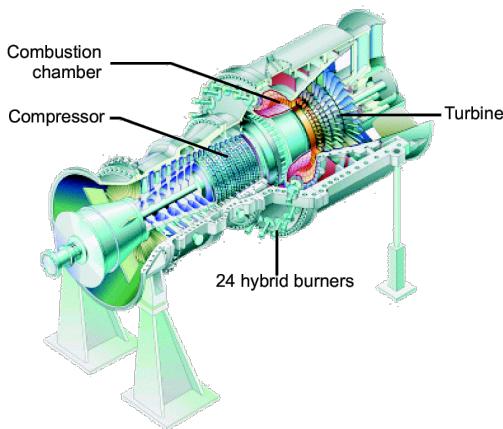


# Roadmap Engineering Thermodynamics

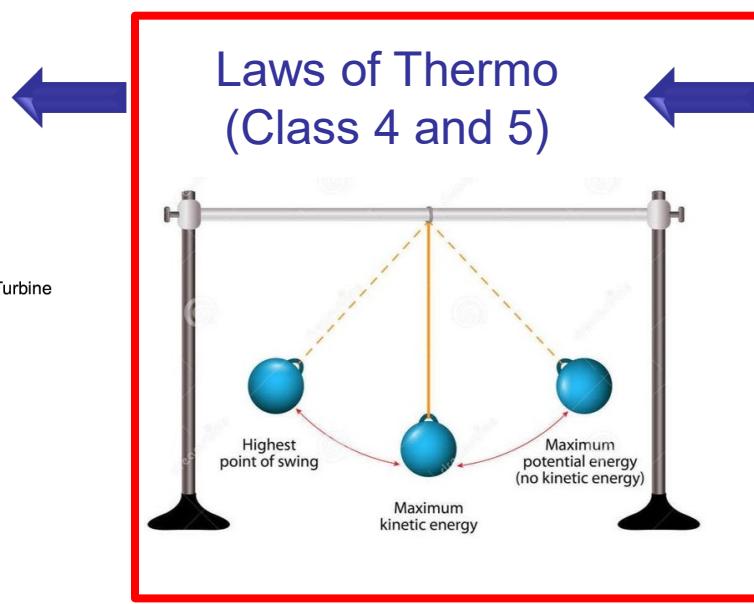
- Using thermodynamics for practical applications requires knowledge of:  
Concepts and definitions (Class 1)    ➔    Various forms of energy (Class 2)



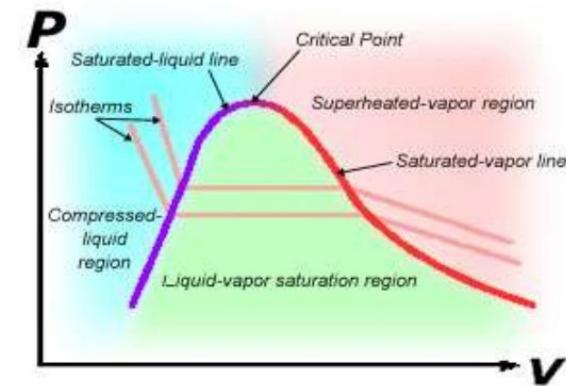
- Power cycles  
(Class 6 – 11)



- Laws of Thermo  
(Class 4 and 5)

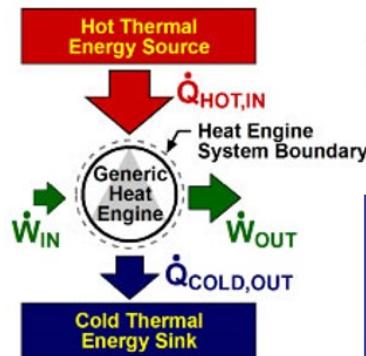


- Properties of Substances  
(Class 3, 9)

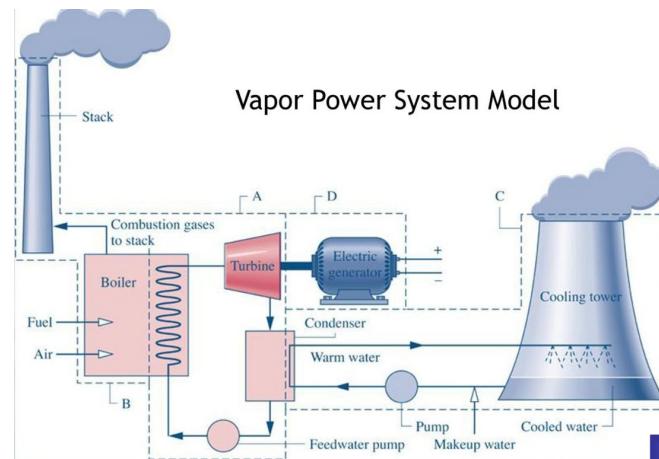


# Roadmap Engineering Thermodynamics

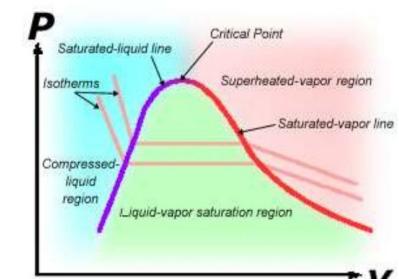
Thermodynamic cycles (Class 6)



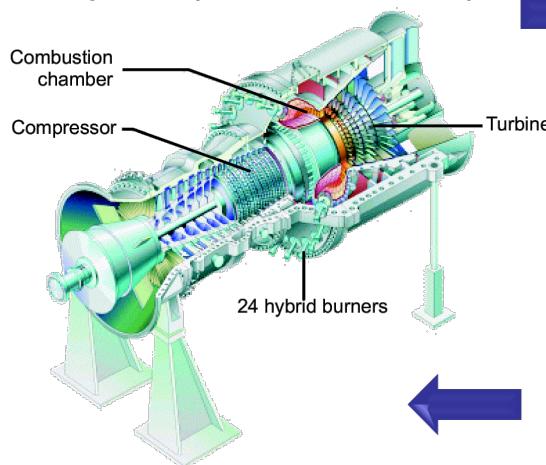
Vapor power cycles – Rankine cycle (Class 7, 8)



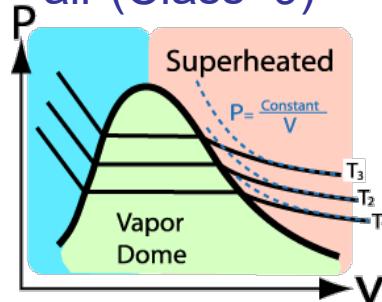
Properties of water (Class 3)



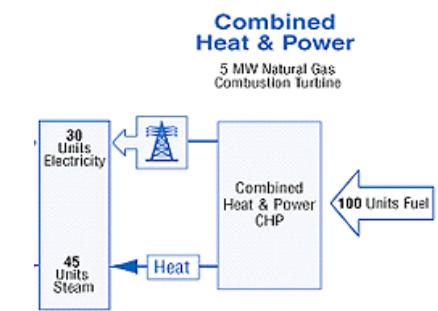
Gas power cycles – Brayton cycle (Class 10, 11)



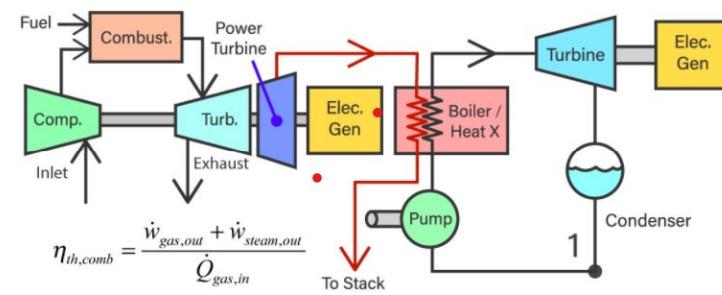
Properties of air (Class 9)



Combined cycles  
Combined heat & power (Class 8, 11)



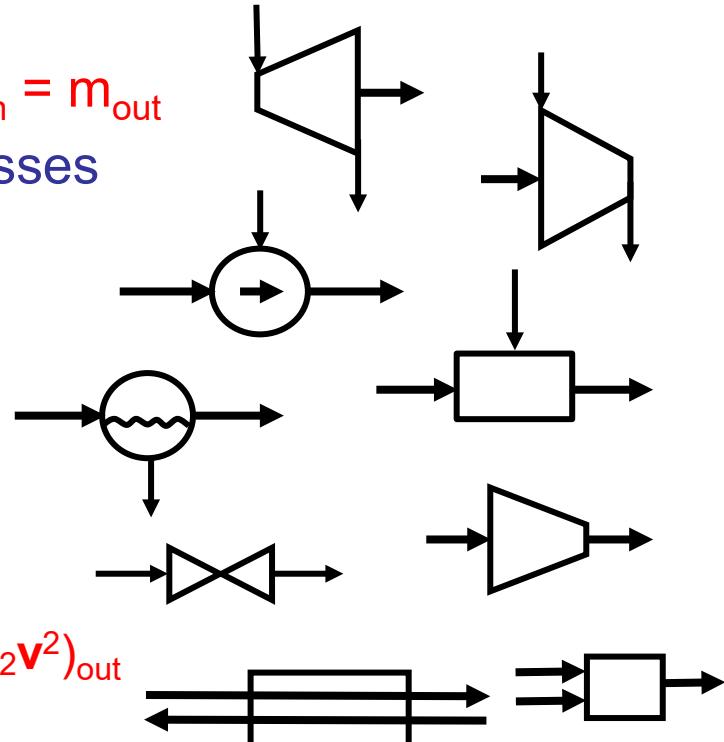
75% OVERALL EFFICIENCY



# Recapitulate Class 4

- **Conservation of energy, first law of thermodynamics**
  - Closed system  $du = \delta q - \delta w \rightarrow \Delta u = q_{\text{net}} - w_{\text{net}} \rightarrow \Delta U = Q_{\text{net}} - W_{\text{net}}$
  - Open system  $q_{\text{in}} + w_{\text{in}} + (h + ke + pe)_{\text{in}} = q_{\text{out}} + w_{\text{out}} + (h + ke + pe)_{\text{out}}$
- **Conservation of mass in open systems**  $m_{\text{in}} = m_{\text{out}}$
- Application to steady-state steady-flow processes
  - Turbines
  - Compressors
  - Pumps
  - Blowers
  - Boilers
  - Condensers
  - Nozzles and diffusers
  - Throttling valves
  - Heat exchangers
  - Mixing device

$w_{\text{out}} = h_{\text{in}} - h_{\text{out}}$   
 $w_{\text{in}} = h_{\text{out}} - h_{\text{in}}$   
 $w_{\text{in}} = v(P_{\text{out}} - P_{\text{in}})$   
 $w_{\text{in}} = h_{\text{out}} - h_{\text{in}}$   
 $q_{\text{in}} = h_{\text{out}} - h_{\text{in}}$   
 $q_{\text{out}} = h_{\text{in}} - h_{\text{out}}$   
 $(h + \frac{1}{2}v^2)_{\text{in}} = (h + \frac{1}{2}v^2)_{\text{out}}$   
 $h_{\text{in}} = h_{\text{out}}$   
 $\dot{m}_{\text{cold}}(h_{\text{out,cold}} - h_{\text{in,cold}}) = \dot{m}_{\text{hot}}(h_{\text{in,hot}} - h_{\text{out,hot}})$   
 $\dot{m}_1 h_1 + \dot{m}_2 h_2 = \dot{m}_3 h_3$

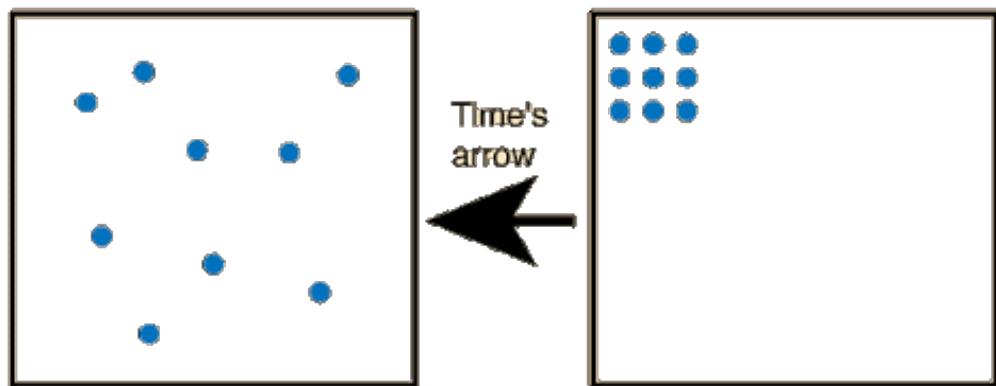


# Content Class 5

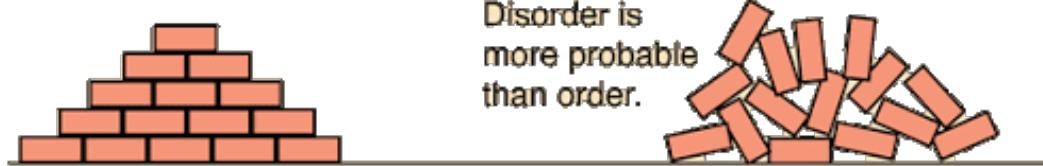
- **The second law of thermodynamics and entropy**

- Direction of processes
- Reversible and irreversible processes
- Entropy
- Second law of thermodynamics
- Second law applied to processes
- Isentropic efficiencies
- **Learning goal:** apply the concept of entropy in analysing thermodynamic systems, explain the second law of thermodynamics, apply it to thermodynamic systems and interpret the effects

If the particles represent gas molecules at normal temperatures inside a closed container, which of the illustrated configurations came first?



If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?



# The second law of thermodynamics & entropy

- The **first law** is very universal and powerful, however it **is not a complete description of all thermodynamic processes**
- Not all processes obeying the first law are possible, many processes that are likely to occur in one direction are unlikely to occur in reverse, even they do not violate the first law
- From observations in our everyday life we know what happens in a lot of processes, but how can this be predicted and why does the reversed process not occur although the first law of thermodynamics, conservation of energy is still obeyed
- How can this thermodynamically be described?



# Impossible processes

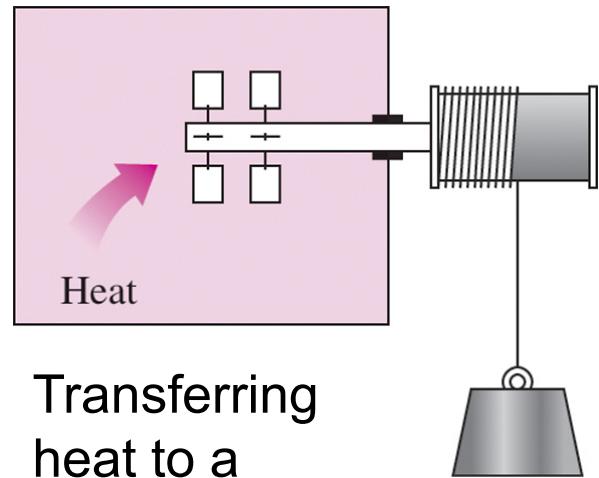
- A lot of processes cannot occur even though they are not in violation with the first law
- Why? Energy is conserved



A cup of hot coffee does not get hotter in a cooler room

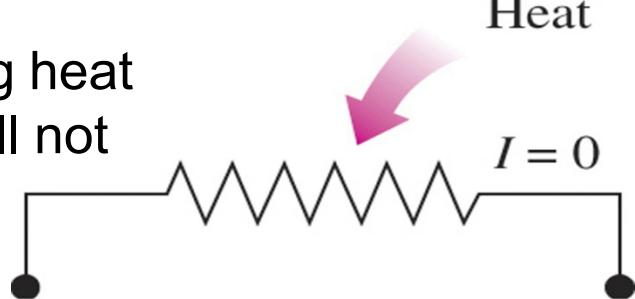


Ice cubes will not be created at room temperature



Transferring heat to a paddle wheel will not cause it to rotate

Transferring heat to a wire will not generate electricity

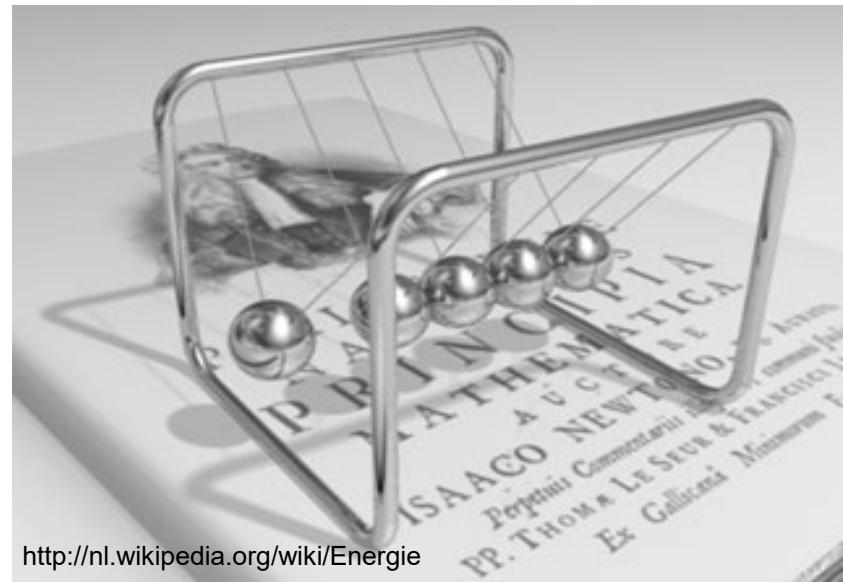


# Direction of processes

- Processes occur in a certain direction, and not in the reverse direction
- Why can these process not be reversed?
- No extra energy is needed to reverse the process, energy is still conserved reversing the process



- The energy is converted to a form with less potential to create work, a form which has less quality
- The process is called to be **irreversible**



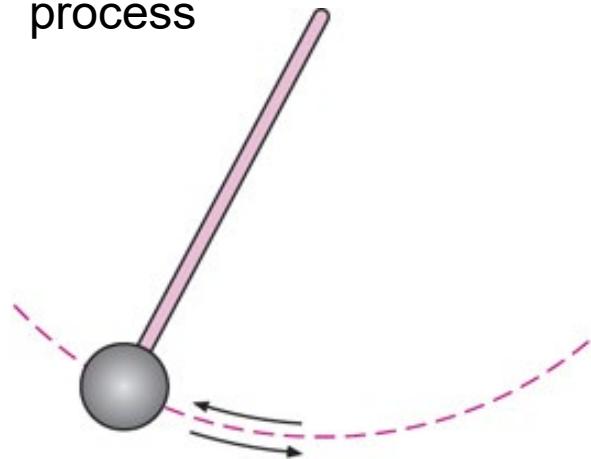
<http://nl.wikipedia.org/wiki/Energie>

Potential, kinetic and strain (internal) energy are successively converted into each other till the motion stops and all potential energy is converted into internal energy. The quality of the energy decreased till it has no potential anymore to perform work

# Reversible and irreversible processes

- **Reversible process:** A process that can be reversed without leaving any trace on the surroundings
- **Irreversible process:** A process that is not reversible
- All the processes occurring in nature are irreversible
- Reversible processes are only possible in theory and only in very limited cases a process can be approached as a reversible process

Frictionless pendulum  
a familiar reversible  
process

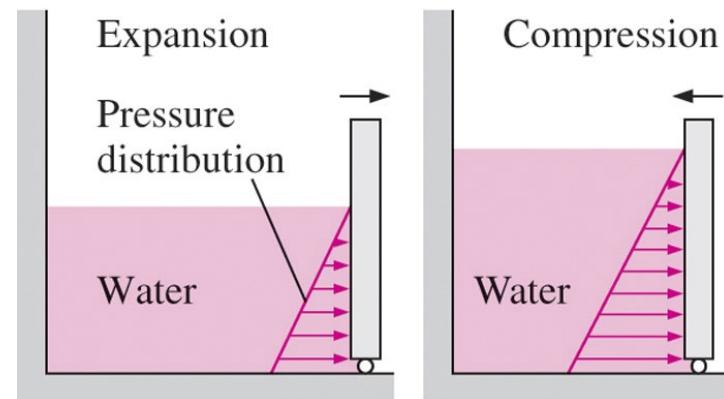


**Why should we be  
interested in reversible  
processes?**

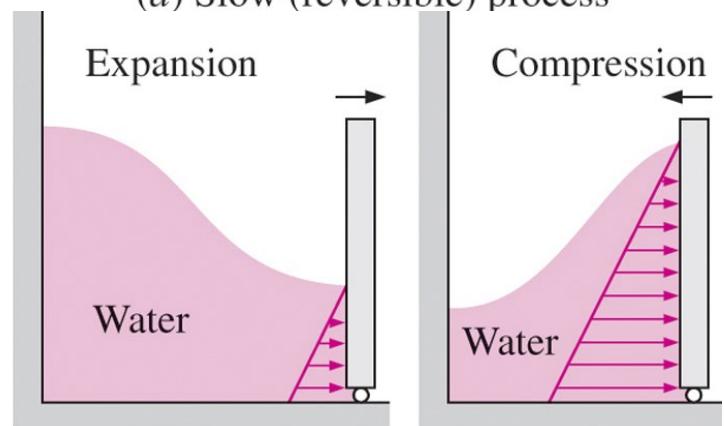
Quasi-equilibrium expansion and compression of a gas, is often used in thermodynamics to approach a reversible process

# Reversible and irreversible processes

- Why are we interested in reversible processes as all processes occurring in nature are irreversible?
  1. they are easy to analyze
  2. they serve as idealized models (theoretical limits) to which actual processes can be compared
- Some processes are more irreversible than others
- Why we try to approximate reversible processes?
- **Reversible processes deliver the most and consume the least work**



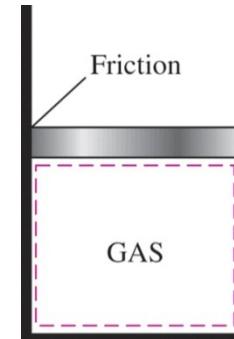
(a) Slow (reversible) process



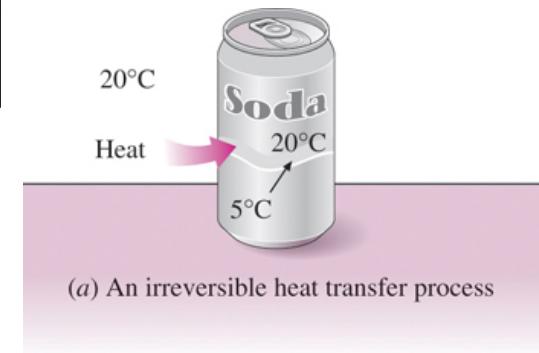
(b) Fast (irreversible) process

# Reversible and irreversible processes

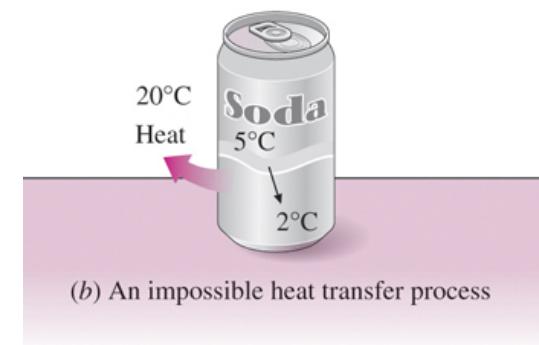
- **Irreversibilities** are the factors that cause a process to be irreversible, they include:
  1. friction
  2. heat transfer across a finite temperature difference
  3. unrestrained expansion
  4. mixing of two fluids
  5. electric resistance
  6. inelastic deformation of solids
  7. chemical reactions
  8. fluid viscosity and turbulence
- The presence of any of these effects renders a process irreversible



Friction renders a process irreversible.



(a) An irreversible heat transfer process



(b) An impossible heat transfer process

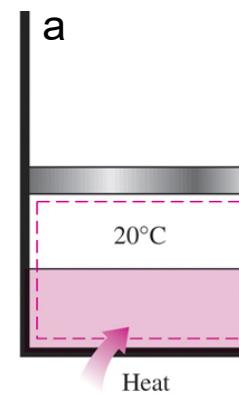
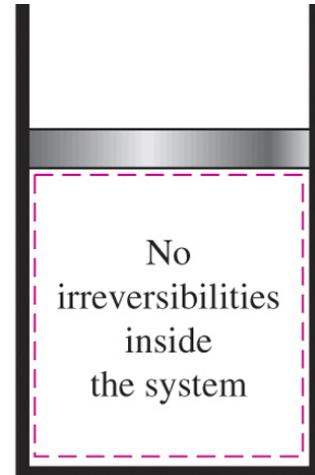
(a) Heat transfer through a temperature difference is irreversible, (b) the reverse process is impossible.

# Internally and externally reversible processes

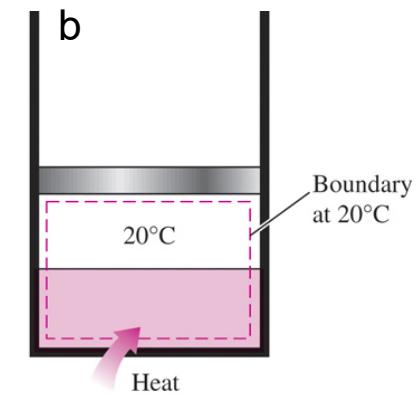
- **Internally reversible process:** If no irreversibilities occur within the boundaries of the system during the process
- **Externally reversible:** If no irreversibilities occur outside the system boundaries
- **Totally reversible process:** It involves no irreversibilities within the system or its surroundings.
- A totally reversible process involves no heat transfer through a finite temperature difference, no non quasi-equilibrium changes, and no friction or other dissipative effects.

No  
irreversibilities  
outside  
the system

A reversible process  
involves no internal  
and external  
irreversibilities



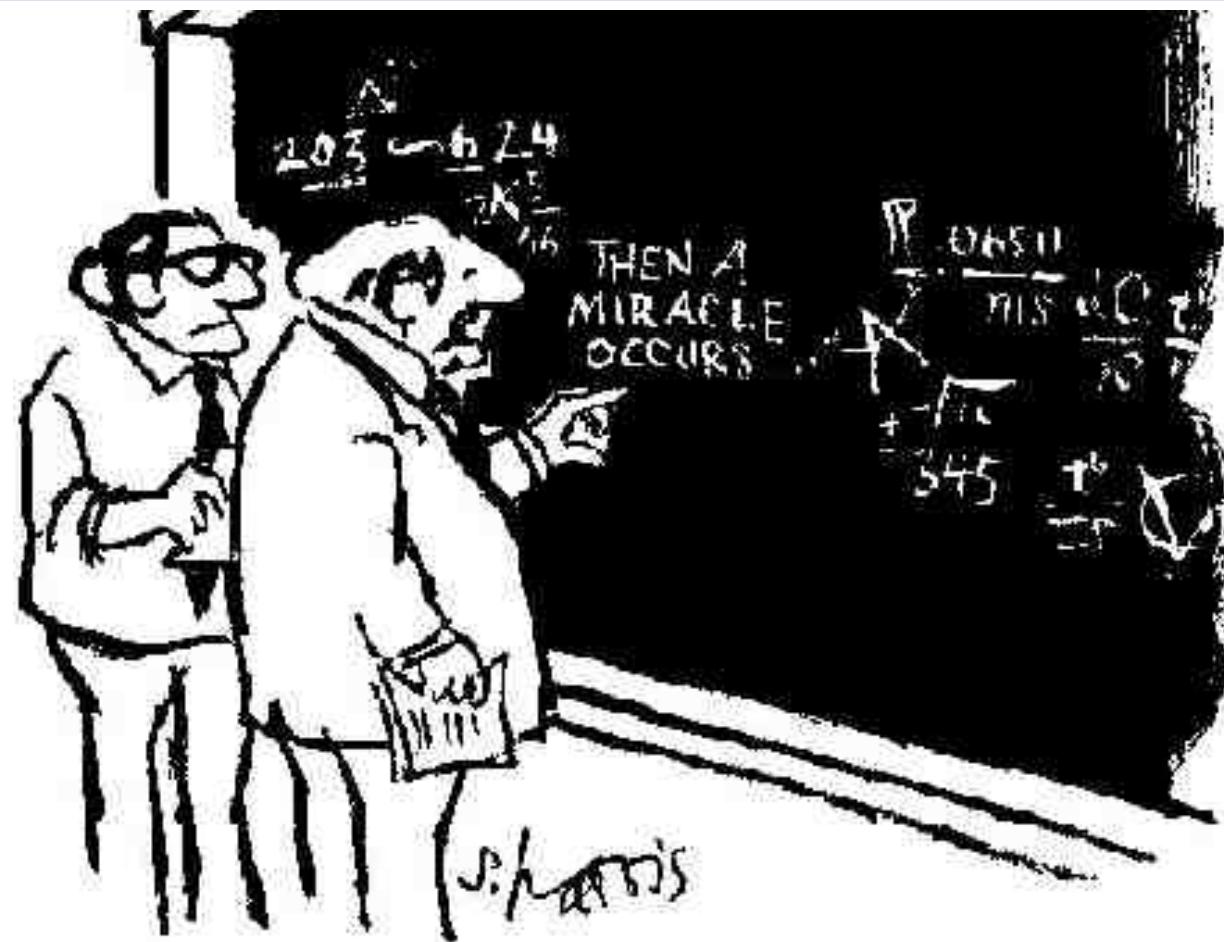
Totally (a) and internally (b) reversible  
heat transfer processes



# Accounting for irreversibility's in thermo

- Processes with **friction** and/or **heat transfer across a finite temperature difference** (or other irreversibilities) loss energy that can not be recovered in a reverse process
- **Questions to be answered:**
  - How to deal with irreversibility?
  - How can we describe (quantitatively) the progress of real processes?
  - Can we predict if a process is reversible or irreversible?
  - Can we predict the allowable direction of a process?
  - Calculate  $w_{OUT}$  from real processes accounting for irreversibility's?
- In the next part we will introduce:
  1. The property, **entropy,  $s$** , that can handle irreversibility's
  2. The **second law of thermodynamics** to be able to study real processes

# Entropy: The measure of irreversibility



"I THINK YOU SHOULD BE MORE EXPLICIT HERE IN STEP TWO."

<http://star.psy.ohio-state.edu/coglab/Miracle.html>

- In the 19<sup>th</sup> century a lot of scientist looked for a property that could measure irreversibility's
- It was Clausius who in 1865 the key concept of thermodynamics discovered
- The 'mystery' property is called nowadays **entropy**
- Still most people understand entropy intuitively based on expected direction of processes and find **quantification of entropy abstract**

# Entropy: The measure of irreversibility

- Entropy is a **thermodynamic property** (like temperature, pressure, enthalpy and internal energy), denoted by  $s$  or  $S$
- Entropy is an **extensive property** (like energy and depends on the size of the system)
- Entropy is a **state function** (exact differential and depends only on the state the system is in)
- The **unit** of specific entropy is  $\text{J/kgK}$  (or  $\text{kJ/kgK}$ ) (or for total entropy  $\text{J/K}$  or  $\text{kJ/K}$ )
- Entropy values can be found in the tables, read from a graph or calculated

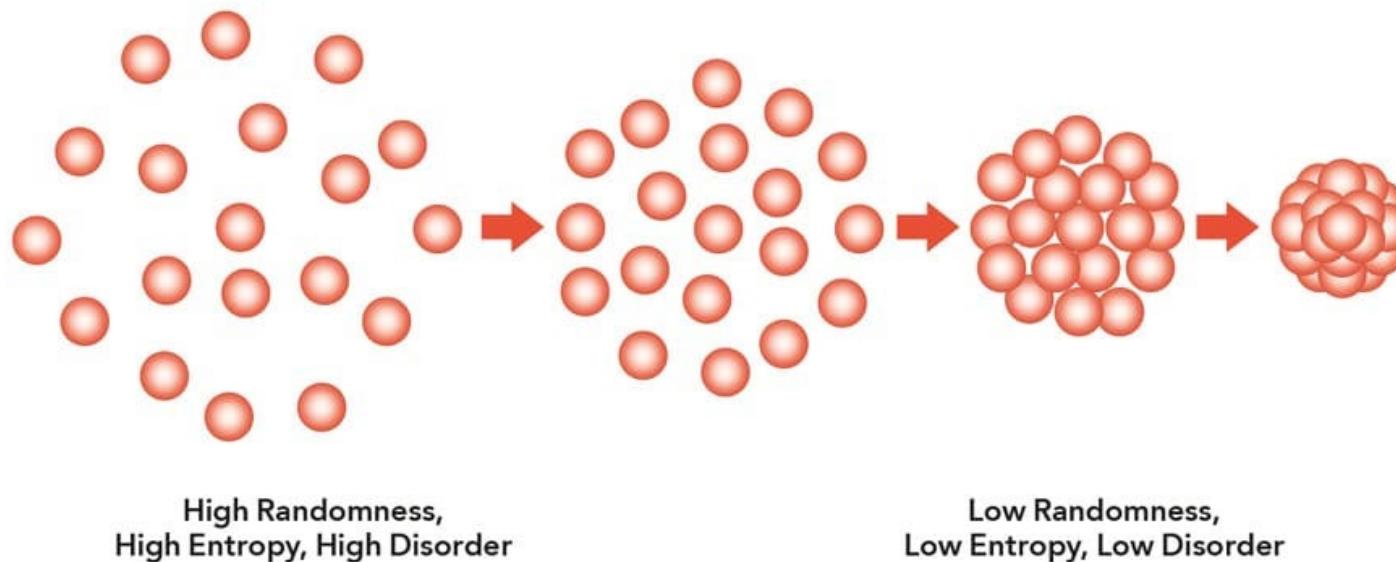


**Ice melting:** a classic example of the increase of entropy described in 1865 by Rudolf Clausius

# Entropy: The measure of irreversibility

- Entropy gives information about irreversibility
- At the **microscopic level** entropy is a measure of the degree of randomization or disorder of energy in a system
- The lower the entropy the more ordered and less random it is

## Energy, Entropy, the 2<sup>nd</sup> law of Thermodynamics



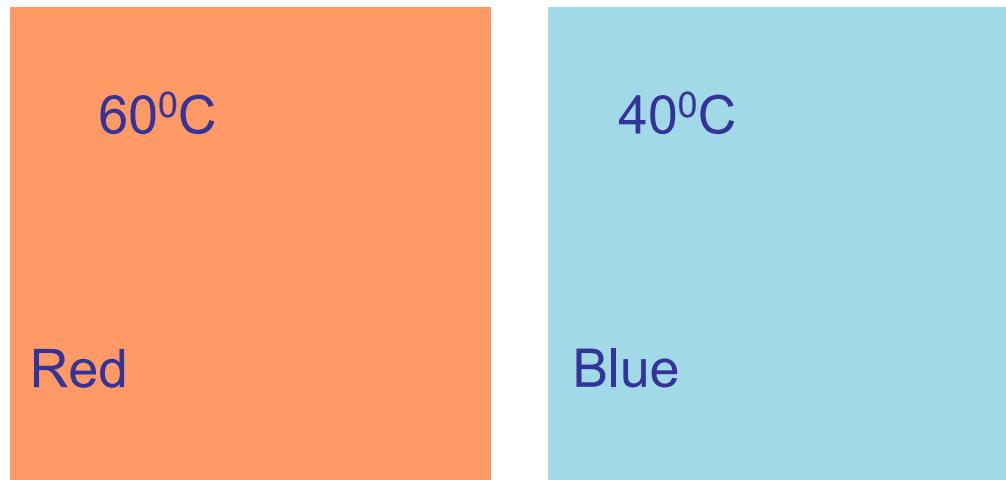
- In **equilibrium** entropy is at a **maximum**, most disorder

# Entropy: The measure of irreversibility

- To understand entropy a bit first we try to understand it more intuitively by connecting entropy to the direction that we would expect processes to occur spontaneously
- In the next few slides we see some examples of two states with one different property
- Try to find out which state is more random at the microscopic level; this is the state that has the most entropy
- Spontaneously the process between the states can only occur in one direction
- Realize that this is always the direction of increasing disorder and thus of increasing entropy

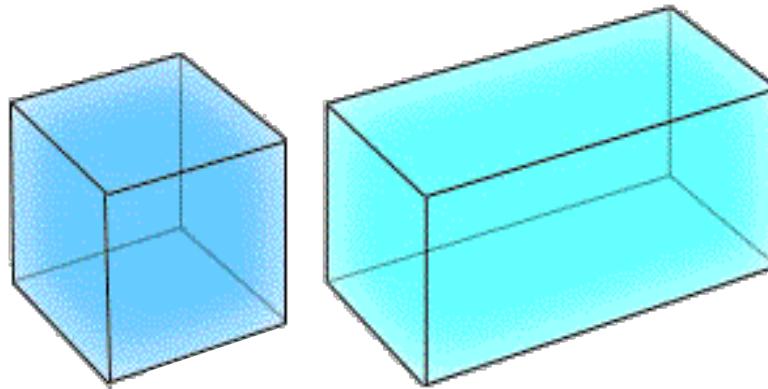
# Describing our intuition about reality

- **Entropy and temperature**
  - Red has more entropy, molecules move faster, more chaos, more random
  - Entropy increase with temperature



# Describing our intuition about reality

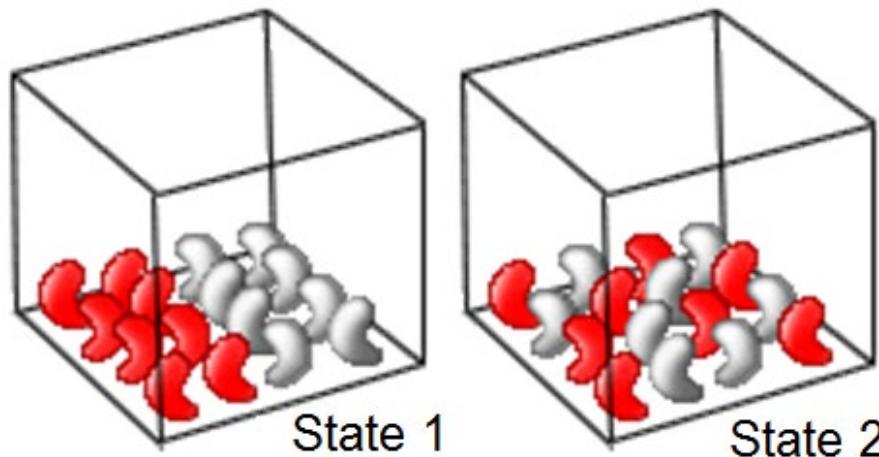
- **Entropy and pressure**
  - The small box is at a higher pressure
  - The large box has more entropy (in the large box there are less molecules per volume, they have more freedom to move and therefore they are more random)
  - Entropy increases with decreasing pressure



Two boxes with the same temperature and the same mass of an ideal gas but different volume

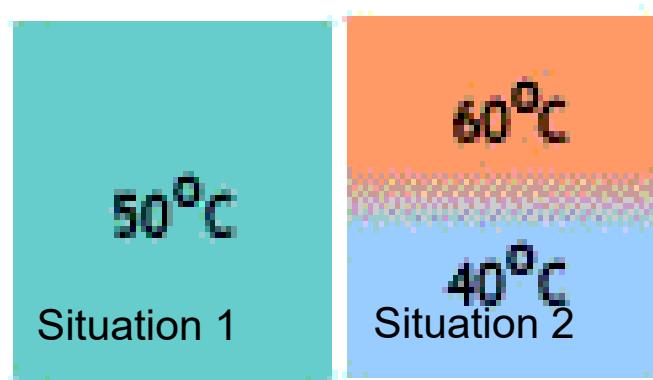
# Describing our intuition about reality

- Entropy and mixing
  - Spontaneously  $1 \rightarrow 2$   
(to reach  $2 \rightarrow 1$ , you really must work)
  - State 2 has more entropy (more random)



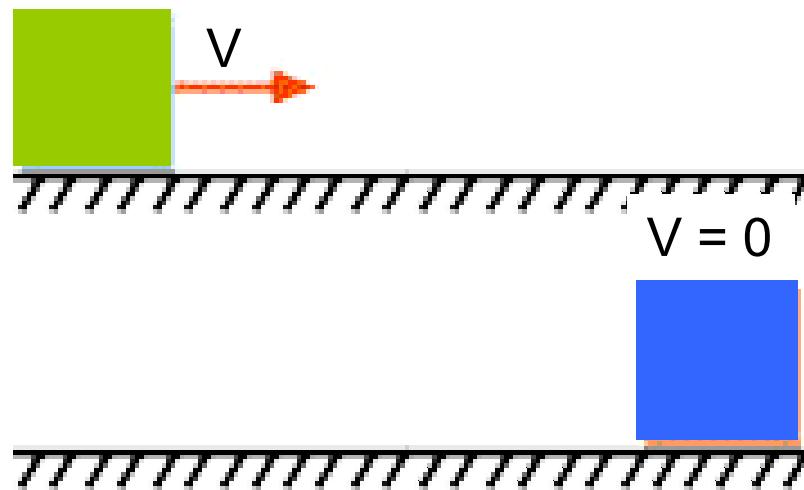
# Describing our intuition about reality

- Isothermal and non-isothermal
  - Spontaneously  $2 \rightarrow 1$
  - Situation 1 has more entropy (equilibrium)



# Describing our intuition about reality

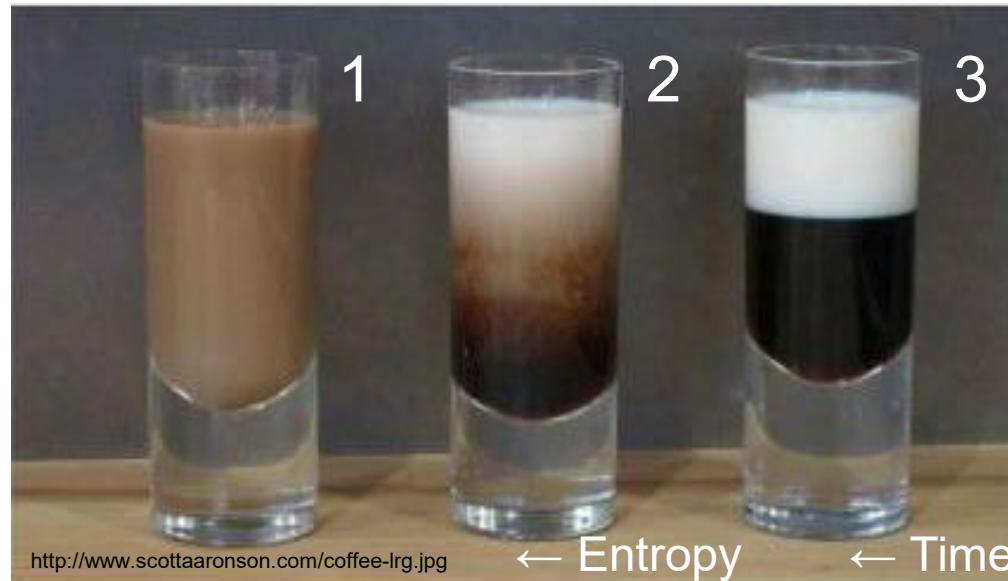
- Entropy, internal energy and kinetic energy
  - Spontaneously Green  $\rightarrow$  Blue
  - Blue one has more entropy (equilibrium)
  - $U$  has more entropy than KE



Two blocks with equal mass, temperature and energy. The green block has both internal and kinetic energy while the blue block has only internal energy

# Describing our intuition about reality

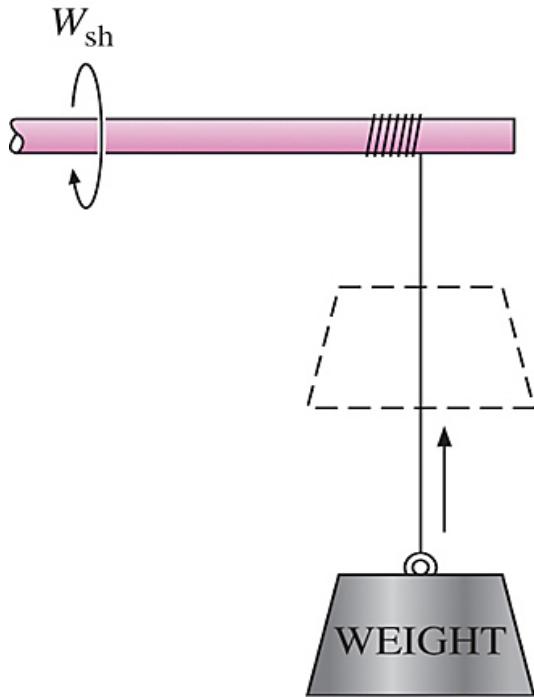
- Entropy and mixing of coffee and milk
  - Spontaneously  $3 \rightarrow 2 \rightarrow 1$
  - Glass 1 has more entropy (completely mixed, most random)



# Describing our intuition about reality

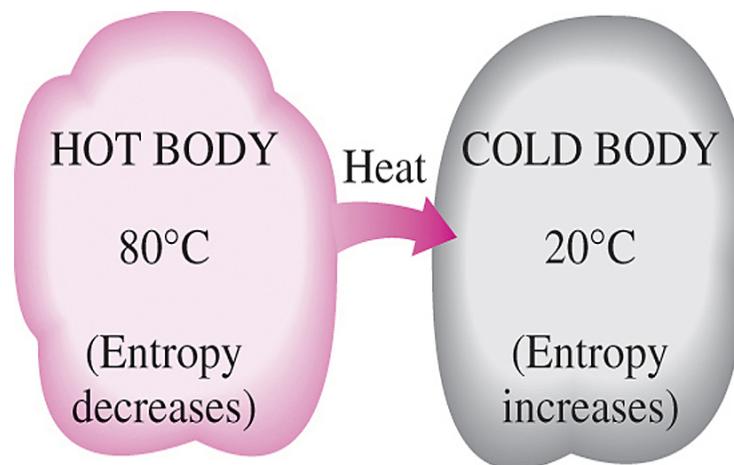
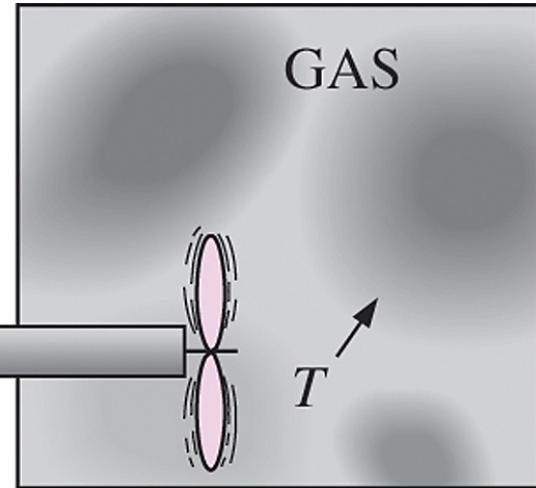
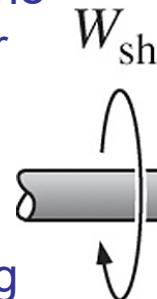
- We saw several processes and can conclude that:
  - Entropy increases with temperature
  - Entropy decreases with increasing pressure
  - Internal energy has more entropy than kinetic energy
  - Systems with uniform properties (isothermal, isobaric) have more entropy than systems with non-uniform properties (they are in equilibrium)
- Processes spontaneously always go to equilibrium
- In equilibrium everything is more randomly distributed
- Entropy is a measure of randomness
- The more random a state the more entropy it has
- In equilibrium the entropy is at a maximum
- Entropy always increase in spontaneous processes, this is stated in the **second law of thermodynamics**

# What is entropy?



In the absence of friction, raising a weight by a rotating shaft does not create any disorder (entropy), and thus energy is not degraded during this process.

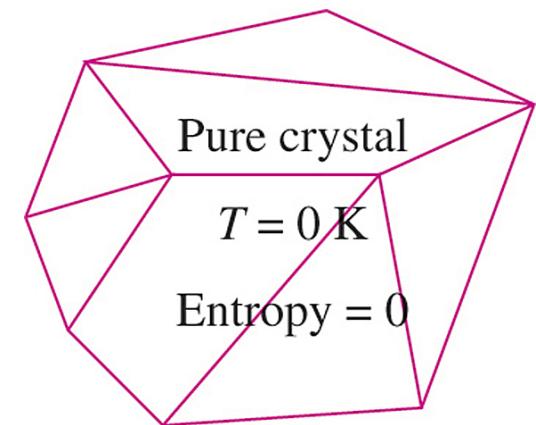
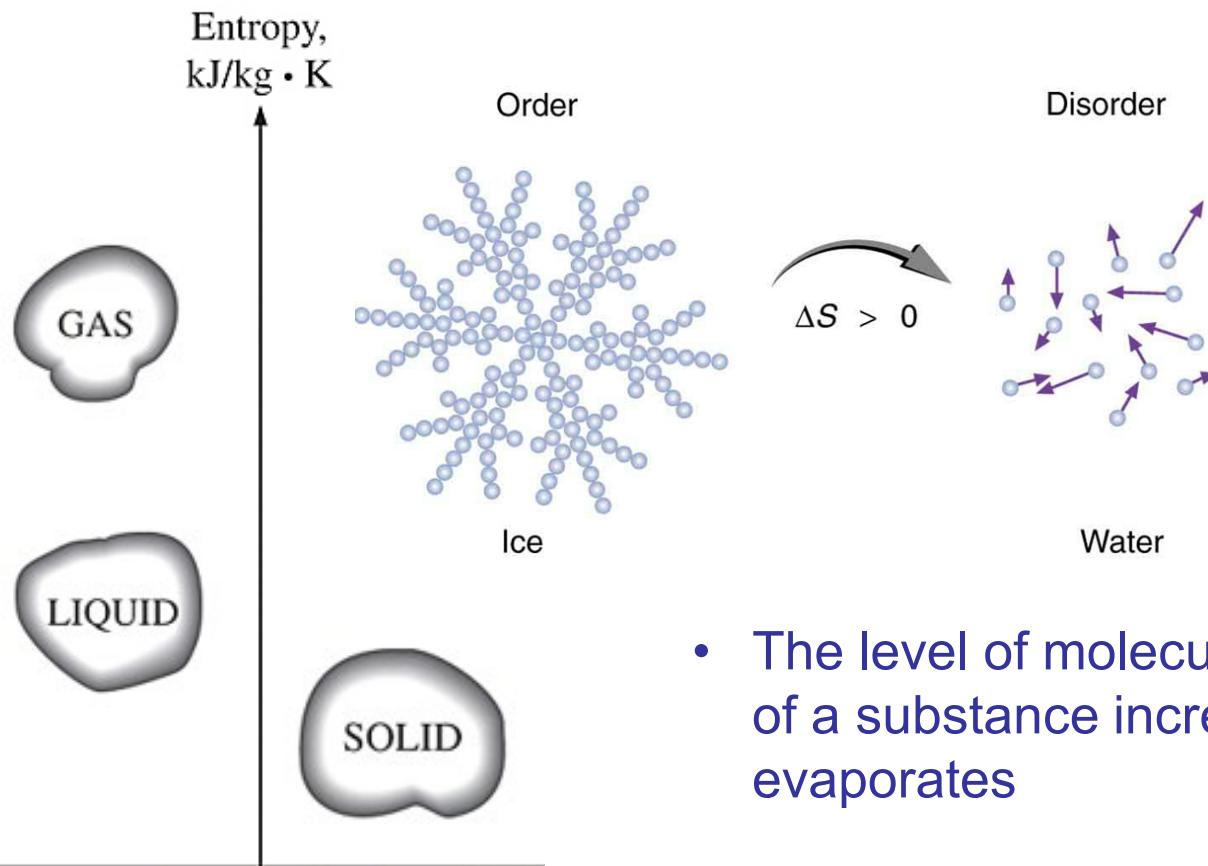
The paddle-wheel work done on a gas increases the level of disorder (entropy) of the gas, and thus energy is degraded during this process.



During a heat transfer process, the net entropy increases. (The increase in the entropy of the cold body more than offsets the decrease in the entropy of the hot body.)

# Third Law of Thermodynamics

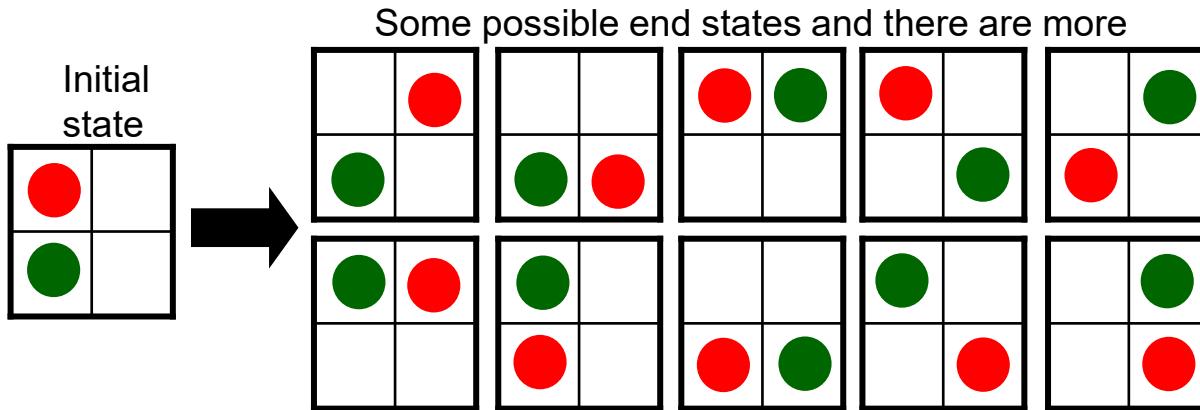
- **Third law of thermodynamics:** a pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero



- The level of molecular disorder (entropy) of a substance increases as it melts or evaporates

# Entropy on microscopic level

- At the **microscopic level** entropy is a measure of the degree of randomization or disorder of the energy of a system
- Ludwig Boltzmann first stated the logarithmic connection between entropy and probability in his kinetic theory of gases
- His famous formula for entropy  $S \rightarrow S = k_b \ln W$ 
  - $k_b = 1,38065 \times 10^{-23} \text{ J/K}$ , Boltzmann's constant
  - $W$  is the *Wahrscheinlichkeit*, the number of possible microstates corresponding to the macroscopic state of a system



Boltzmann's grave in the Zentralfriedhof, Vienna, with bust and entropy formula

# Entropy: The measure of irreversibility

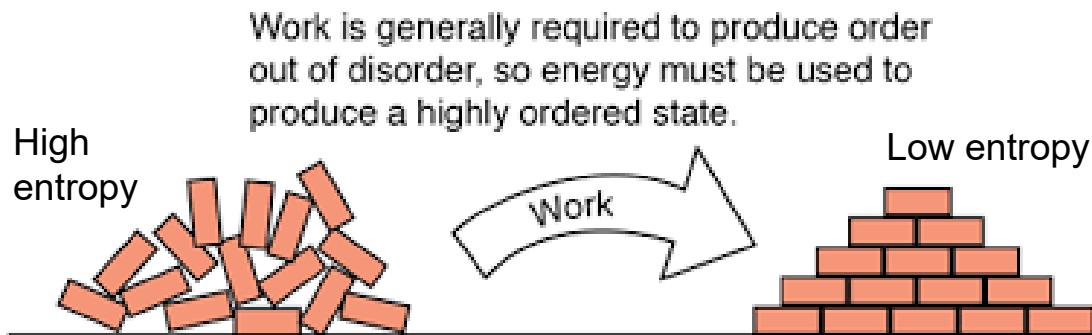
**FOKKE & SUKKE**  
LEIDEN HUN COLLEGA ROND

Entropy is one of the fifty subjects of the beta canon  
(<http://www.foksuk.nl/betacanon> en  
<http://extra.volkskrant.nl/betacanon/>)



# Some concluding remarks about entropy

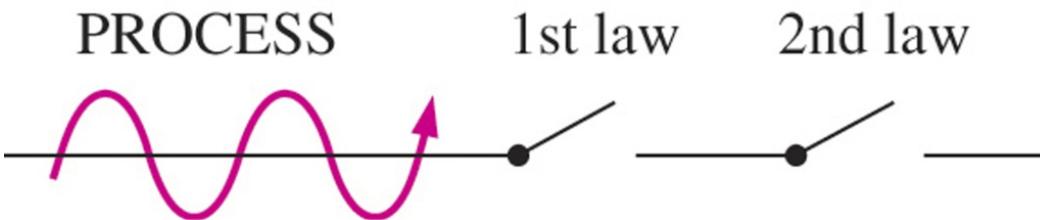
1. Spontaneous processes can occur in a certain direction only, not in any direction. A process must proceed in the direction that complies with the increase of entropy principle, that is,  $S_{gen} \geq 0$ . A process that violates this principle is impossible.
2. Entropy is a non conserved property, and there is no such thing as the conservation of entropy principle. Entropy is conserved during the idealized reversible processes only and increases during all actual processes.
3. The performance of engineering systems is degraded by the presence of irreversibilities, and entropy generation is a measure of the magnitudes of the irreversibilities during that process. It is also used to establish criteria for the performance of engineering devices.



Note: you can go to a state of lower entropy, but you must put some effort (work) in it. To perform this work somewhere else more entropy is produced

# The second law of thermodynamics

- Conservation of mass and conservation of energy (the first law), are not sufficient to describe thermodynamic processes as they cannot guarantee that a process is possible although both conditions are fulfilled
- The second law of thermodynamics had to be added to indicate the direction a process will proceed spontaneously
  - The property entropy can determine the direction of a process
- The second law of thermodynamics states that
  - Entropy can be created, but never destroyed in a spontaneous process
  - The entropy in the universe must remain constant or increase, but can never decrease



A process must satisfy both the first and second laws of thermodynamics to proceed.

# No exception on the second law

NRC Handelsblad Donderdag 8 maart 2012

Sorry this article is in Dutch, it is about a scientific test that proves, after 145 years, that there is no exception on the second law of thermodynamics.

Wetenschap 19

## Maxwells duiveltje is uitgedreven

Een knappe proef bewijst na 145 jaar dat een uitzondering op de tweede hoofdwet van de thermodynamica toch niet bestaat.

Door onze redacteur

MARGRIET VAN DER HEIJDEN

ROTTERDAM. Soms duikt hij nog op. In ietwat *nerdy* stripverhalen, of in de hoofden van fysici. Wie? Het duiveltje van Maxwell dat fysici decennia lang heeft dwarsgezeten.

James Clerk Maxwell (1831-1879), beroemd wegens zijn vergelijkingen die elektromagnetisme beschrijven, bedacht het sluwe duiveltje in 1867 als figurant in een gedachte-experiment. Maxwell wilde ermee aantonen dat de beroemde tweede hoofdwet van de thermodynamica (de warmteleer) niet altijd per se opgaat. Nogal gewaagd, want die tweede hoofdwet heeft in de fysica een enorme status.

„Als je theorie indruist tegen de tweede hoofdwet van de thermodynamica dan is alle hoop verloren: dan moet je in diepste nederigheid je verlies nemen”, zei de bekende fysicus Stanley Eddington ooit.

En inderdaad, zijn hoofd buigen, dat moet ook Maxwells duiveltje. In 1961 weerlegde fysicus Rolf Landauer Maxwells duiveltje paradox al op papier. Antoine Bérut van de École Normale Supérieure in Lyon en zijn collega's bevestigen Landauers gelijk nu nog eens experimenteel. Deze week beschrijven zij hun ingenieuze proef in *Nature*.

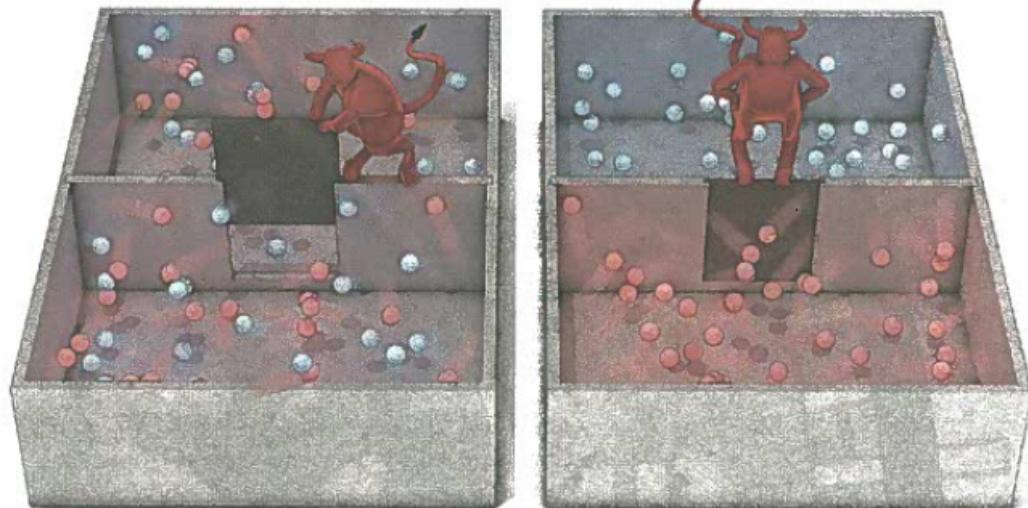
Hoe zit dat? Eerst die tweede hoofdwet. Een formulering ervan is dat er nooit spontaan warmte van een koud voorwerp naar een warmer voorwerp kan stromen. Een hete kop koffie bijvoorbeeld, koelt af doordat warmte eruit wegstromt naar de omgeving – net zolang tot de koffie en de omgeving even warm zijn. En nooit keert die warmtestroom zo maar om, zodat de koffie zonder stoken of opwarmen weer heet wordt.

Een statistische formulering is dat de moleculen en atomen in het hele systeem (de koffie en de omgeving) zich zo rangschikken dat ze gemiddeld genomen hun bewegingsvrijheid (trillen, draaien of rondsuzen) optimaal benutten. Ook dat bewijst de praktijk telkens weer: als gas een lege ruimte binnenstroomt bijvoorbeeld, dan verdeelt het zich onmiddellijk over die ruimte. Nooit nestelt het zich aan één kant, terwijl het de overige ruimte onbenut laat. Kort door de bocht: de natuur streeft maximale wanorde na.

Behalve dus Maxwells duiveltje dat alles listig leek te omzeilen. Maxwell plaatste het in een met gas gevulde ruimte met in het midden een scheidingswand.

Stel, zei Maxwell, dat het duiveltje daar van elk gasdeeltje meet hoe snel het beweegt en in welke richting. En stel verder dat het duiveltje moeite-loos een luikje in het scheidingswandje kan openen. Dan kan het, door het luikje tijdig te openen of te sluiten, alle snelle deeltjes aan één kant van de wand verzamelen (warm), en alle trage deeltjes aan de andere kant (koud).

Second law



Illustratie Roland Blokhuizen

Zonder arbeid te verrichten, brengt het duiveltje zo warmte naar één helft van de ruimte. Of: zonder er energie in te steken, schept het toch orde (warm links, koud rechts). Tegen de tweede hoofdwet in.

De fysici uit Lyon bevestigen nu de tegenwerping die Rolf Landauer in 1961 formuleerde. Het punt is niet, zei Landauer, dat het duiveltje energie verbruikt bij zijn deeltjesmetingen, en zo zelf warmte produceert. Zelfs dat is op te lossen. Alleen: de volgende valkuil is dat het duiveltje de informatie over die deeltjes dan in

zijn werkgeheugen moet opslaan. Én daarna weer moet wissen, want anders kan hij op enig moment geen nieuwe deeltjes meer meten. Zelfs niet als zijn geheugen enorm is, zo bleek in 1982 na veel denkwerk.

Maar, zo betoogde Landauer: als je informatie wist, komt er warmte (energie) vrij. En omdat extra warmte tot toenemende bewegelijkheid van de deeltjes in het systeem leidt, en daarmee tot groeiende wanorde, is de tweede hoofdwet gered.

Klopt, zeggen de fysici uit Lyon. Zij stelden vast hoeveel warmte mi-

nimaal vrijkomt als één bit aan informatie wordt gewist – de Landauerlimiet. Ze gebruikten daarbij een minuscule silicium bolletje dat in een vloeistof zweefde. Dat pinden ze vast met laserlicht (ze noemden dat één informatiebit), daarna bevrijdden ze het (de informatie werd gewist) en maten de vrijkomende warmte. De zo gevonden Landauerlimiet stemt perfect overeen met de verwachting, schrijven zij. Minstens zo cruciaal: de proef demonstreert opnieuw de nauwkeurige band tussen thermodynamica en informatietheorie.

# Summary: The four Laws of Thermodynamics

- We now have met the four **laws of thermodynamics**. They define fundamental physical quantities (like temperature, energy, and entropy) that characterize thermodynamic systems. The laws describe how these quantities behave under various circumstances, and forbid certain phenomena (such as perpetual motion).
  - The **zeroth** law of thermodynamics is concerned with the properties of systems in thermal equilibrium, the concept of temperature follows of it. **If two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other.**
  - The **first** law of thermodynamics deals with the conservation of energy. **Different forms of energy can be transformed into each other, but the total energy is constant.** The internal energy of a system can change by transfer of heat, work and/or mass into the system. Equivalently, perpetual motion machines of the first kind are impossible.
  - The **second** law of thermodynamics states that **spontaneous natural processes increase entropy overall**, or in another formulation **that heat can spontaneously go only from a higher-temperature region to a lower-temperature region, but not the other way around.** Equivalently, perpetual motion machines of the second kind are impossible.
  - The **third** law of thermodynamics is concerned with the entropy of a system at absolute zero Kelvin. **The entropy of a system approaches a constant value as the temperature approaches zero.** It is typically zero for one ground state and in all cases is determined only by the number of different ground states it has.

[http://en.wikipedia.org/wiki/Laws\\_of\\_thermodynamics](http://en.wikipedia.org/wiki/Laws_of_thermodynamics)

# The second law of thermodynamics

- Entropy in universe increases due to **entropy generation ( $S_{GEN}$ )** in irreversible processes
  - $S_{GEN} = 0$  for reversible process
  - $S_{GEN} > 0$  for irreversible process
  - $S_{GEN} < 0$  for impossible process



## Major uses of the second law of thermodynamics

1. The second law may be used to identify the direction of processes.
2. The second law also asserts that energy has quality as well as quantity. The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality. The second law provides the necessary means to determine the quality as well as the degree of degradation of energy during a process.
3. The second law of thermodynamics is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators, as well as predicting the degree of completion of chemical reactions.

# Energy, mass, entropy balances

- Total **mass** in universe is **constant** (for engineering applications)
- Total **energy** in universe is **constant**
- Total **entropy** in universe must remain **constant or increase**
- Compare mass and energy (conservative) balances to entropy balance (non-conservative) for a system:
  - Mass balance:  $\dot{m}_{IN} - \dot{m}_{OUT} = \frac{dm_{CV}}{dt}$   $\xrightarrow{\text{sssf}}$   $\dot{m}_{OUT} - \dot{m}_{IN} = 0$
  - Energy balance:  $\dot{E}_{IN} - \dot{E}_{OUT} = \frac{dE_{CV}}{dt}$   $\xrightarrow{\text{sssf}}$   $\dot{E}_{OUT} - \dot{E}_{IN} = 0$
  - Entropy balance:  $\dot{S}_{IN} - \dot{S}_{OUT} + \dot{S}_{GEN} = \frac{dS_{CV}}{dt}$   $\xrightarrow{\text{sssf}}$   $\dot{S}_{OUT} - \dot{S}_{IN} = \dot{S}_{GEN}$
  - Entropy generation cannot be measured directly, but it can be calculated using the entropy balance or looked up in a table or diagram

# Entropy of sat. liquids and sat. vapors

- Entropy values with respect to P and T can be found in tables
- Entropy saturated phases tabulated just like v, u and h
  - Table A4 or A5

Properties of Saturated Water - Pressure Table (SI)

P kPa	T °C	Internal Energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/(kg·K)		
		$u_L$	$u_{LV}$	$u_V$	$h_L$	$h_{LV}$	$h_V$	$s_L$	$s_{LV}$	$s_V$
45	78.736	329.58	2150.4	2480.0	329.62	2311.3	2640.9	1.0603	6.5684	7.6287
50	81.339	340.49	2142.8	2483.3	340.54	2304.8	2645.3	1.0912	6.5016	7.5928
60	85.949	359.84	2129.2	2489.0	359.90	2293.1	2653.0	1.1454	6.3856	7.5310
70	89.956	376.68	2117.3	2494.0	376.75	2282.9	2659.6	1.1920	6.2869	7.4789
80	93.511	391.63	2106.7	2498.3	391.71	2273.6	2665.3	1.2330	6.2009	7.4339

ThermoNet:Wiley

- For saturated mixtures s can be calculated using the quality (x)  
 $\rightarrow s = s_L + x(s_V - s_L) = s_L + xs_{LV}$   
(recall x = quality of the saturated mixture:  $0 < x < 1$ )

# Entropy of Superheated Vapors

- Entropy values with respect to P and T can be found in tables
- Entropy of superheated vapors tabulated just like v, u and h
  - Table A6

Properties of Superheated Steam (SI)

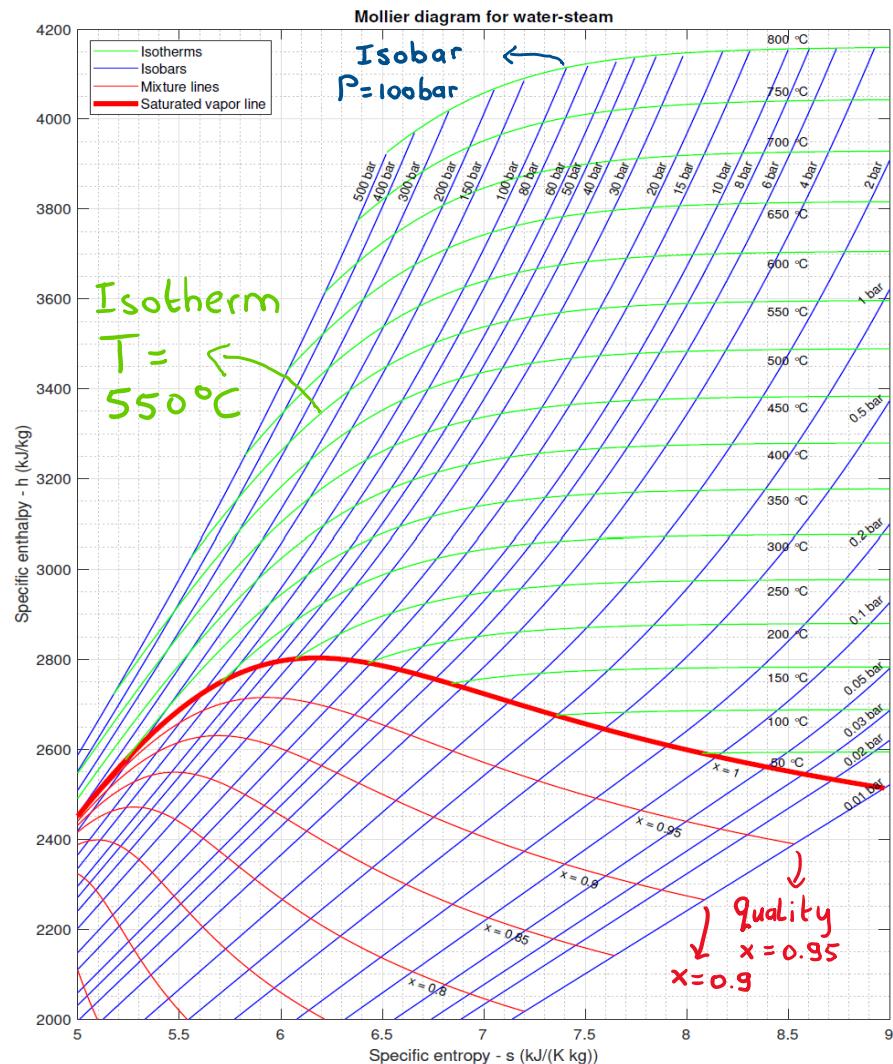
T °C	v m <sup>3</sup> /kg	u kJ/kg	h kJ/kg	s kJ/(kg·K)
<b>P = 8000 kPa</b>				
(295.04)	(0.0235)	(2569.6)	(2757.8)	(5.7431)
300	0.02426	2590.5	2784.6	5.7901
350	0.02995	2746.7	2986.3	6.1286
400	0.03431	2863.5	3138.0	6.3630
450	0.03816	2966.9	3272.2	6.5554
500	0.04174	3064.6	3398.5	6.7243

ThermoNet: John Wiley

- Entropy values for the superheated region and the high-quality part of the saturated mixture can also be found in a Mollier diagram (hs-diagram)
- Less accurate but a lot faster for the mixture region as it is not necessary to calculate the quality and it gives a clear overview of the process (i.e. you can see if the expansion process in the turbine is acceptable)
- You can read the quality from the diagram

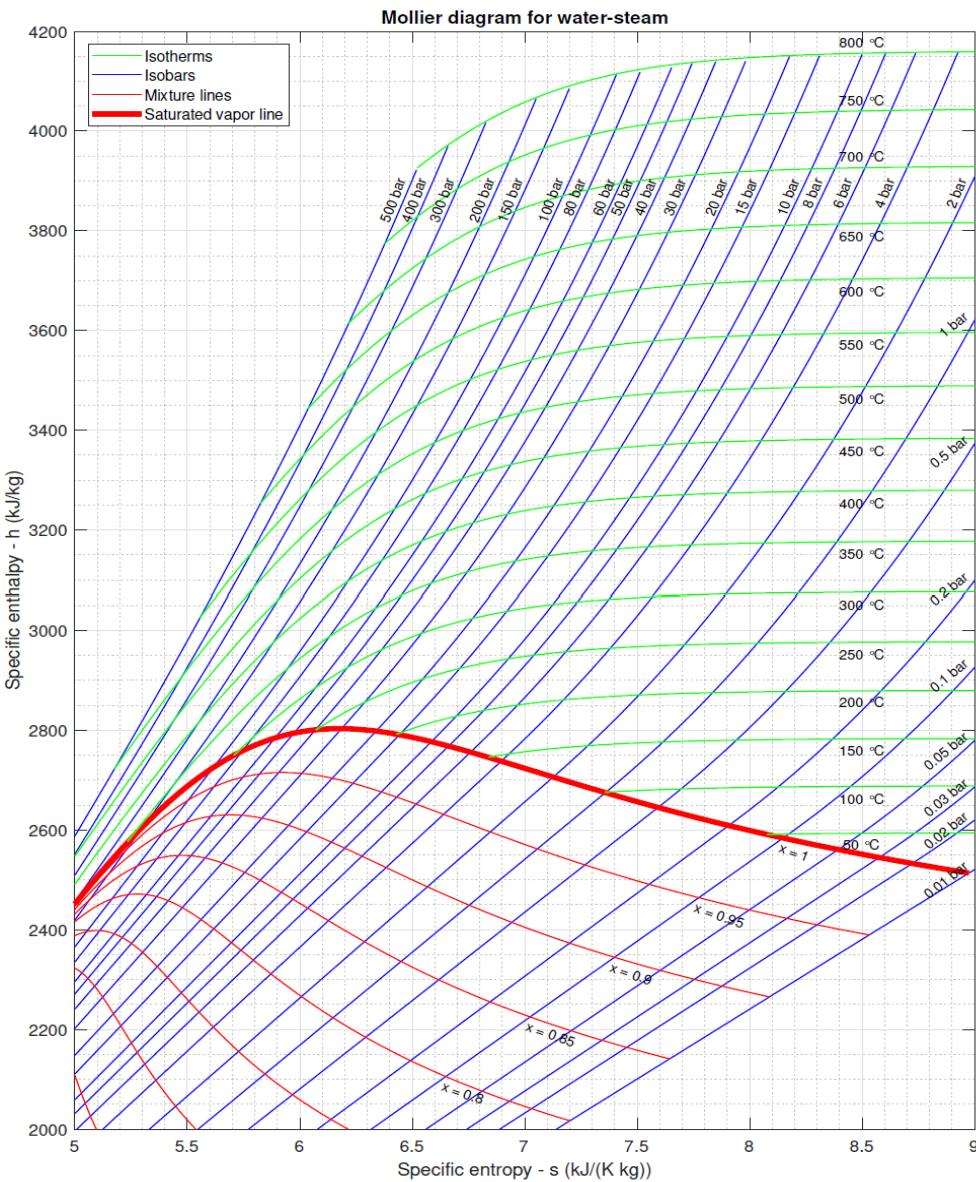
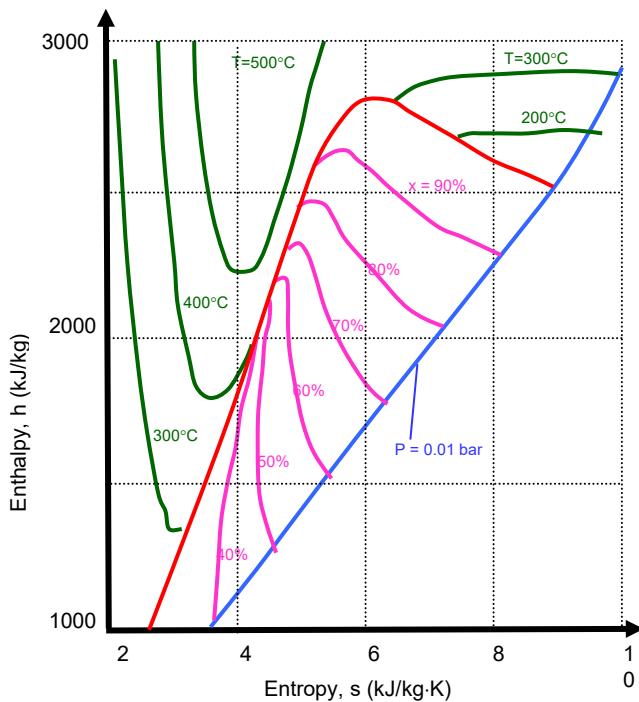
# Mollier Diagram Water for Rankine Cycle

- The hs - diagram of water, the enthalpy on the y-axis and the entropy on the x-axis
- Mollier Diagram** named, after Professor Richard Mollier who recognized the importance of the combination  $u + Pv = h$  in the analysis of steam turbines and in the representation of properties of steam in tables and diagrams
- The Mollier diagram is used to analyze the Rankine cycle
- The advantage over the table is that values in the mixture region can be found faster
- Do you recognize the vapor dome (bold red line), isobars in Bar (blue), isotherms (green), vapor mass fraction (red)?



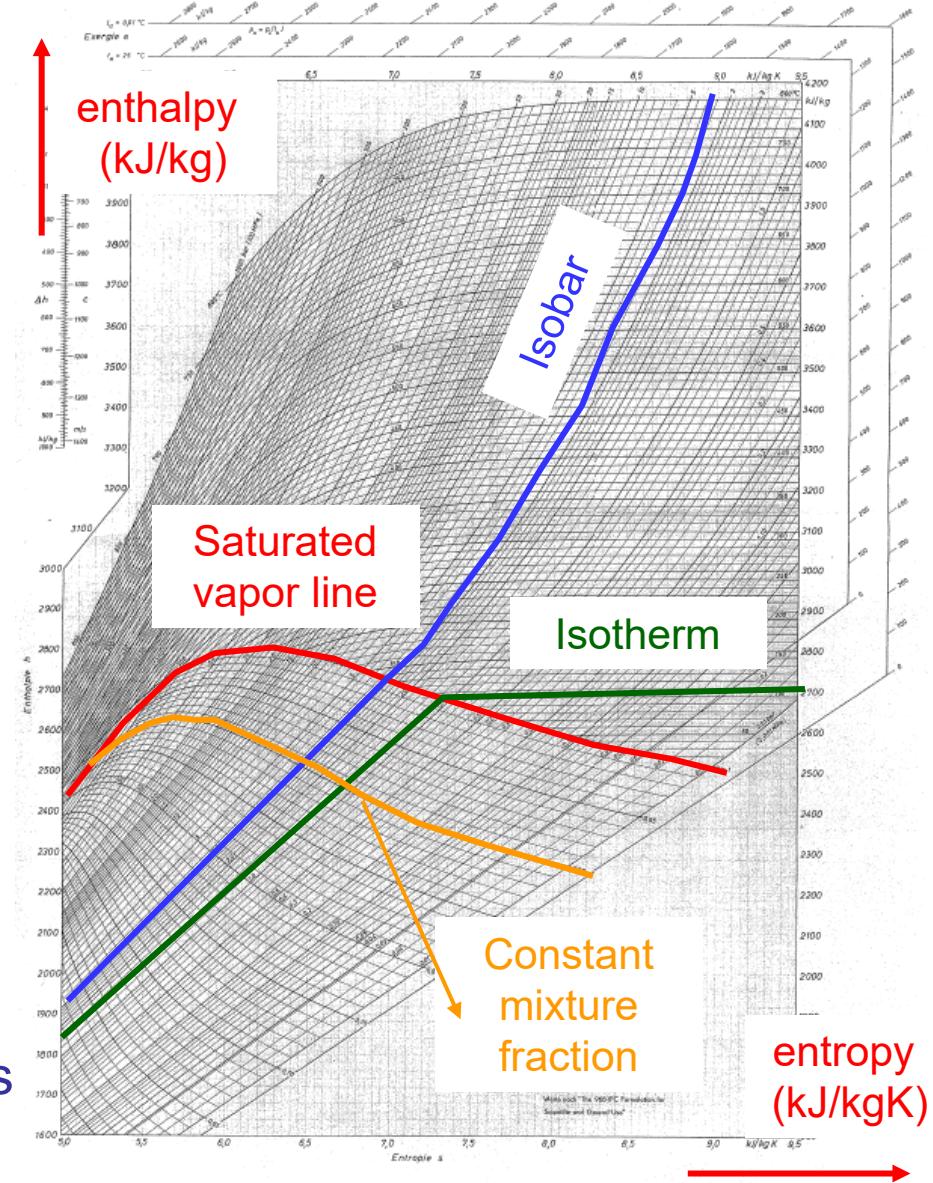
# Mollier Diagram Water for Rankine Cycle

- Only the superheated region and part of the vapor dome is shown, however this is the part where the expansion process takes place
- The compressed liquid region is not shown, isobars are too close to each other



# Mollier Diagram Water for Rankine Cycle

- Scanned version of the Mollier diagram for water used to analyze the Rankine cycle
  - Enthalpy (kJ/kg) on the y-axis, horizontal line  $\rightarrow dh = 0$
  - Entropy (kJ/kgK) on the x-axis, vertical line  $\rightarrow ds = 0$
  - Saturated vapor line divides superheated vapor and mixture region
  - Isobars (in Bar !!)
  - Isotherms (in degree Celsius)
  - Constant mixture fraction lines
- Compressed liquid area not shown, lines are too close to each other  $\rightarrow$  diagram is not usable, use tables
- This diagram is used in the solutions of the assignment bundle



# Entropy of solids and compressed liquids

- Entropy of compressed liquids, if compressed liquid tables are available, entropy tabulated like v, u and h (table A7)
- If only saturated tables are available, apply incompressible liquid approximation (ICL):  $s_{\text{ICL}}(T, P) \approx s_L(T)$
- For incompressible substance,  $dv = 0$  and  $ds = \frac{c_V}{T} dT + \frac{R}{v} dv$ 
$$ds = c_V \frac{dT}{T} \Rightarrow s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_V}{T} dT$$
- If  $c_V$  is independent of temperature and recalling  $c_V = c_P = c$  for an incompressible substance

$$s_2 - s_1 = c \ln \left( \frac{T_2}{T_1} \right)$$

(Relations will be derived later when treating gasses)

# Definition of entropy

- Applying the entropy balance to isolated / closed / open systems and calculating the entropy generation of heat, work and mass flowing in or out of the system gives an expression for the entropy
- It is found that entropy can only enter or leave a system with heat or mass (therefore entropy can not leave or enter a closed isolated system, energy generated in such a system stays in the system)
- Reversible work does not change the entropy of a system
- **Definition of entropy**
  - for an internally reversible system  $ds = \left( \frac{\delta q_{net}}{T_{out}} \right)_{int.rev}$
  - for all other (irreversible) systems  $ds \geq \left( \frac{\delta q_{net}}{T_{out}} \right)_{irrev}$  or  $q_{net} \leq T_{out} ds$

(definitions will be derived later)

# General relations for entropy

- General relations for entropy can be derived based on
  - Entropy is a state function (a thermodynamic property)
  - $s = s(u,v)$  [Thermodynamic state principle, two variables]
- Therefore the entropy,  $s$ , can be written as a total differential of the variables  $u$  and  $v$  (in chapter 12 (module 3) more about this)

$$ds = \left(\frac{\partial s}{\partial u}\right)_v du + \left(\frac{\partial s}{\partial v}\right)_u dv$$

- Expressions must be found for the partial derivatives
- Based on observations and smart thinking
  - Increasing internal energy  $\rightarrow$  increasing entropy
  - Increasing volume  $\rightarrow$  increasing entropy

(Derivation of this formula is not part of the exam)

# General relations for entropy

- Total differential:  $ds = \left(\frac{\partial s}{\partial u}\right)_v du + \left(\frac{\partial s}{\partial v}\right)_u dv$
- Partial derivatives are **defined** as:

$$\left(\frac{\partial S}{\partial U}\right)_V \equiv \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

These definitions are based on observations.  
More in module 3

- This results in the Gibbs equations for entropy

$$ds = \frac{1}{T}du + \frac{P}{T}dv \quad \rightarrow \quad Tds = du + Pdv$$

$$dh = du + Pdv + vdP \quad \rightarrow \quad Tds = dh - vdP$$

- Used to calculate changes in entropy
- Entropy is tabulated

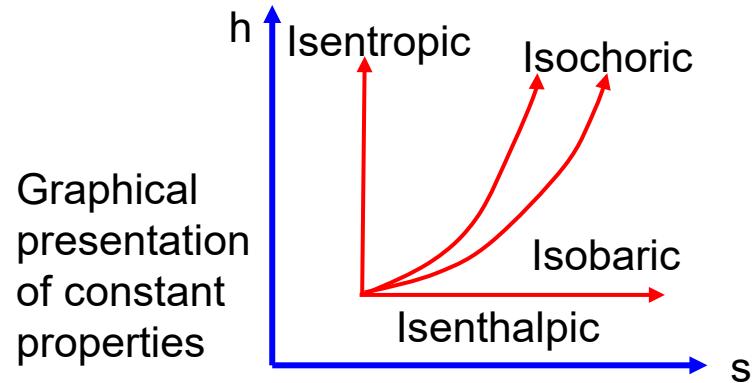
Temperatuur  $\left(\frac{\partial U}{\partial S}\right)_V \equiv T$

(Derivation of this formula is not part of the exam)

# Application: Isentropic process, pump

- In an isentropic process the entropy does not change ( $ds = 0$ )

- Isentropic process: Constant s**
- Isothermal: Constant T
- Isobaric: Constant P
- Isochoric: Constant v
- Isenthalpic: Constant h



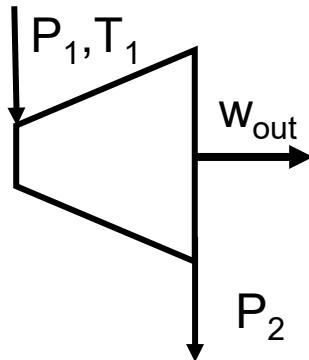
- For an isentropic processes for an incompressible substance follows from the Gibbs Equation ( $Tds = dh - vdP$ )

$$\cancel{ds^0_{ISENTROPIC}} = \frac{dh}{T} - \frac{v}{T} dP \Rightarrow dh = vdP \\ \Rightarrow \Delta h = v(P_2 - P_1)$$

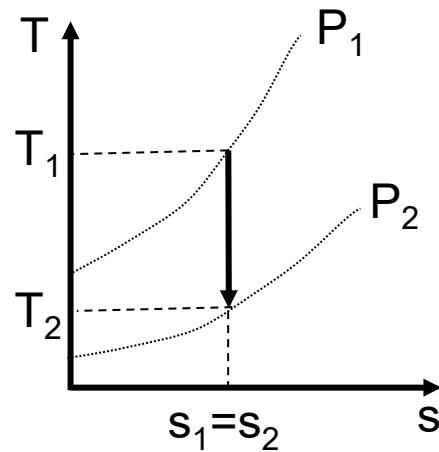
- The relation  $\Delta h = v(P_2 - P_1)$  is used for analyzing ideal pumps (and often forgotten at the exam.....)

# Application: Isentropic process, turbine

- In **isentropic processes** states can be related using  $s_2 = s_1$
- Example: isentropic expansion process in a steam turbine from  $(T_1, P_1)$  to  $P_2$  at unknown  $T_2$
- What is  $T_2$ ?
  - $s_1 = s(T_1, P_1)$  (given)
  - $s_2 = s_1$  (because isentropic)
  - $T_2 = T(P_2, s_2)$  (can be found)



Isentropic expansion  
 $ds=0$  or  
 $s_1 = s_2$



Steam Turbine Blades from a Calpine Geothermal Plant

DK

# 2<sup>nd</sup> law applied to thermodynamic devices

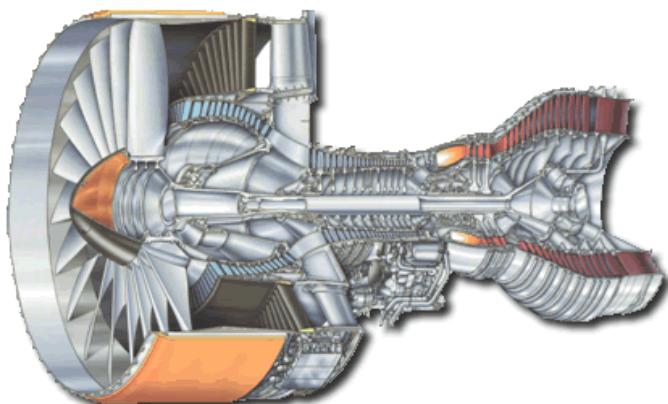
- So far, we have introduced:
  - The thermodynamic property entropy
  - The second law of thermodynamics
- They determine the direction of processes
- Now we will apply the second law to engineering devices to see how it is used in calculations
  - Idealized devices with no irreversibility's, provide limits for real devices
  - Real devices with irreversibility's
  - **Isentropic efficiency**

An ideal, reversible turbine delivers the maximum amount of work. A real, irreversible turbine working between the same end states produces less than the maximum amount of work



# 2<sup>nd</sup> law applied to thermodynamic devices

- An **ideal device** which is reversible has the **highest possible efficiency** and can be used as a **benchmark for real processes**
- Define behavior of idealized devices with no irreversibility's
- Define how real devices depart from ideal behavior when irreversibilities are present
- This leads to **isentropic efficiency**



Pratt and Whitney PW 4000 Turbofan Engine

A real turbofan engine produces less thrust than an ideal turbofan engine due to irreversibility's

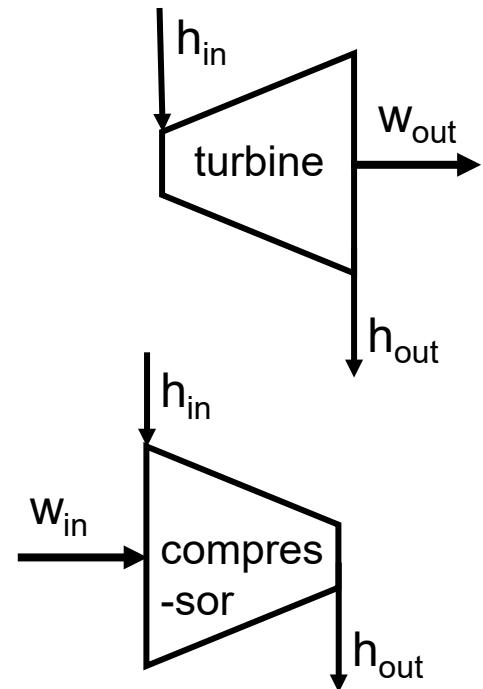


A real pump requires more power than an ideal one due to irreversibility's

# Ideal devices

- First consider **ideal devices**
- With a few exceptions (e.g. throttling) ideal devices
  - Are frictionless
  - Have isothermal heat transfer
  - Have completely reversible process ( $\delta s_{gen} = 0$ )

- **Ideal output producing device:**
  - Produces **more** power than a real device
  - e.g. turbine  $W_{out,ideal} > W_{out}$
- **Ideal input requiring device:**
  - Requires **less** power than a real device
  - e.g. compressor  $W_{in,ideal} < W_{in}$



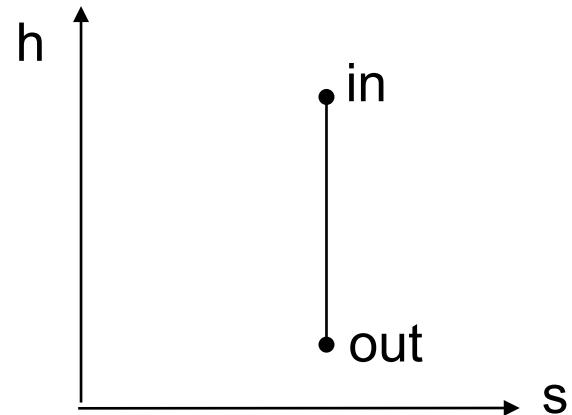
# Ideal devices: open systems

- For **ideal (reversible) adiabatic** devices can be derived
  - **Open system with single in- and outlet**

$$w_{NET,S} = h_{IN} - h_{OUT,S} \quad \text{with} \quad h_{OUT,S} = h(P_{OUT}, s_{OUT} = s_{IN})$$

$$\dot{W}_{NET,S} = \dot{m}(h_{IN} - h_{OUT,S}) \quad \text{with} \quad h_{OUT,S} = h(P_{OUT}, s_{OUT} = s_{IN})$$

- Isentropic process,  $ds = 0$
- Outlet state is denoted by the subscript s
- Entropy (s) outlet state same as s inlet state ( $s_2 = s_1$ )
- Vertical line in a hs-diagram



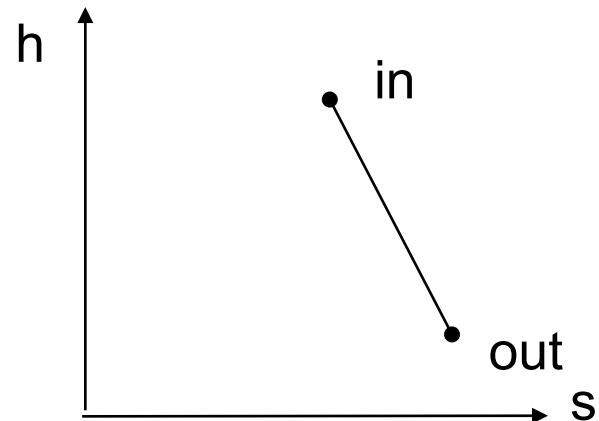
# Real devices: open systems

- Real (irreversible) adiabatic device
- Open system with single in- and outlet

$$w_{NET,A} = h_{IN} - h_{OUT,A} \quad \text{with} \quad h_{OUT,A} = h(P_{OUT}, s_{OUT})$$

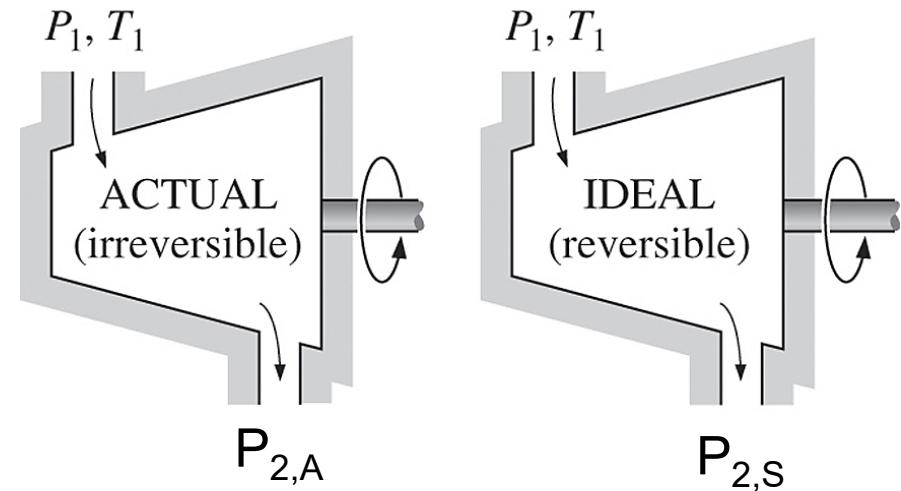
$$\dot{W}_{NET,A} = \dot{m}(h_{IN} - h_{OUT,A}) \quad \text{with} \quad h_{OUT,A} = h(P_{OUT}, s_{OUT})$$

- Outlet state is denoted by the subscript a
- Entropy increases,  $ds > 0$
- Entropy (s) outlet state larger than s inlet state ( $s_2 > s_1$ )
- Decreasing line in a hs-diagram



# Real devices: Isentropic efficiencies

- Now that relations for ideal systems (frictionless and reversible heat transfer) and real system (friction, irreversible heat transfer) are available we can look at the **behavior of real systems compared to ideal systems**
- The **isentropic efficiency** is a comparison of the actual (denoted by A) and the ideal performance (denoted by S)
- The isentropic efficiency is defined **different** for input requiring (compressor) and output producing (turbine) systems



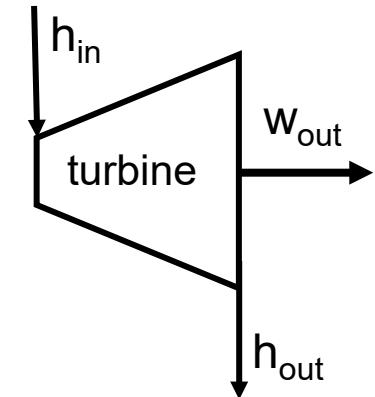
The isentropic process involves no irreversibilities and serves as the ideal process for adiabatic devices.

# Real devices: Isentropic efficiencies

- The isentropic efficiency is defined **different** for input requiring (compressor) and output producing (turbine) systems
- The **isentropic efficiencies**:

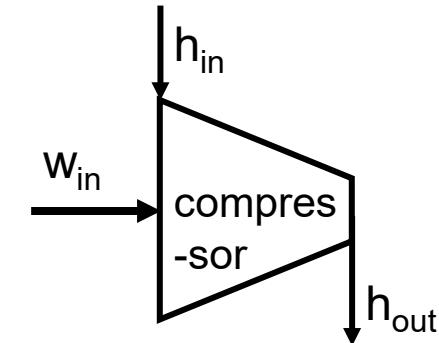
- Output, producing device (e.g. turbine)

$$\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}} \quad \text{note always} \quad w_{OUT,A} \leq w_{OUT,S}$$



- Input, requiring device (e.g. compressor / pump)

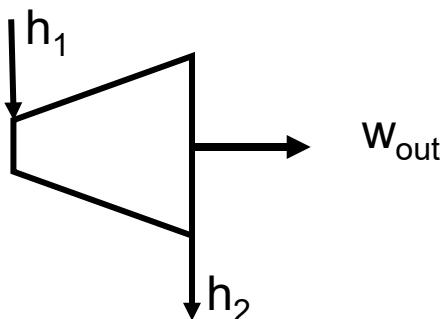
$$\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}} \quad \text{note always} \quad w_{IN,S} \leq w_{IN,A}$$



- Isentropic efficiencies are always less than 1:  $\eta_s \leq 1$

# Isentropic efficiencies: open output system

- Consider a **turbine** as an example of an **open system** device with shaft **work output**

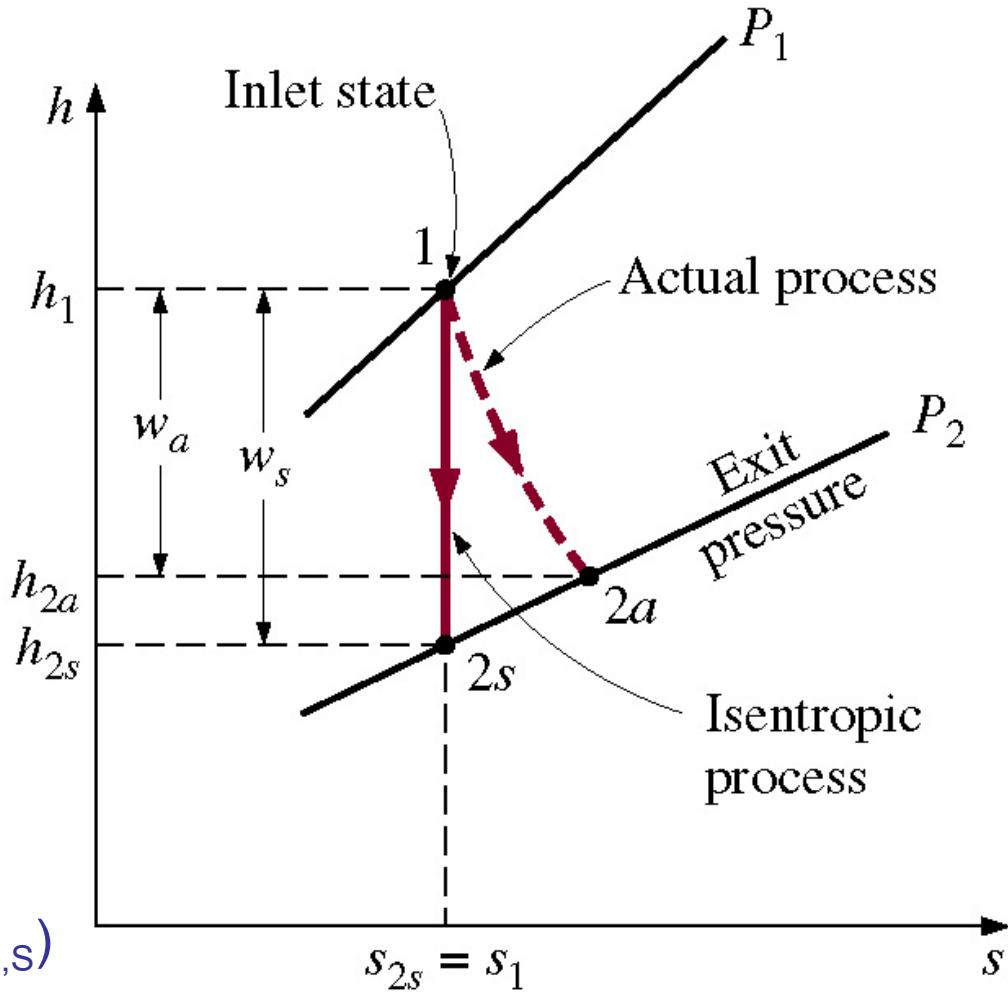


- Actual process  $1 \rightarrow 2,A$
- Isentropic process  $1 \rightarrow 2,S$   
ideal process  
where  $P_{2,S} = P_{2,A}$   
and  $s_{2,S} = s_1$

$s_{2,A} > s_{2,S}$  (Entropy increases)

$h_{2,A} > h_{2,S}$

$$w_A = (h_1 - h_{2,A}) < w_S = (h_1 - h_{2,S})$$

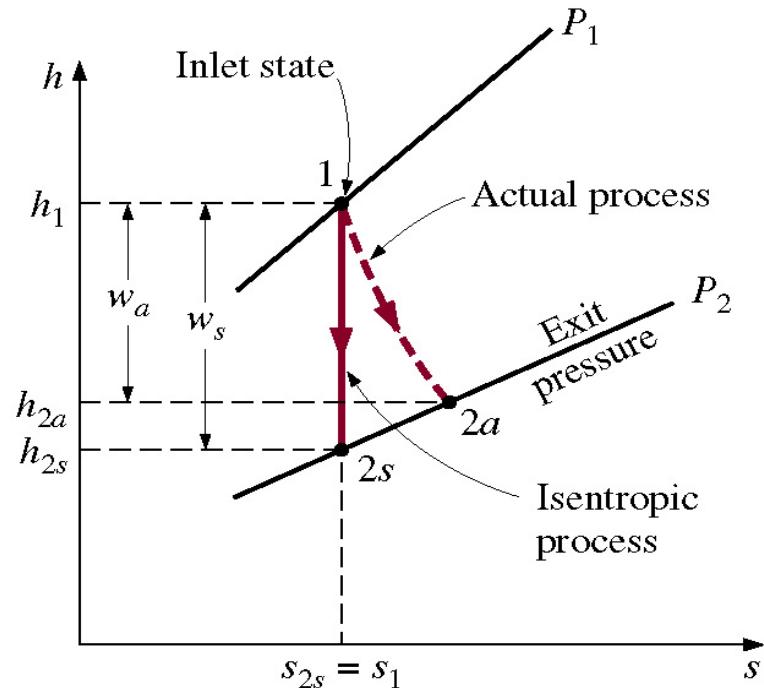


# Isentropic efficiencies: open output system

- Consider a **turbine** as an example of an **open system** device with shaft **work output**

- Actual process IN → OUT,A
- Isentropic process IN → OUT,S  
where  $P_{OUT,S} = P_{OUT,A}$   
and  $s_{OUT,S} = s_{IN}$

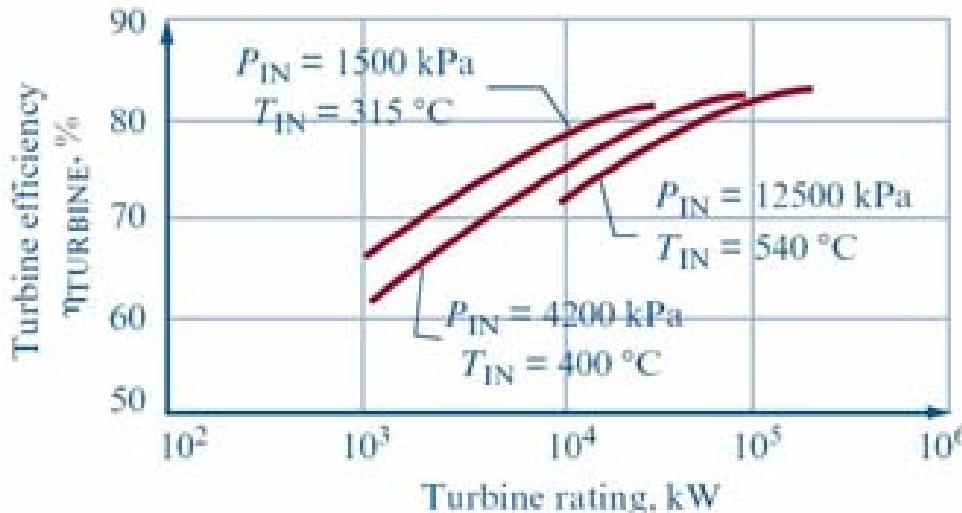
- The **isentropic efficiency**



$$\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}} = \frac{h_{IN} - h_{OUT,A}(P_{OUT})}{h_{IN} - h_{OUT,S}(P_{OUT}, s_{IN})}$$

# Isentropic efficiency of a turbine

- The isentropic efficiency of a turbine is usually measured and provided by the manufacturer
- Efficiencies depend on the conditions where the turbine is used and vary with the turbine's power rating, inlet- and outlet conditions and turbine revolutions per minute
- The best performance is on the design conditions, often more turbines are placed behind each other to have optimal performance in each pressure range

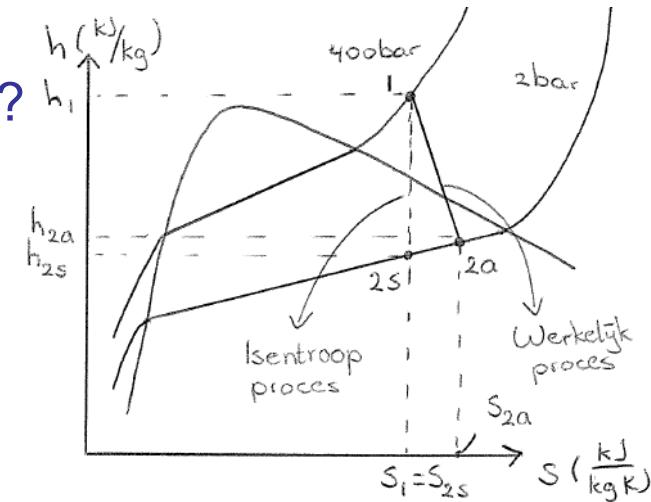


Typical condensing steam turbine isentropic efficiency curves, as supplied by the manufacturer,  $P_{out} = 15 \text{ kPa}$  at 3600 rpm

# Example: Isentropic efficiency steam turbine

- Consider an adiabatic steam turbine with an isentropic efficiency of 85%
- Inlet conditions:  $T_1 = 400 \text{ C}$ ,  $P_1 = 40 \text{ bar}$  and exit conditions:  $P_2 = 2 \text{ bar}$
- Draw the process in a hs-diagram
- How much work is produced by the steam turbine?
- What is the entropy change?

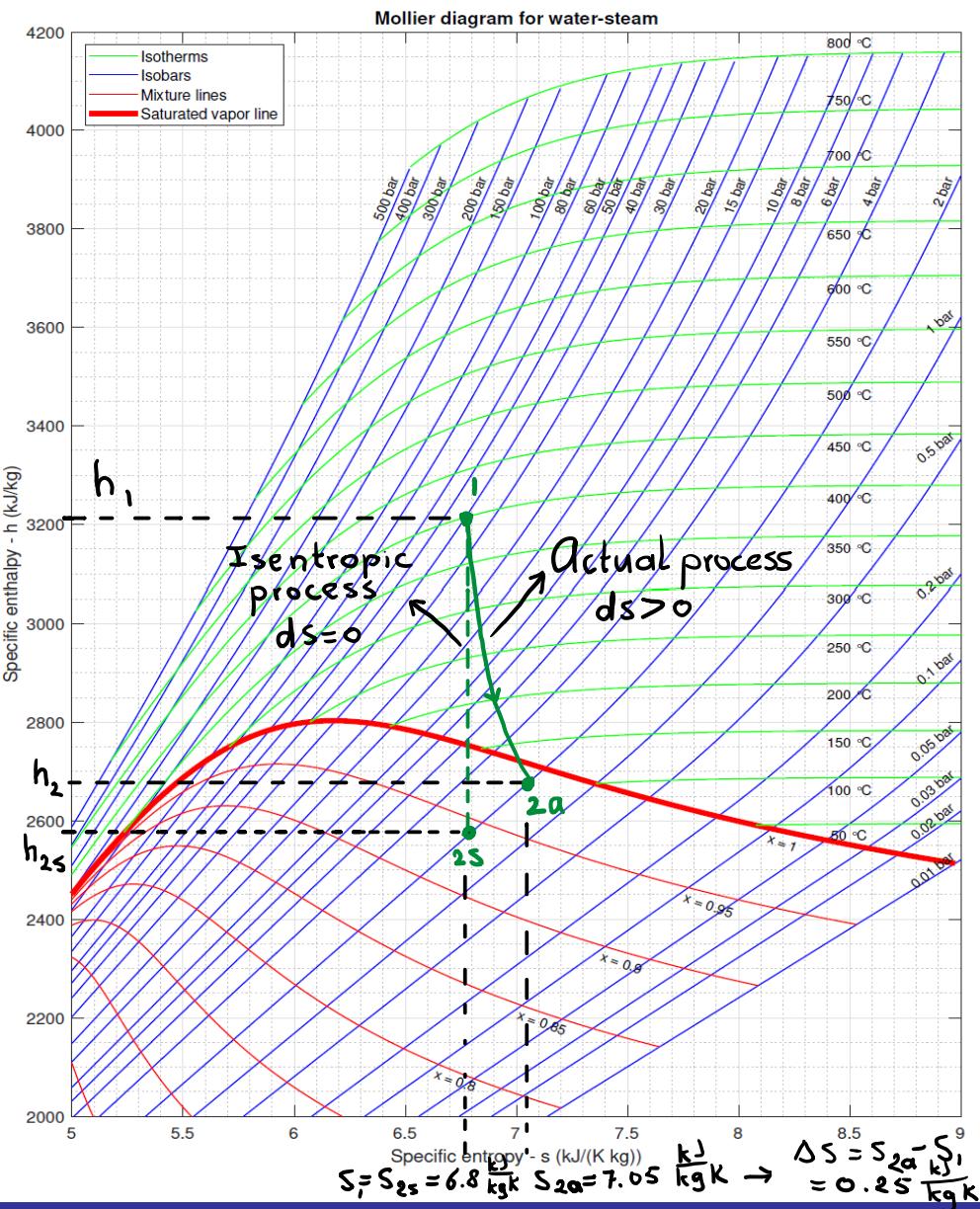
**Solution:**  $\eta_{\text{OUTPUT},s} = \frac{w_{\text{OUT},A}}{w_{\text{OUT},s}} = \frac{h_1 - h_{2,A}}{h_1 - h_{2,s}}$   
 $\rightarrow w_{\text{OUT},A} = h_1 - h_{2,A} = \eta_{\text{OUTPUT},s}(h_1 - h_{2,s})$



- Table 6  $\rightarrow h_1 = 3213.4 \text{ kJ/kg}$ ,  $s_1 = 6.7688 \text{ kJ/kgK}$
- $h_{2,s} = h_{2,s}(P_2, s_1)$  in saturated mixture region as  $s_v@2\text{bar} = 7.1272 \text{ kJ/kgK}$
- $s_L@2\text{bar} = 1.5304 \text{ kJ/kgK} \rightarrow x_s = \frac{s_1 - s_l}{s_v - s_l} \rightarrow x_s = 0.94$
- $h_L@2\text{bar} = 504.8 \text{ kJ/kg}$ ,  $h_v@2\text{bar} = 2706.5 \text{ kJ/kg} \rightarrow h_{2,s} = h_l + x_s(h_v - h_l) = 2574.4 \text{ kJ/kg}$
- $W_{\text{out},A} = \eta_{\text{output},s}(h_1 - h_{2,s}) = 542.3 \text{ kJ/kg}$
- $h_{2,A} = h_1 - \eta_{\text{output},s}(h_1 - h_{2,s}) = 2670.3 \text{ kJ/kg} \rightarrow x_a = \frac{h_{2,a} - h_l}{h_v - h_l} \rightarrow x_a = 0.98$
- $\Delta S = s_{2,A} - s_1 = s_{2,A} - s_{2,s}$
- $s_{2,A} = s_l + x_a(s_v - s_L) = 7.015 \text{ kJ/kgK} \rightarrow \Delta s = 0.246 \text{ kJ/kgK}$

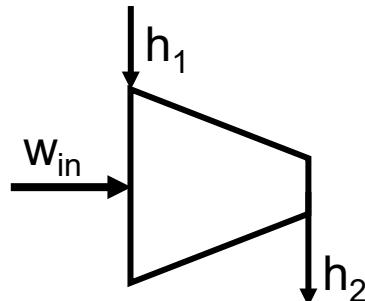
# Example: Isentropic efficiency steam turbine

- Steam turbine work output
- Previous slide solved using tables
- Now solved using hs-diagram
  - Gives more insight, is faster but numbers are less accurate
- Point 1:**  $T_1 = 400 \text{ C}$ ,  $P_1 = 40 \text{ bar}$   
 $\rightarrow h_1 = 3210 \text{ kJ/kg}$
- Point 2s:**  $P_2 = 2 \text{ bar}$ ,  $s_{2s} = s_1$   
 $\rightarrow h_{2s} = 2575 \text{ kJ/kg}$  and  $x = 0.94$
- Point 2a:**  $\eta_{S,TURB} = \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$   
 $\rightarrow h_{2a} = h_1 - \eta_{s,turb}(h_1 - h_{2s}) = 2670 \text{ kJ/kg}$   
 add to diagram and find  $x = 0.98$
- Work:**  $w = h_1 - h_{2a} = 540 \text{ kJ/kg}$   
 (tables result:  $w = 542.3 \text{ kJ/kg}$ )
- Entropy difference:**  $\Delta s = s_{2a} - s_1 = s_{2a} - s_{2s} = 7.05 - 6.8 = 0.25 \text{ kJ/kgK}$   
 (tables result:  $\Delta s = 0.25 \text{ kJ/kgK}$ )



# Isentropic efficiencies: Open input system

- Consider a **compressor** as an example of an **open system** device with **shaft work input**



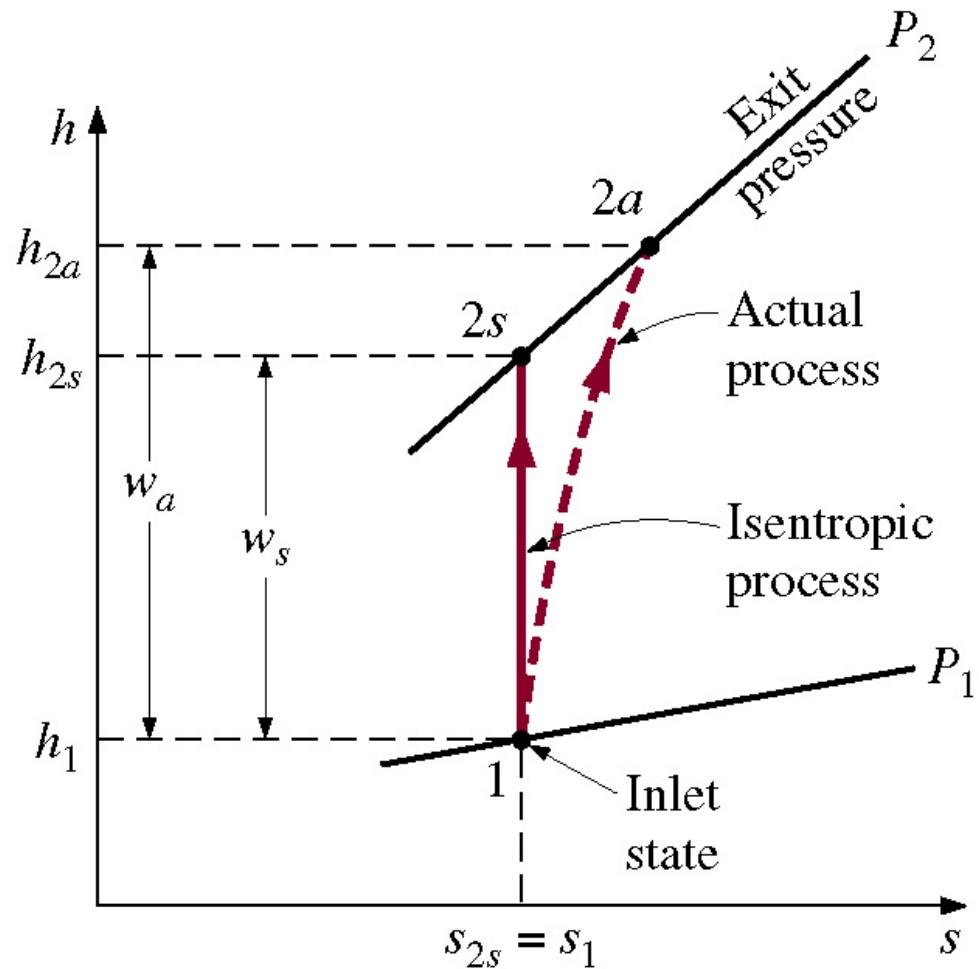
- Actual process  $1 \rightarrow 2,A$
- Isentropic process  $1 \rightarrow 2,S$   
ideal process

where  $P_{2,S} = P_{2,A}$   
and  $s_{2,S} = s_1$

$$s_{2,A} > s_{2,S}$$

$$h_{2,A} > h_{2,S}$$

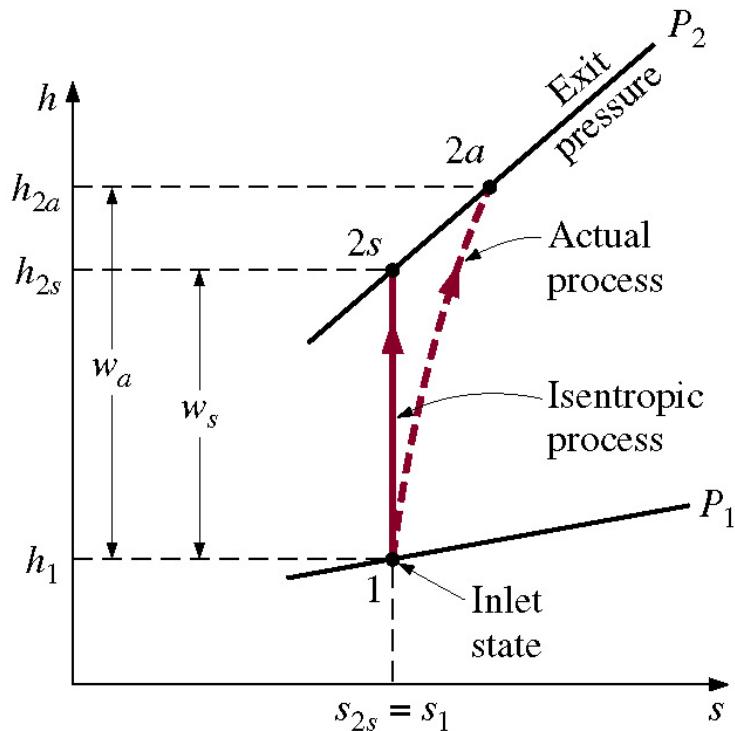
$$w_A = (h_{2,A} - h_1) > w_S = (h_{2,S} - h_1)$$



# Isentropic efficiencies: Open input system

- Consider a **compressor** as an example of an **open system** device with **shaft work input**
  - Actual process:  $1 \rightarrow 2a$
  - Isentropic process:  $1 \rightarrow 2s$  where  $P_{2s} = P_{2a}$  and  $s_{2s} = s_1$
- The **isentropic efficiency**

$$\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}} = \frac{h_{2s}(P_2, s_1) - h_1}{h_{2a}(P_2) - h_1}$$



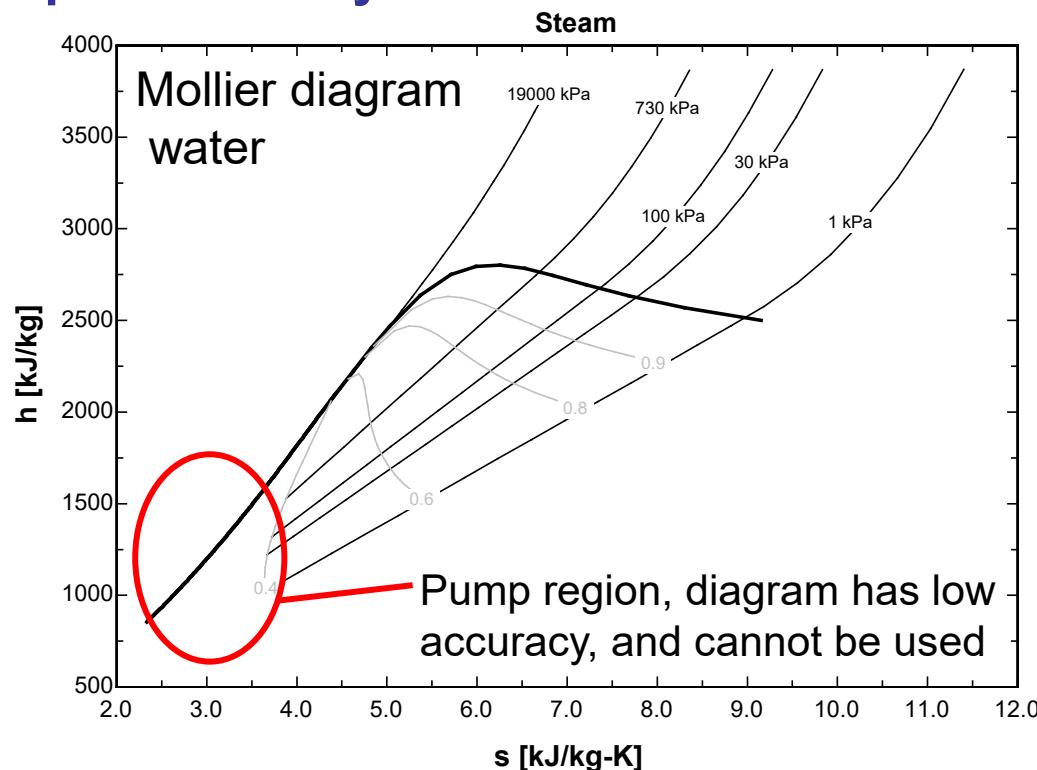
# Isentropic efficiencies: Open input system

- Consider an adiabatic pump as an example of an **open system** device with **shaft work input**
  - Actual process  $1 \rightarrow 2A$  and isentropic process  $1 \rightarrow 2s$  where  $P_{2s} = P_{2A}$  and  $s_{2,s} = s_1$
- Like for a compressor the **isentropic efficiency** is

$$\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}} = \frac{h_{2,s}(P_2, s_1) - h_1}{h_{2,A}(P_2) - h_1}$$

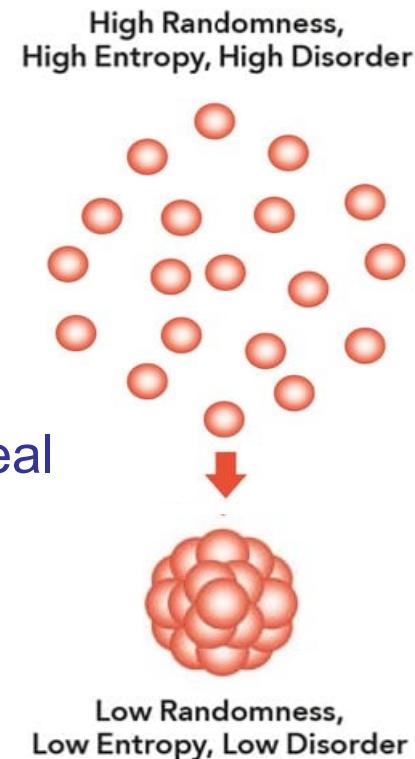
- Ideal pump ( $ds=0$ ) used for incompressible ( $dv=0$ ) fluid therefore (Gibbs equation)

$$h_{2,s} - h_1 = \int_1^2 dh = \int_1^2 (Tds + vdp)$$
$$= \int_1^2 vdp = v(P_2 - P_1)$$



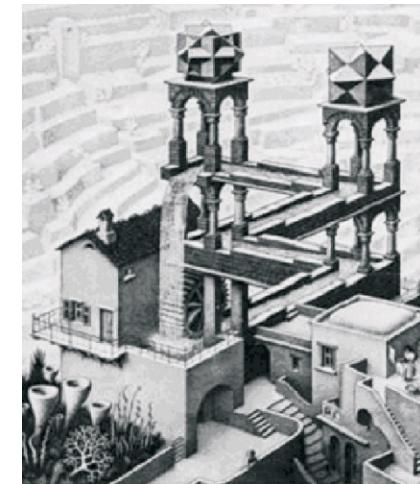
# Recapitulate class 5

- Entropy ( $s$  [ $\text{kJ/kgK}$ ]), is a measure of the randomness, disorder of the energy of a system, it gives information about irreversibility and is used to describe the direction of processes
- The second law of thermodynamics states that actual processes proceed in direction of overall increasing entropy
- Entropy is not conserved, in real processes it increases, entropy is generated:  $\delta s_{\text{gen}} = ds_{\text{system}} + ds_{\text{surroundings}} \geq 0$
- Inequality of Clausius:  $ds \geq \left( \frac{\delta q_{\text{net}}}{T_{\text{out}}} \right)_{\text{irrev}}$  (= reversible process)
- Heat transfer  $\delta q_{\text{net}} \leq T ds$ , reversible  $\delta q_{\text{rev,net}} = T ds$
- Gibbs equations  $T ds = du + P dv$  and  $T ds = dh - v dP$
- **ISENTROPIC efficiency**, gives information on how close a real device or processes is to an ideal (=optimal) behavior
  - Output producing systems:  $\eta_{\text{OUTPUT},s} = \frac{w_{\text{OUT},A}}{w_{\text{OUT},s}}$
  - Input requiring systems:  $\eta_{\text{INPUT},s} = \frac{w_{\text{IN},s}}{w_{\text{IN},A}}$

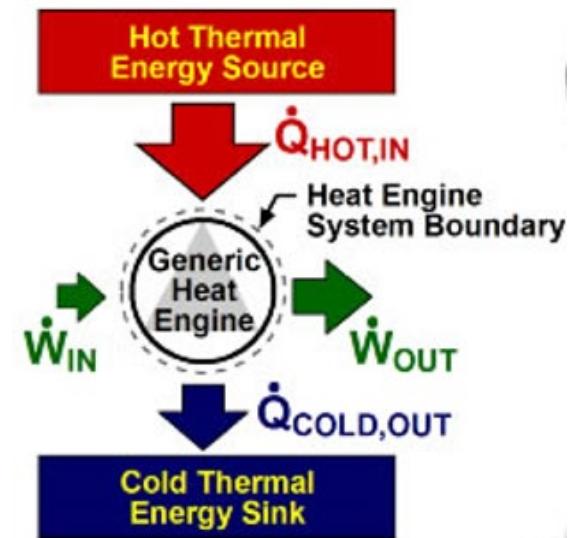


# Next Class 6: Cycles for work, cold and heat, Carnot

- Processes and devices are combined to make practical cycles (engines / installations)
  1. Heat power cycles
  2. Refrigeration / heat pump cycles
- The laws of thermodynamics for cycles
- Thermal efficiency of a heat power cycle
- Carnot cycle and Carnot efficiency
- COP of refrigeration and heat pump cycles
- Kelvin-Planck and Clausius statement
- Perpetual - Motion Machines
- What is the highest possible efficiency of a heat engine? Can it be 100% (in theory)?
- Can we get rid of the heat rejected to the cold environment?



A perpetual – motion machine, an impossible cycle (M.C. Escher)



# Keep in mind: Important formulas

- Specific volume  $v=V/m$  [ $m^3/kg$ ] and density  $\rho=1/v=m/V$  [ $kg/m^3$ ]
- Volume work  $\delta w = Pdv$  or  $\delta W = PdV$
- Enthalpy  $h = u + Pv$ , where  $u$  is internal energy,  $P$  is pressure,  $v$  is volume
- Efficiency  $\eta_{thermal} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Mixture fraction  $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
- Conservation of mass  $m_{in} = m_{out}$ , mass flow rate  $\dot{m} = \rho v A$
- Conservation of energy, first law of thermodynamics
  - Closed system:  $du = \delta q - \delta w \rightarrow \Delta u = q_{net} - w_{net}$
  - Open system:  $q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$
- S increases, second law  $ds_{total} = ds_{system} + ds_{surroundings} = \delta s_{gen} \geq 0$
- Inequality of Clausius  $ds \geq \left( \frac{\delta q_{net}}{T_{out}} \right)_{irrev}$  (= for reversible process)
- Gibbs equations  $Tds = du + Pdv$  and  $Tds = dh - vdP$
- Isentropic efficiencies  $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$ ,  $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$

