

Class 1: Introduction and basic thermodynamic concepts



Navy Shipyard Fire Department Vehicle (1881)

Manufactured in England by Merryweather & Sons – London. The steam which set in motion the water pumps to the fire hose was provided by the coal boiler. In less than 10 minutes it produced the required pressure, which happened while the car was on its way to the fire. The car was pulled either by man or mules.

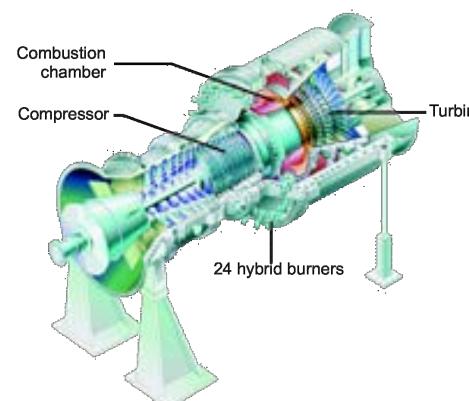
(Museu de Marinha, Lisbon)

Recap Objectives Eng. Thermodynamics

- **Engineering thermodynamics:** application of thermodynamics to solve technological problems that engineers face
- Analysis of transport and conversion of various forms of energy (work \leftrightarrow electricity \leftrightarrow heat \leftrightarrow cold)
- **The objectives are:**
 1. Conversion of heat into work / electricity (heat engine)
 2. Transportation of heat using work / electricity (cooling / heat pump)



Heat converted into work (electricity) [1]



Heat converted into work to generate power [1]

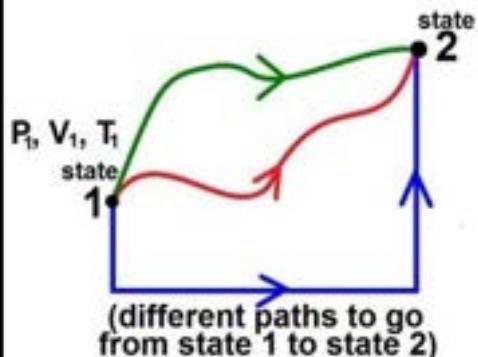
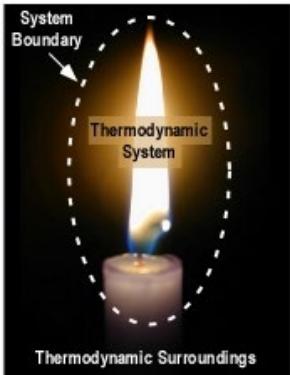


Work (electricity) converted into cold [2]

Roadmap Engineering Thermodynamics

- Using thermodynamics for practical applications requires knowledge of:

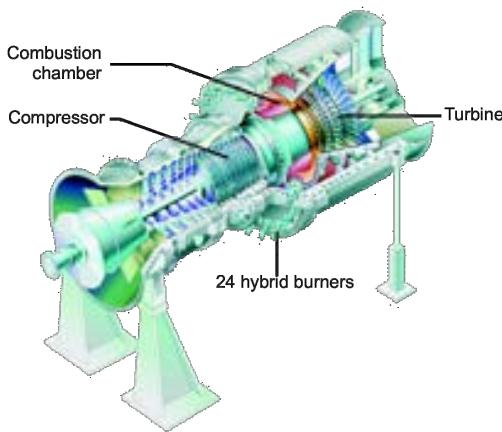
Concepts and definitions (Class 1)



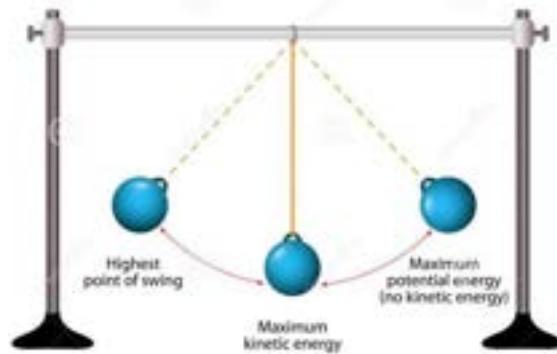
Various forms of energy (Class 2)



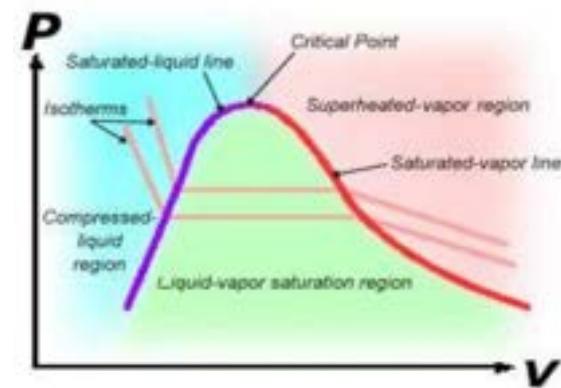
Power cycles
(Class 6 – 11)



Laws of Thermo
(Class 4 and 5)

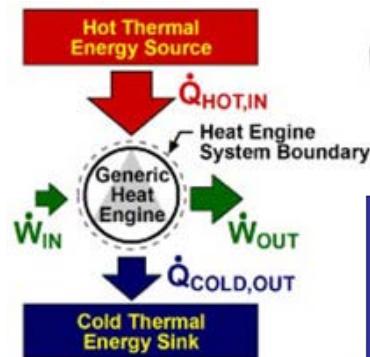


Properties of Substances
(Class 3, 9)

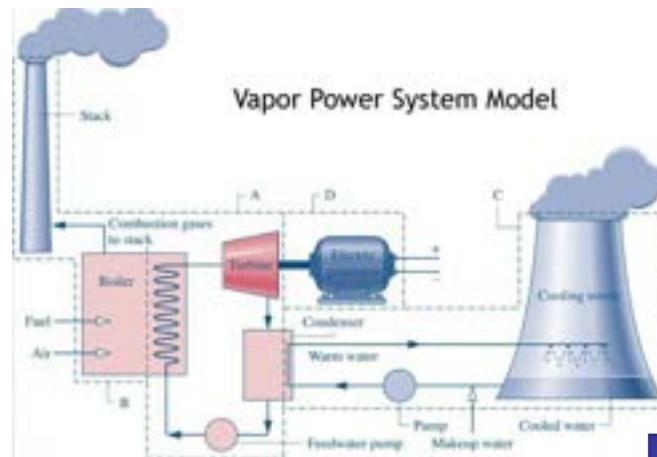


Roadmap Engineering Thermodynamics

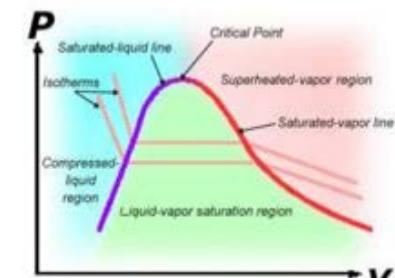
Thermodynamic cycles (Class 6)



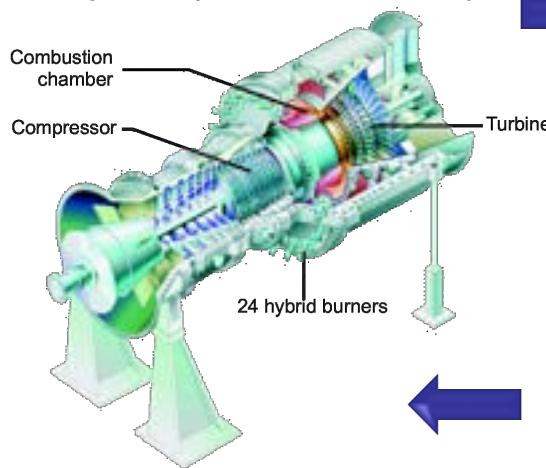
Vapor power cycles – Rankine cycle (Class 7, 8)



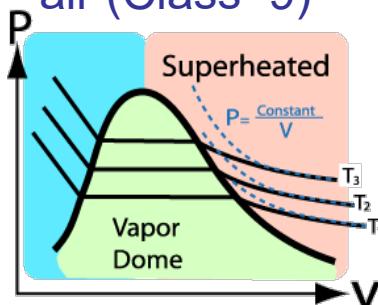
Properties of water (Class 3)



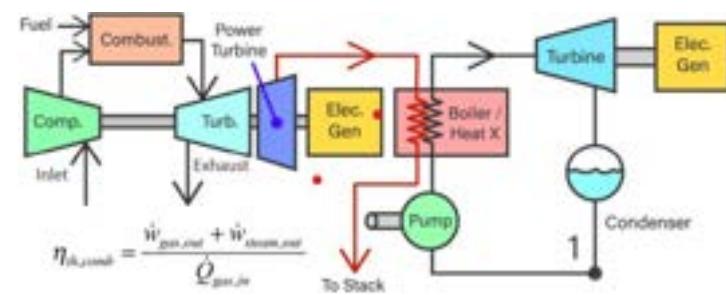
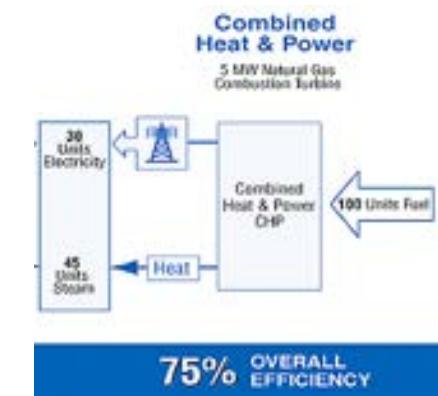
Gas power cycles – Brayton cycle (Class 10, 11)



Properties of air (Class 9)

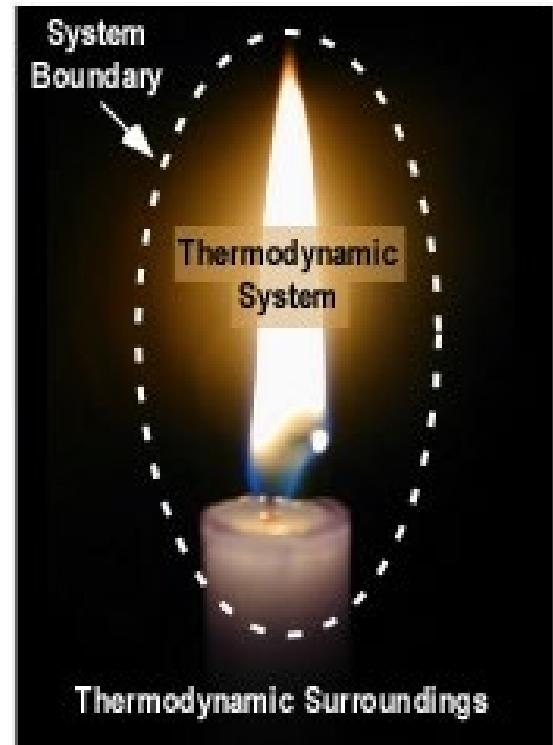


Combined cycles
 Combined heat & power (Class 8, 11)



Content Class 1

- **Important definitions, concepts and terminology**
- Systems and boundaries
 - Open / closed / isolated systems
- Properties
 - Extensive / intensive / specific
- States and State Postulate
- Equilibrium and quasi-equilibrium
- Processes and cycles
 - Isobaric / isotherm / isochoric / adiabatic
 - Process diagrams
- Metric system and fundamental units
- Temperature and the zeroth law of thermodynamics
- Pressure (absolute and gauge pressure)
- **Learning goal:** explain thermodynamic concepts, processes & definitions



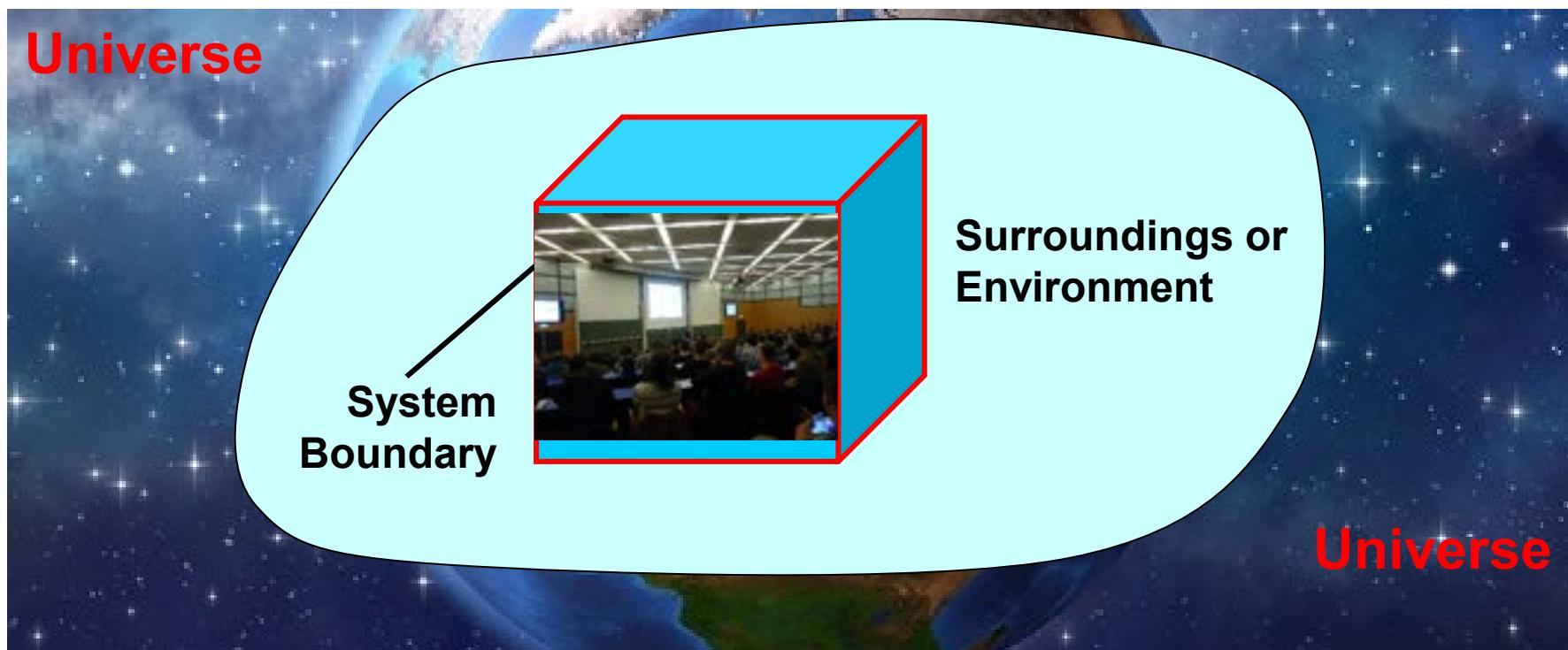
Systems: Definitions

- **System:** part of the universe that we want to analyze



Systems: Definitions

- **System:** part of the universe that we want to analyze
- **Surroundings / Environment:** part of universe that is affected or influenced by the system
- **System boundary:** separates the system from the surroundings
(note: system boundary can be rigid, deformable or move)

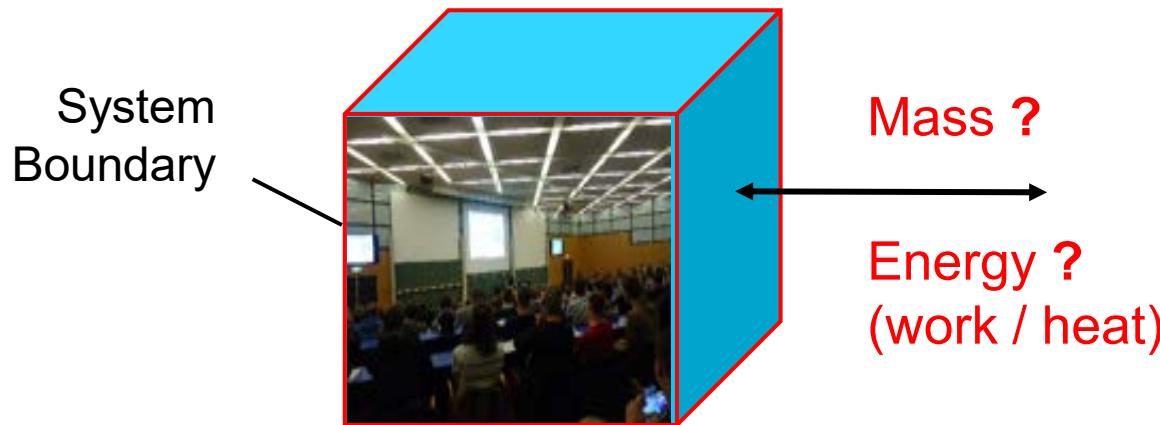


Systems: Examples



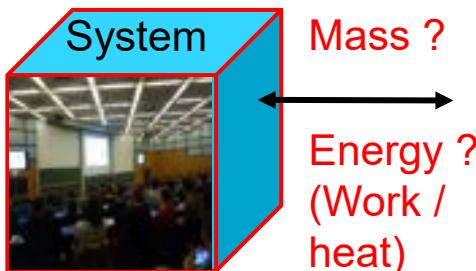
System Types

- **Different types of systems:** difference based on the **transport of mass and energy** across the system boundary



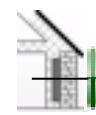
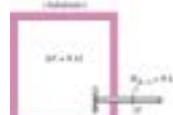
- **Open system:** Mass and energy (work and heat) can cross the boundary
- **Closed system:** Only energy (work and heat) can cross the boundary
- **Isolated system:** No mass or energy (work and heat) can cross the boundary
- **Insulated system:** Mass cannot cross the boundary, heat cannot cross the boundary, but work can

Systems Types



Transferred across system boundary

Note: a boundary can be rigid, deformable or move

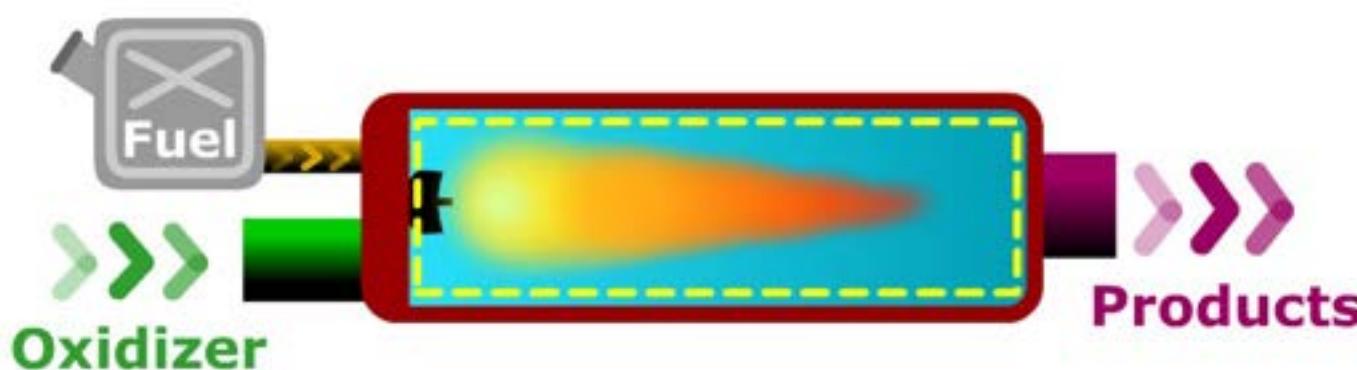
Type of System	Mass	Energy	Example
Open System / Control Volume (CV)	Yes	Yes	   
Closed System / Control Mass (CM)	No	Yes	   
Isolated System	No	No	 
Insulated System	No	Work yes Heat no	 

- Thermodynamic relations for closed or open systems are different

Combustion in Open & Closed Systems



- **Closed system:** Combustion in a closed system, only heat can cross the system boundary mass stays inside the system
- **Open system:** Combustion in an open system, also mass (fuel, oxidizer and combustion products) can cross the system boundary

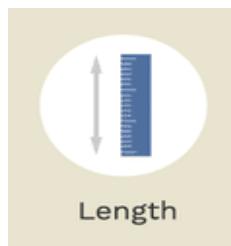


Properties: Definitions

- **Property:** any defining characteristic of a system
- **Thermodynamic properties:** properties that describe mass and energy of systems (e.g. T, P, v, ρ and U)

- **Extensive properties**

Depend on system size, vary if the size of the system changes (e.g. V, U)



Length



Volume



Size



Weight

- **Intensive properties**

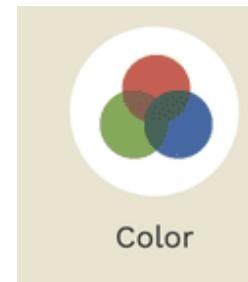
Independent of system size, do not vary if the size of the system changes (e.g. T, P, ρ)



Temperature



Boiling Point



Color

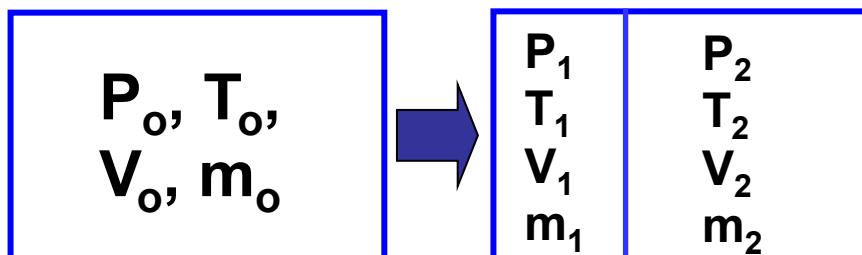


Hardness

Intensive and Extensive Properties

- The value of an **extensive property** is dependent of the mass / size of the system
- The value of an **intensive property** is independent of the mass / size of the system

- The box will be divided in two parts
- How will the properties change?



$P_0 = P_1 = P_2 \rightarrow$ Intensive prop
 $T_0 = T_1 = T_2 \rightarrow$ Intensive prop
 $V_0 \neq V_1 \neq V_2 \rightarrow$ Extensive prop
 $m_0 \neq m_1 \neq m_2 \rightarrow$ Extensive prop

Total and Specific Properties

- Besides **intensive** and **extensive** properties, **total** and **specific** properties can be distinguished
- **Total properties**
 - Describe the total value of a system
 - Depend on the size of the system, i.e. extensive properties
 - Denoted by upper case letter
- **Specific properties**
 - Dividing an extensive property by mass gives a specific one
 - Specific properties are intensive properties as they are not dependent on the size of the system
 - Denoted by lower case letter
- Total volume: V [m^3]
- Specific volume: $v = V/m$ [m^3/kg]



$$\begin{aligned}V &= 3 \text{ liters} = 0.003 \text{ m}^3 \\m &= 2.76 \text{ kg} \\v &= 0.003/2.76 = 0.00109 \text{ m}^3/\text{kg}\end{aligned}$$

Specific Properties

- **Why we use specific properties?**

- The size of the system is not important to know something of it
- Everyday life example: shopping



- Fresh fruit, vegetables and meat are priced in Euro per kg
 - you buy Y kg and you pay Y kg \times euro/kg (price is independent of the amount of vegetables or meat that the shopkeeper has)
 - You don't want to know the total price of a big piece but you need to know what to pay if you buy 200 grams.

Total and Specific Properties

- Example for volume
- Total volume: V [m³] • Specific volume: $v = V/m$ [m³/kg]
(note: $v = 1/\rho$)

A	B
$\frac{2}{3}V$	$\frac{1}{3}V$
$\frac{2}{3}m$	$\frac{1}{3}m$

$$v_{A+B} = v_A + v_B$$
$$m_{A+B} = m_A + m_B$$
$$v = \frac{V_{A+B}}{m_{A+B}} = \frac{V_A}{m_A} = \frac{V_B}{m_B}$$

- Specific volume, $v = V/m = 1/\rho$ is the same for A and B
- This also holds for energy properties
 - Total energy: E [J]
 - Specific Energy: $e = E/m$ [J/kg]

Note: in handwriting the difference between upper and lower case is not always clear

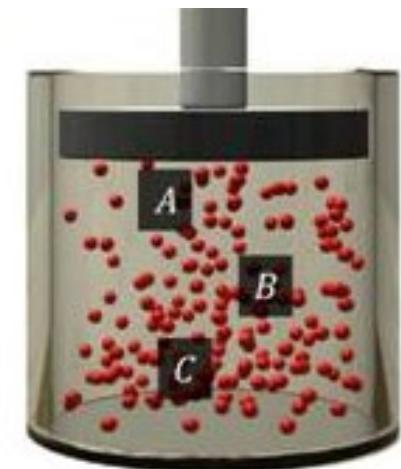
Intensive, Extensive and specific properties

Property	Extensive	Intensive
Mass	m	-
Temperature	-	T
Volume	V	$v = V/m$ (specific volume)
Pressure	-	P
Internal Energy	U	$u = U/m$ (specific internal energy)
Enthalpy	H	$h = H/m$ (specific enthalpy)

- Any extensive property can be made intensive by dividing by mass
- This is a **specific property**

Thermodynamic State

- A set of thermodynamic properties that describe the condition of a system
- At a given state all the properties of the system have fixed values
- The ability to define the state of a system is essential in thermodynamics
- Using the state postulate, only a limited set of property data is needed to determine all property data of a thermodynamic state



T, P, v, m, e,

State Postulate

- Knowing any two independent properties of a state one can determine any other property of the state (more in class 3)

State postulate: The state of a simple compressible system is completely specified by two independent, intensive properties

- Simple compressible system: If a system involves no electrical, magnetic, gravitational, motion and surface tension effects

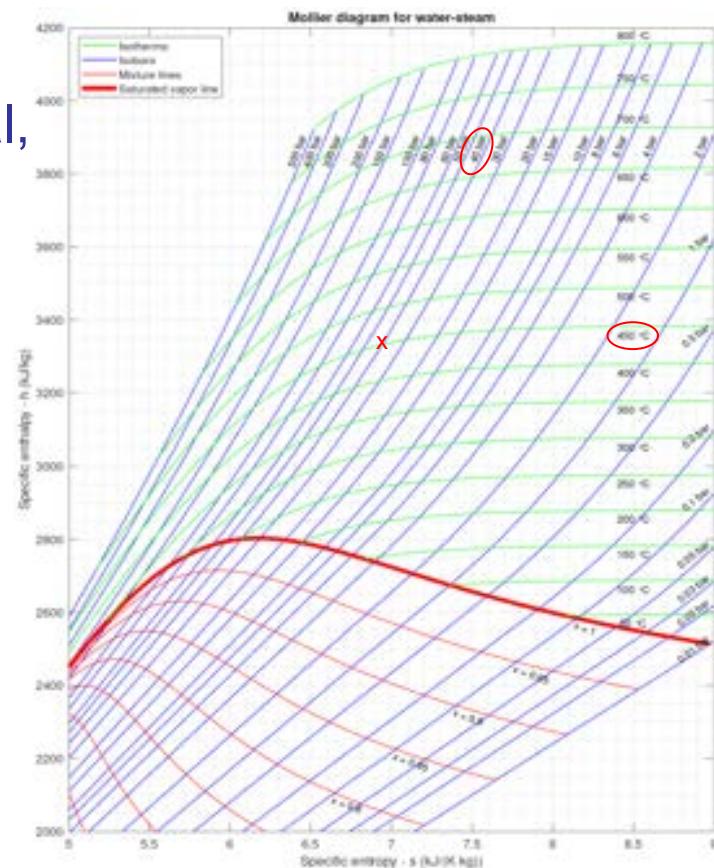
Table of Steam Properties

P (kPa)	T (°C)	v (m³/kg)
100	100	1.696
100	120	1.793
100	160	1.984

ThermoNet: John Wiley Publishers



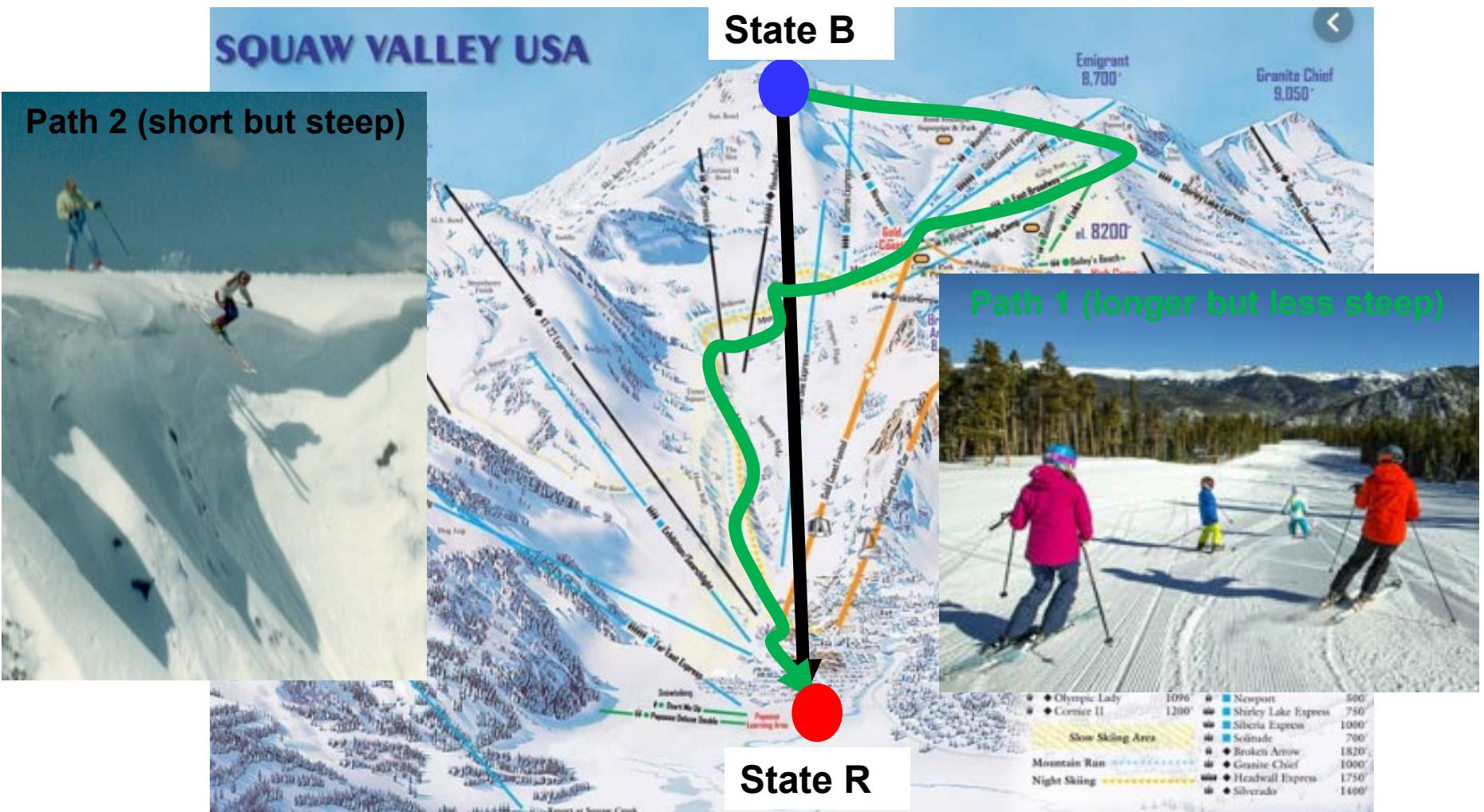
The state of nitrogen is fixed by two independent properties



Changing the state of a system: Processes



Changing the state of a system: Processes

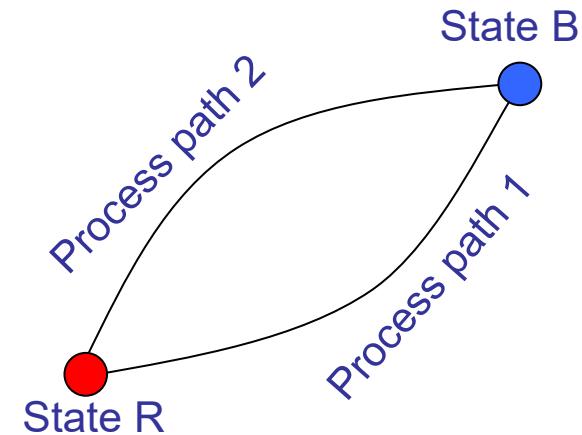


- A change of the system, state B to R is also a change of its properties (T, P, ...)
- The process, the way the change is accomplished, can differ (different the paths) but the change in the state (properties) will be the same

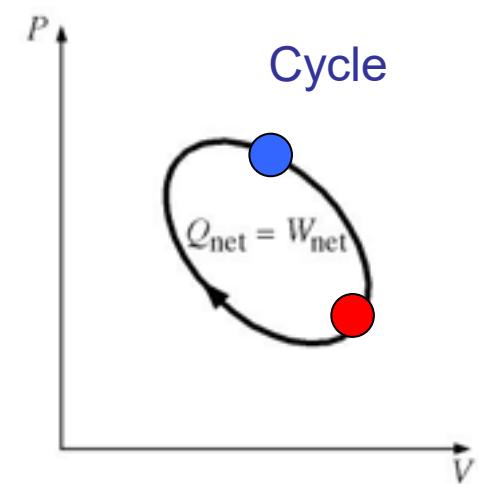
Changing the state of a system: Processes

- Change of the **state** of the system is reflected in a change of the properties of the system

- Process:** Changing the state of a system



- The system undergoes a **cycle** if it undergoes a process to a different state and returns to the original state via a different process path



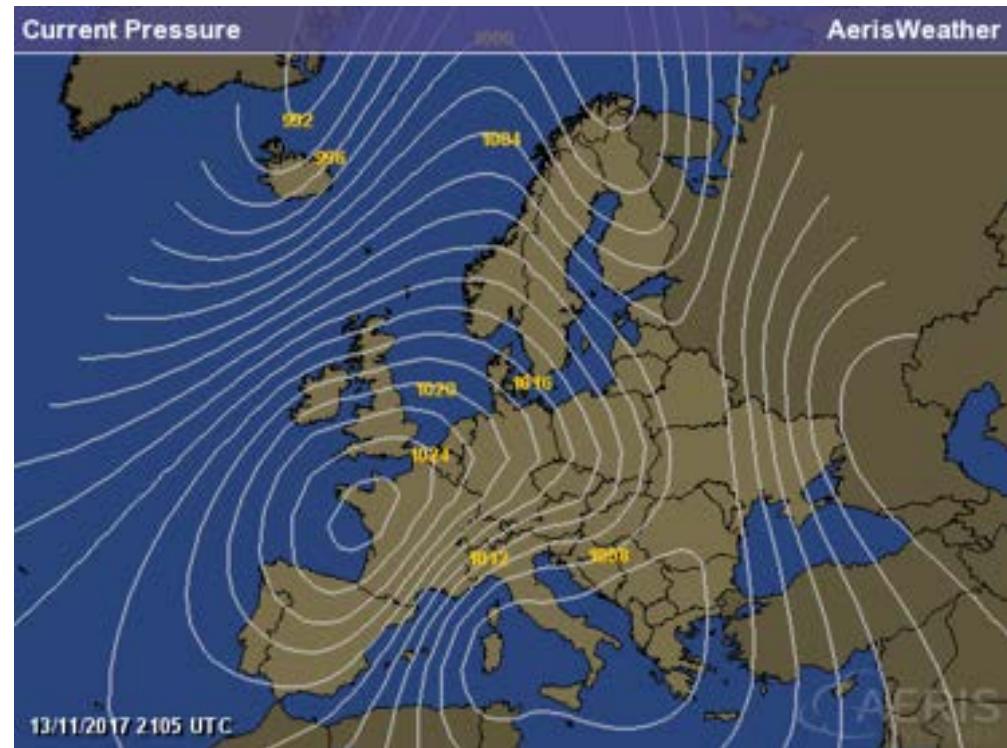
Types of Processes

- **Isothermal:** constant temperature
- **Isobaric:** constant pressure
- **Isometric or isochoric:** constant volume
- **Adiabatic:** no heat transfer



This does not imply that the temperature is constant, the temperature can still change by heating up or cooling down as a result of work added or subtracted to the system

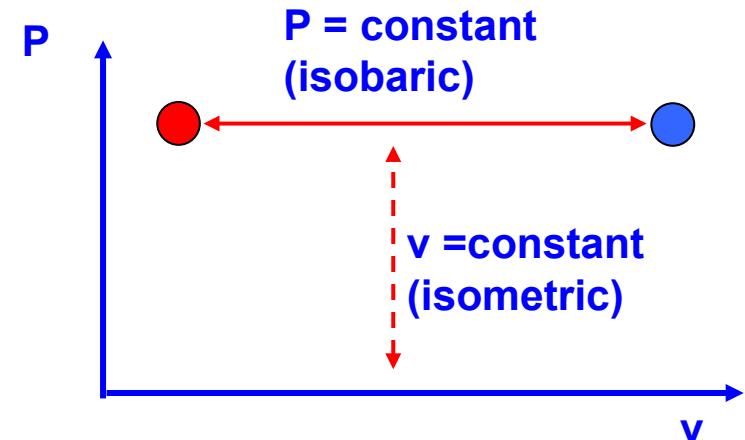
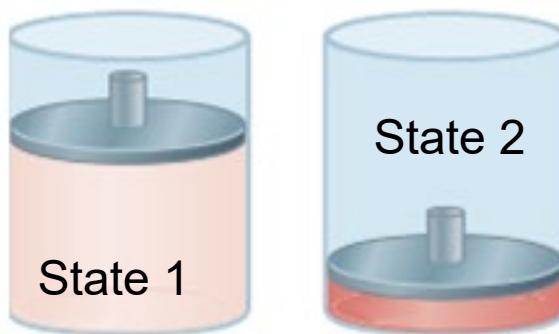
Isobars, lines of constant pressure on a weather map



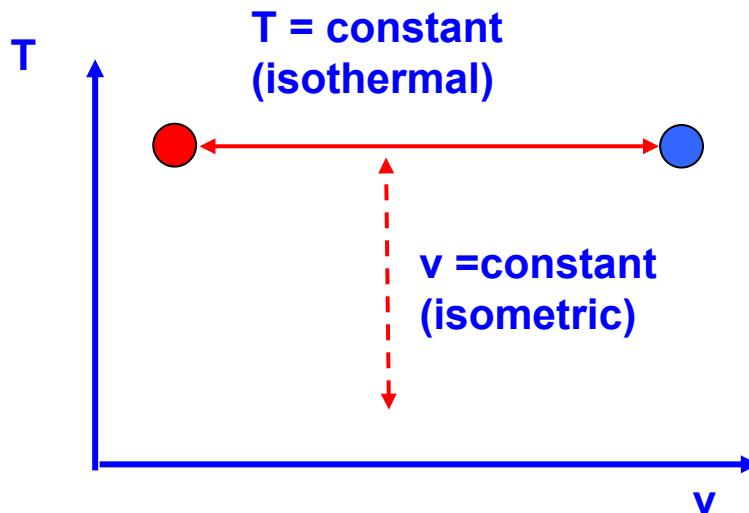
Processes: property diagrams

- Thermodynamic processes displayed in property diagrams

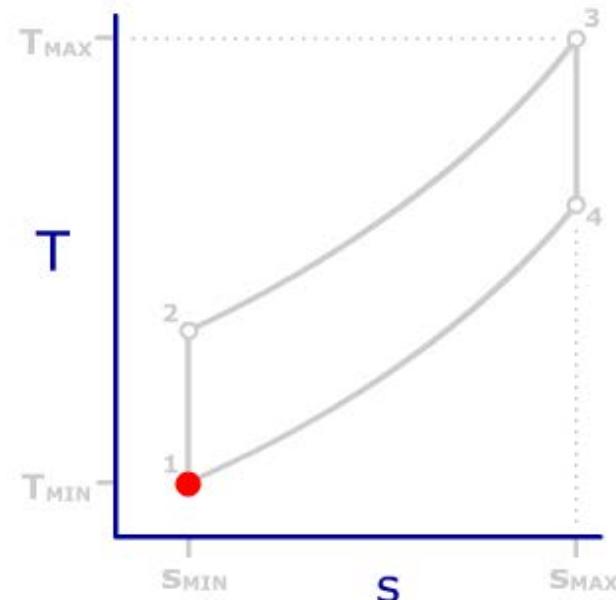
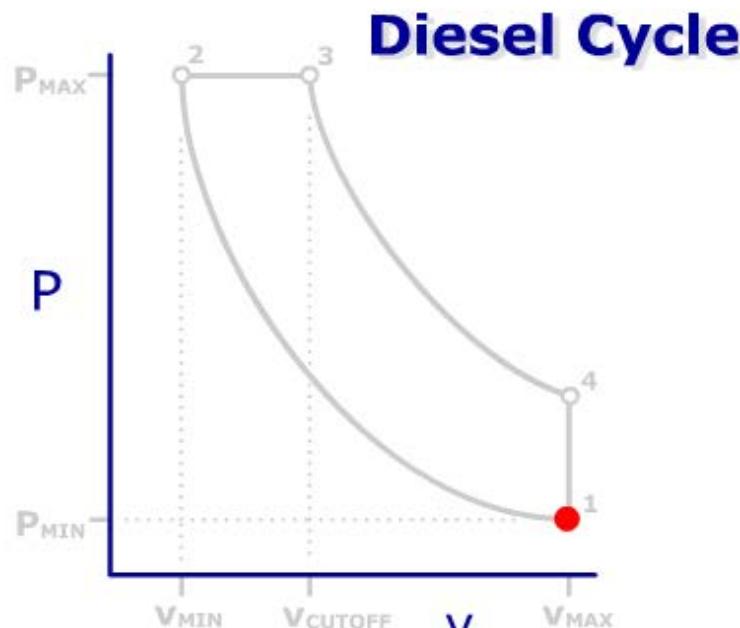
- Pv-diagram



- Tv-diagram



Example: Isobaric, Isentropic & Isometric Processes



ThermoNet: Wiley

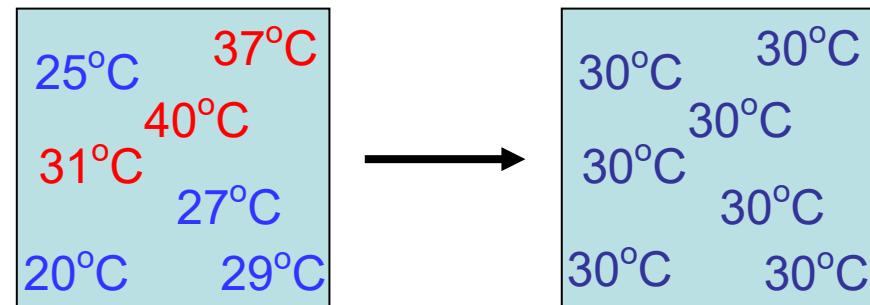
- Isobaric process (2-3) and isochoric (isometric) (1-4) process
- Processes (1-2) and (3-4) are isentropic (class 5)
- The four processes together make a complete cycle

Thermodynamic Equilibrium

- **Equilibrium** of a system implies a state of balance of the system, where there are no driving forces within the system

- **Types of equilibrium**

- Thermal equilibrium
- Mechanical equilibrium
- Phase equilibrium
- Chemical equilibrium

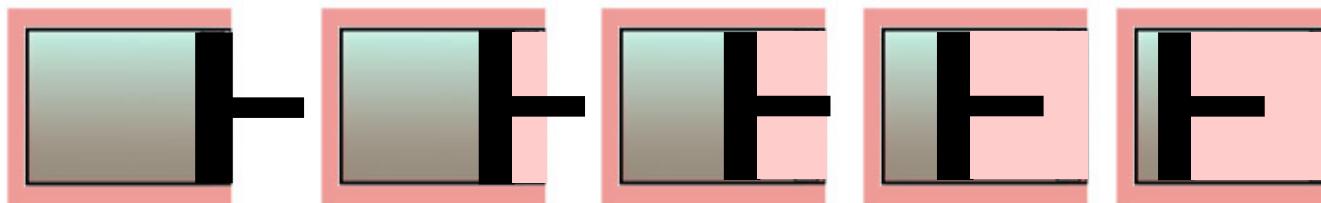


Closed system reaching thermal equilibrium

- A system is only in equilibrium when all relevant equilibrium criteria are satisfied
- If the properties of a system (like pressure and temperature) are not changing with time the system is in **thermodynamic equilibrium**

Quasi-Equilibrium

- A system's equilibrium changes during a process
- During the process, the system passes a series of states
- Describe the system at any point in time → always consider a system to be in quasi-equilibrium
- Quasi-equilibrium
 - Idealized process, not a true representation of an actual process
 - Modeling tool



Slow compression:
every step quasi-equilibrium is reached

- All steps can be considered infinitesimal small and the process occurs between the upper and lower limit
- Mathematics: differentials and integrals

Unit Systems / Dimensions

- **Fundamental units or dimensions:** defined by reproducible physical measurements
 - SI: metric international system
 - Base units: time (s), length (m), temperature (K), mass (kg)
- **Derived units or dimensions:** derived from base units
 - Force (N) is a derived unit from mass via:
Newton's Law: $F = m \cdot a$ [N] = [kg.m/s²]
- Always give units with values, without a unit the answer is useless
- Note: Other unit system, U.S. Conventional System or English System (USCS)
 - Base Units: time (s), length (ft), **force (lbf)**
 - **Mass (lbm)** is a derived unit from force
- Although it is handy to know how to convert units, it not part of this course



Property Units: Time (t)

- Time (t) in seconds (s)
 - Since 1967 the second is defined as the time required for cesium-133 atoms to resonate 9.192.631.770 cycles in a cesium resonator



1 second is 9.192.631.770 trillingen in cesium-133

<https://www.youtube.com/watch?v=oPLirFEFfIY&feature=youtu.be>

Property Units: Time (t)

FOKKE & SUKKE
WERKEN OP DE NATUURKUNDEFACULTEIT

Some Dutch culture

BIJ ONS DUURT
HET ACADEMISCH
KWARTIERTJE

8273368593000
TRILLINGEN VAN HET
CESIUM-133 ATOOM



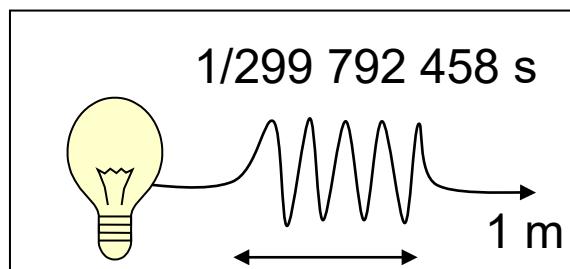
Time is one of the fifty subjects in the beta canon
[\(http://www.foksuk.nl/betacanon\)](http://www.foksuk.nl/betacanon) en
[\(http://extra.volkskrant.nl/betacanon/\)](http://extra.volkskrant.nl/betacanon/)

R.G.U.T.

Property Units: Length (L)

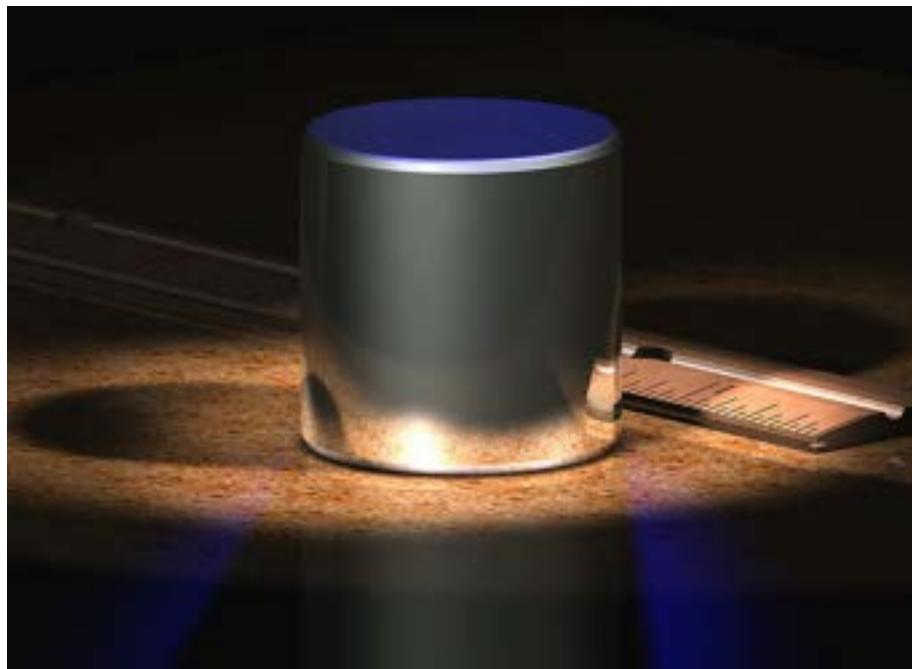
- **Length (L) in meters (m)**

- 1875 International Prototype Meter, the distance between two marks on a platinum-iridium bar under certain prescribed circumstances (the bar is in the International Bureau of Weights and Measures in Serves in France)
- In 1960 a meter is a length equal to 1 650 763.73 wave-lengths in a vacuum of the orange-red line of krypton-86
- In 1983 the meter is the length of the path traveled by light in a vacuum during a time interval of $1/299\ 792\ 458$ (1/c) of a second



Property Units: Mass (M)

- **Mass (M) in kilograms (kg)**
 - Defined in 1889/1901 as the mass of a platinum-iridium cylinder maintained under prescribed conditions. The International Prototype Kilogram is kept at the *Bureau International des Poids et Mesures* (International Bureau of Weights and Measures) in Sèvres on the outskirts of Paris.



A computer-generated image of the **International Prototype kilogram** (IPK), which is made from an alloy of 90% platinum and 10% iridium (by weight) and machined into a right-circular cylinder (height = diameter) of 39.17 mm (the inch ruler is for scale), its edges have a four-angle chamfer to minimize wear.

Property Units: Temperature (T)

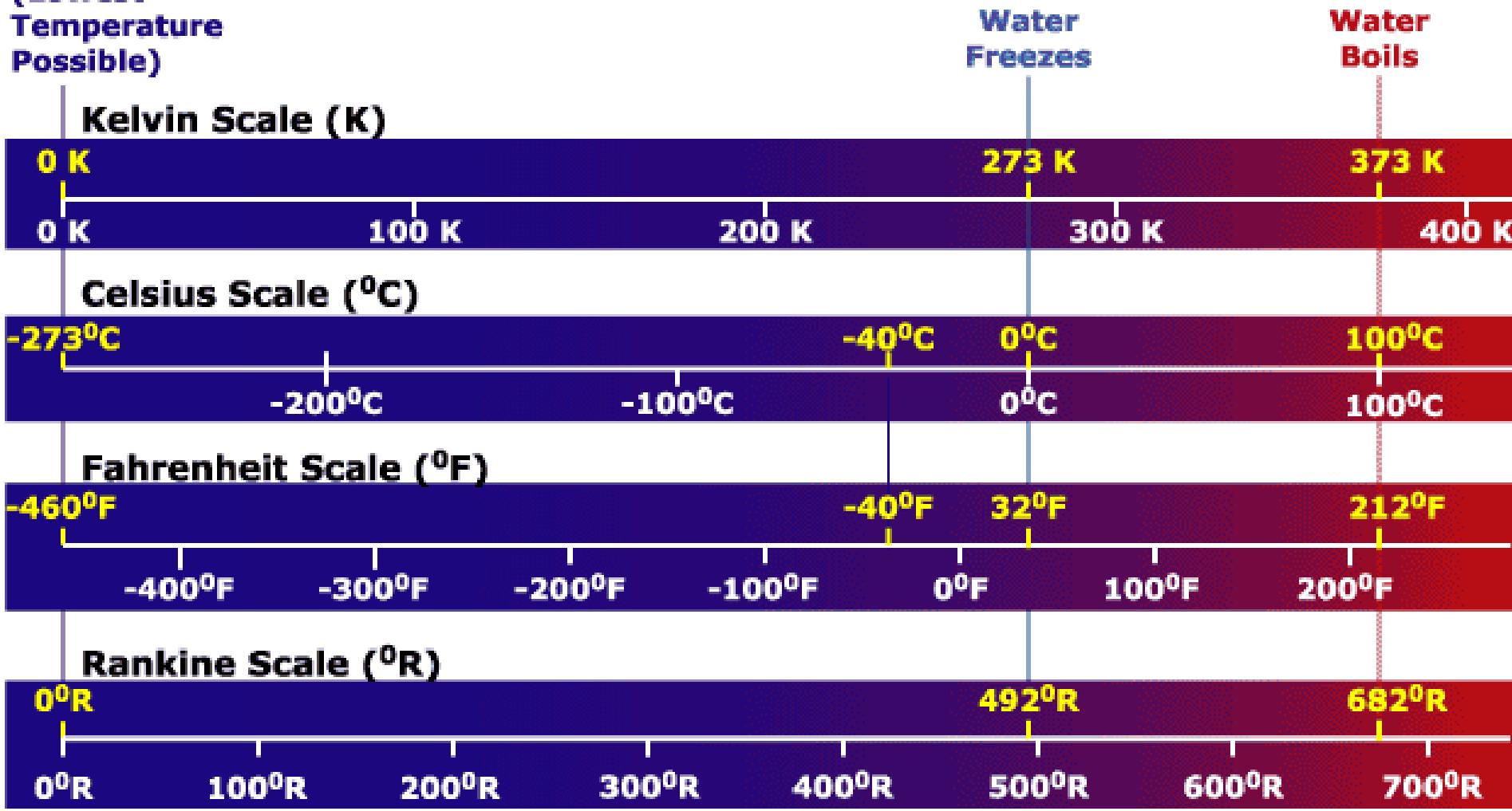
- Temperature (T) in Kelvin (K)
 - Absolute zero temperature
 - Lowest possible temperature
 - Units: Kelvin (K) ($T = 0 \text{ K}$)
 - Can never be negative
 - Relative temperature
 - Temperature measured relative to non-absolute zero temperature
 - Freezing point of water at atmospheric pressure (273.15 K)
 - Units: Degrees Celsius ($^{\circ}\text{C}$)
 - $T(\text{K}) = T(^{\circ}\text{C}) + 273.15$
- The **Kelvin** is defined as the 1/273.16 part of the thermodynamic temperature of the triple point (freezing point) of water



Lord Kelvin (William Thomson)
(1824-1907)

Temperature Scales

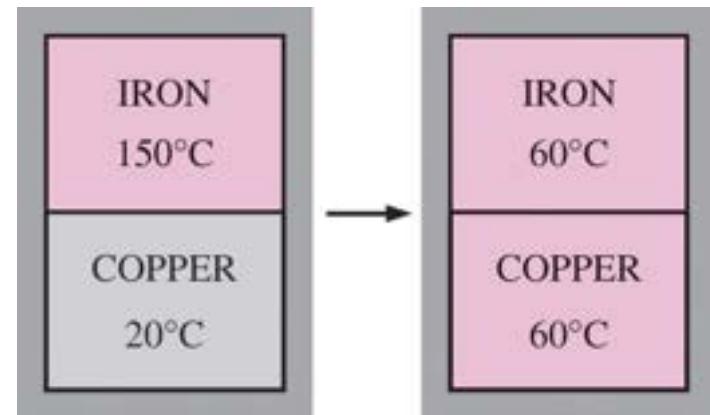
**Absolute Zero
(Lowest
Temperature
Possible)**



ThermoNet: John Wiley

Zeroth law of thermodynamics

- The zeroth law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other
- By replacing the third body by a thermometer it can be restated as, two bodies are in thermal equilibrium if both have the same temperature even if they are not in contact
- It may seem silly that such an obvious fact is called one of the basic laws, however it cannot be concluded from the other laws and serves as a basis for the validity of temperature measurements
- Its value as a fundamental physical principle was recognized after formulation of the first and the second law and therefore called the zeroth law
- The zeroth law was formulated by Fowler in 1931



Two bodies reaching thermal equilibrium after being brought into contact in an isolated enclosure

Property Units: Volume (V) – Density (ρ)

- **Volume, specific volume and density**

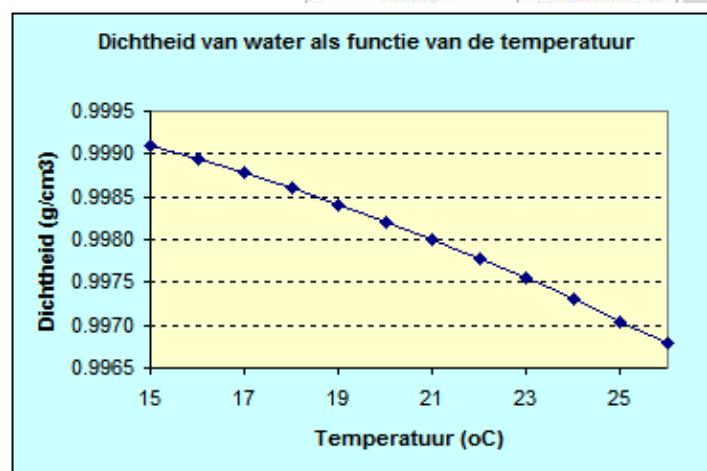
- Volume, V [m^3]
 - Related to meter
- Specific volume, v [m^3/kg]

$$v = \frac{V}{m}$$

- Density, ρ [kg/m^3]

$$\rho = \frac{1}{v} = \frac{m}{V}$$

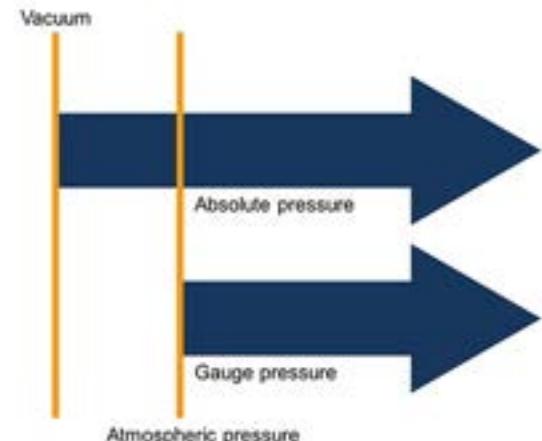
Temperatuur oC	Dichtheid kg/m ³
15	999.1026
16	998.9460
17	998.7779
18	998.5986
19	998.4082
20	998.2071
21	997.9955
22	997.7735
23	997.5415
24	997.2995
25	997.0479
26	996.7867



Density and specific volume depend on temperature

Property Units: Pressure (P)

- **Pressure (P)**
 - $P = \text{Force divided by area } (F / \text{area})$
 - Units: $\text{Pa} = \text{N/m}^2$ ($1 \text{ bar} = 10^5 \text{ Pa}$)
- Two types of pressure
 - **Gauge pressure** (P_{gauge}) measured relative to atmospheric pressure (P_{atm})
 - **Absolute pressure** (P_{absolute}) measured relative to zero pressure (vacuum)

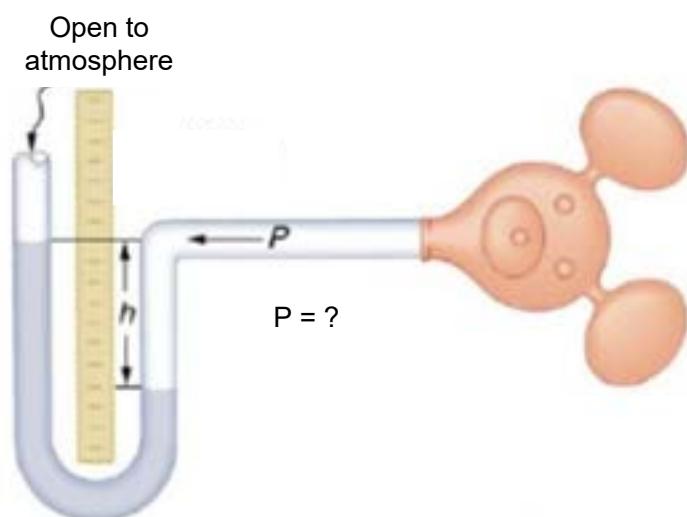


- Measuring pressure with manometer

$$P_{\text{gauge}} = \rho gh$$

$$P_{\text{absolute}} = P_{\text{atm}} + P_{\text{gauge}}$$

- $P_{\text{atm}} = 1 \text{ bar} = 10^5 \text{ Pa}$



Problem Solving (in Thermodynamics)

- **Problem Statement**

- **Analysis**

- Given
- Diagram of system and process
- Assumptions
- Governing relations

- **Solution**

- Derive the answer in symbols → e.g.:
- Fill in the data for a quantitative solution (unit!)

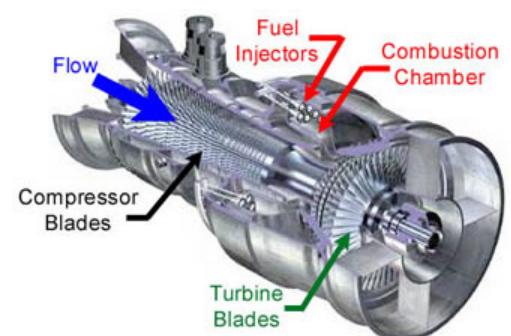
- **Discussion of Results**

- Does the answer make sense?
- What are implications? → this follows from the symbolic solution
- Interpretation and discussion is the most important part for an engineer

$$\begin{aligned}\eta_{th} &= \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_{out} - \dot{W}_{in}}{\dot{Q}_{in}} \\ &= \frac{\dot{m}_3(h_5 - h_6) + \dot{m}_7(h_6 - h_7)}{\dot{m}_3(h_5 - h_4)} \\ &\quad - \frac{\dot{m}_7(h_2 - h_1) + \dot{m}_3(h_4 - h_3)}{\dot{m}_3(h_5 - h_4)}\end{aligned}$$

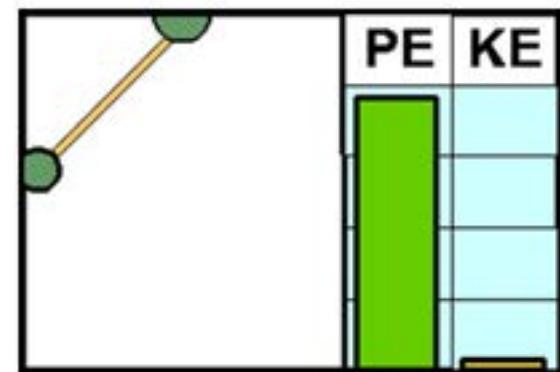
Recapitulate Class 1

- What is thermodynamics? → science on using heat and power, conversion of different forms of energy
- Systems and boundaries
 - Open / closed / isolated systems
- Properties
 - Extensive / intensive / specific
- States and State Postulate
- Equilibrium and quasi-equilibrium
- Processes and cycles
 - Isobaric / isotherm / isochoric / adiabatic
 - Process diagrams
- Metric system and fundamental units
- Temperature and the zeroth law of thermodynamics
- Pressure (absolute and gauge pressure)



Next Class 2: Energy, work, heat, enthalpy, entropy

- Concept of energy and various forms of energy
 - Internal, kinetic and potential energy
- State and path functions
- Mechanisms of energy transfer
 - Heat and heat transfer
 - Work
 - Flow Work (Pv)
- The rate of doing work, heat & mass transfer
- The first law of thermodynamics
- Energy balance
- New properties
 - Enthalpy
 - Entropy
- Efficiencies of energy conversion processes



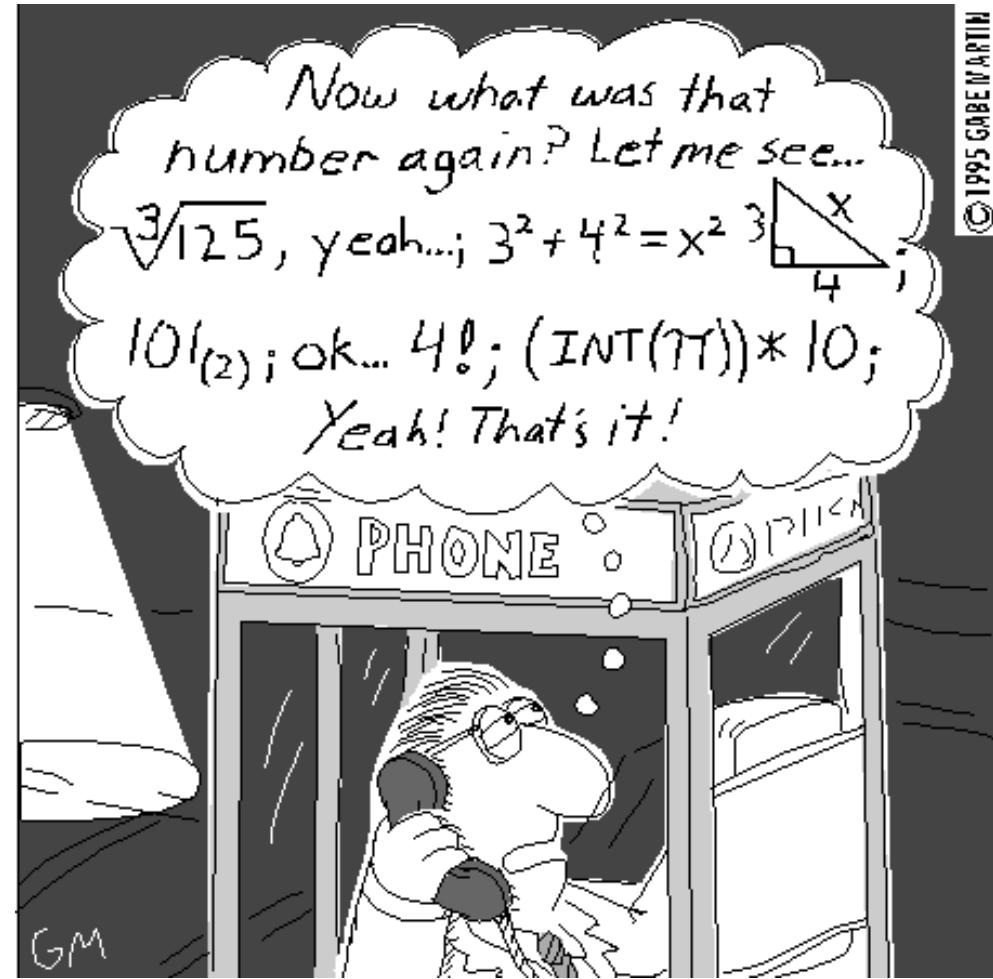
Conservation of mechanical energy, potential energy transforms into kinetic energy and visa versa



But where does the potential energy go in this case? Is the energy not conserved?

Keep in mind: Important Formulas

- Total volume: $V \text{ [m}^3]$
- Specific volume: $v=V/m \text{ [m}^3/\text{kg]}$
- Density: $\rho =1/v=m/V \text{ [kg/m}^3]$
- New formulas will be added every lecture class



Class 2:

Energy, work, heat transfer, enthalpy, entropy, efficiency

Launch of US Air Force early warning satellite - conversion of internal (chemical) energy into kinetic energy

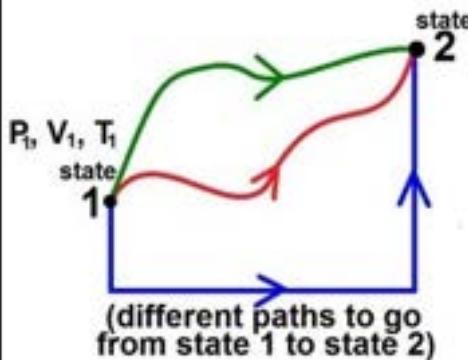
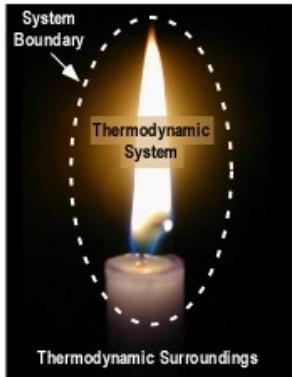
(Courtesy USAF)



Roadmap Engineering Thermodynamics

- Using thermodynamics for practical applications requires knowledge of:

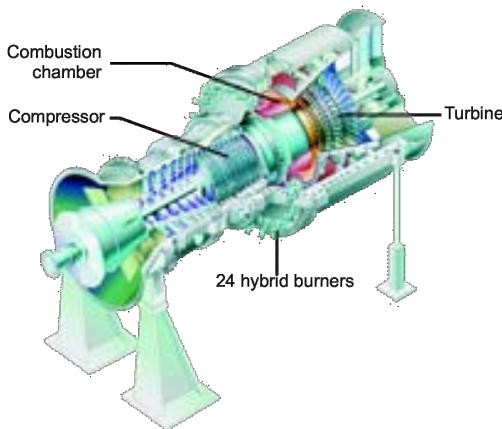
Concepts and definitions (Class 1)



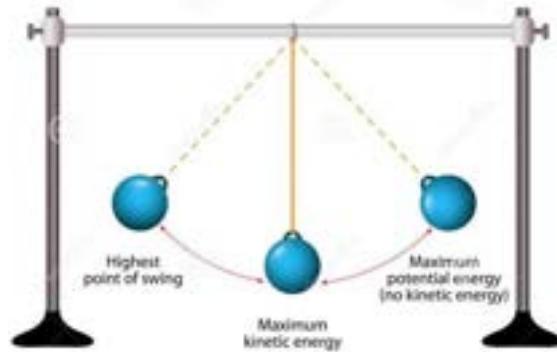
Various forms of energy (Class 2)



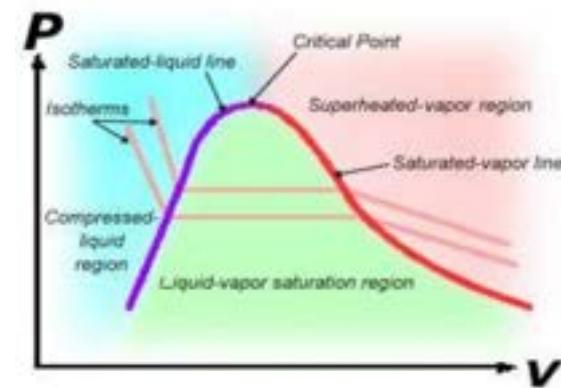
Power cycles
(Class 6 – 11)



Laws of Thermo
(Class 4 and 5)

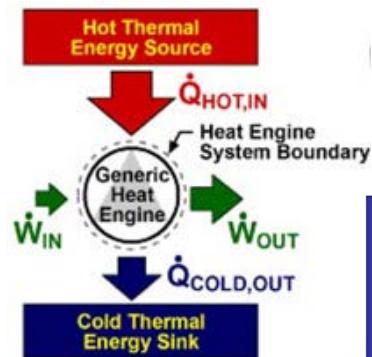


Properties of Substances
(Class 3, 9)

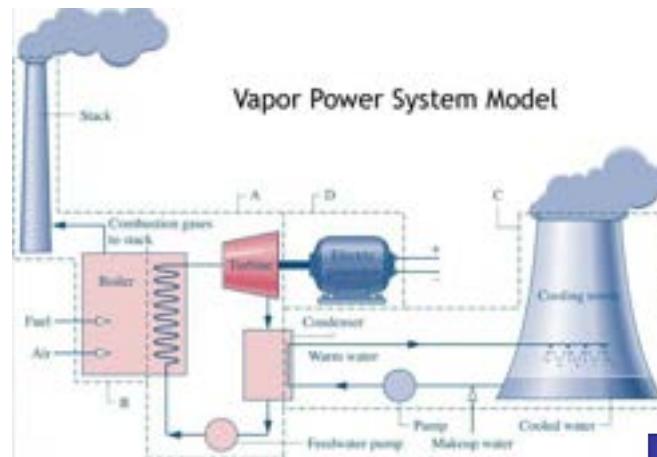


Roadmap Engineering Thermodynamics

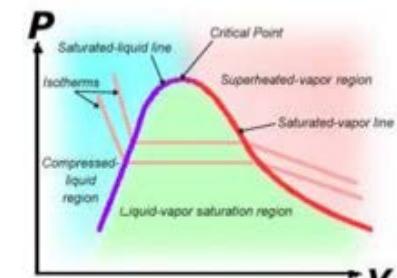
Thermodynamic cycles (Class 6)



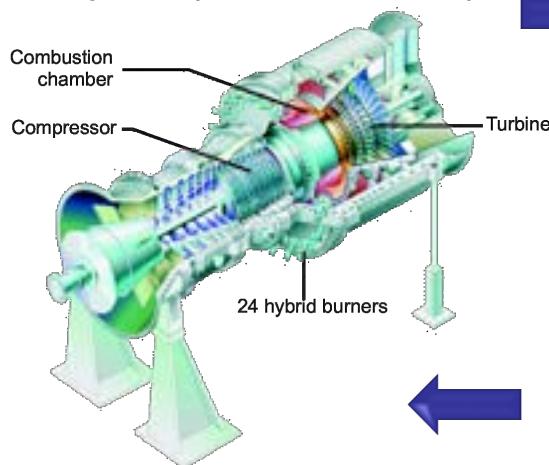
Vapor power cycles –
Rankine cycle (Class 7, 8)



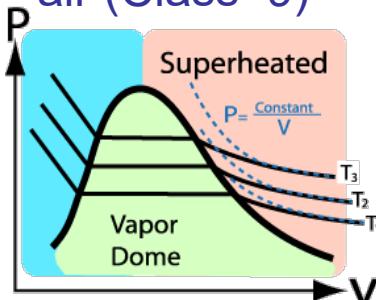
Properties of
water (Class 3)



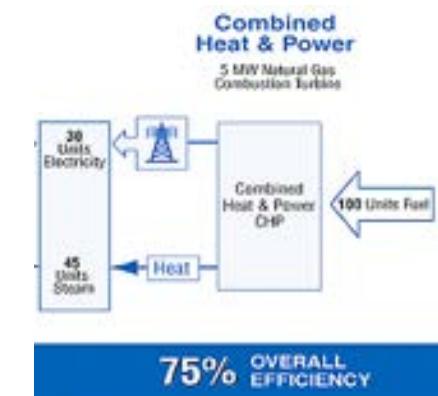
Gas power cycles – Brayton
cycle (Class 10, 11)



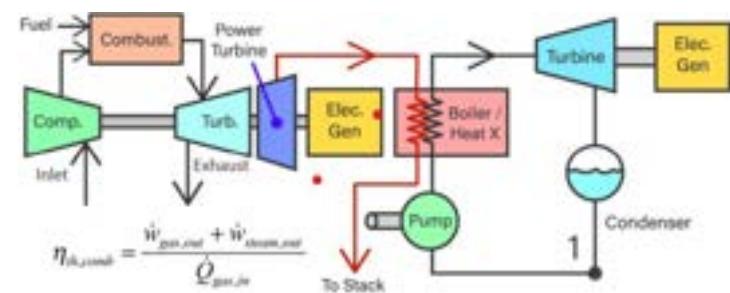
Properties of
air (Class 9)



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

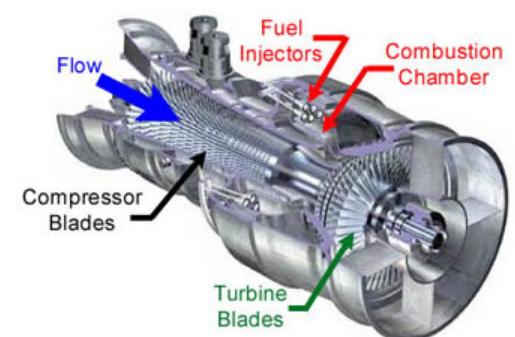


75% OVERALL EFFICIENCY



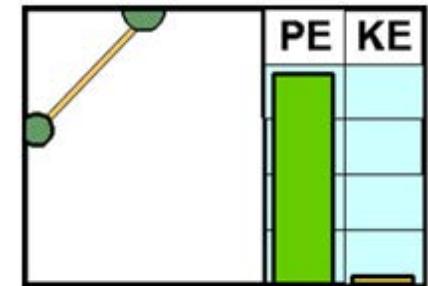
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Content Class 2

- **Energy, work, heat, enthalpy, entropy, efficiency**
- Concept of energy and various forms of energy
 - Internal, kinetic and potential energy
- State and path functions
- Mechanisms of energy transfer
 - Heat and heat transfer
 - Work
 - Flow Work (Pv)
- The rate of doing work, heat & mass transfer
- The first law of thermodynamics
- New properties: Enthalpy & Entropy
- Efficiencies of energy conversion processes
- **Learning goal:** distinguish different kinds of thermodynamic energies and mathematically describe how these can be transformed into each other



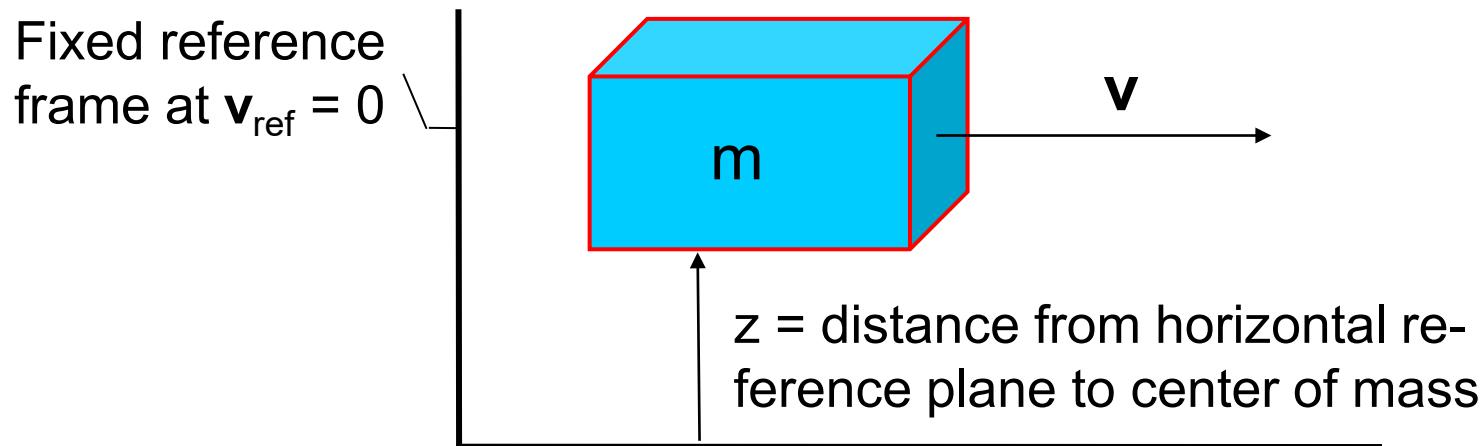
Conservation of mechanical energy: potential energy transforms into kinetic energy and visa versa



But where does the potential energy go in this case? Is the energy not conserved?

Energy within a system boundary: KE & PE

- There are various forms of energy, all have the unit Joule (J)
- Two of them are **kinetic energy (KE) and potential energy (PE)**



- Total kinetic energy of the mass: $KE = \frac{1}{2}mv^2$ [J]
- Total potential energy of the mass: $PE = mgz$ [J]
- The total KE and PE are related to a reference frame in the outside world and therefore macroscopic forms of energy
- They can be calculated if m , v and / or z are known

Energy within a system boundary: KE & PE

- Total kinetic energy (KE): $KE = \frac{1}{2}mv^2$ [J]
- Total potential energy (PE): $PE = mgz$ [J]

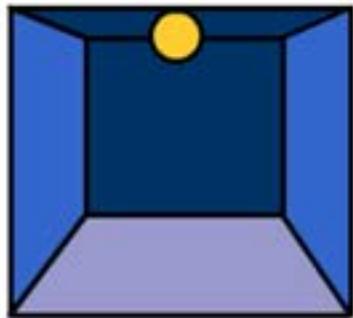
Extensive or Intensive properties?



- The total KE and PE are extensive properties (if you make the system two times larger, i.e. $m \rightarrow 2*m$, the KE and PE gets two times larger)
- They can be made specific (ke and pe), i.e. independent of the mass by division by the mass, m
- Specific kinetic energy (ke): $ke = \frac{KE}{m} = \frac{1}{2}v^2$ [J/kg]
- Specific potential energy (pe): $pe = \frac{PE}{m} = gz$ [J/kg]

Energy within a system boundary: U

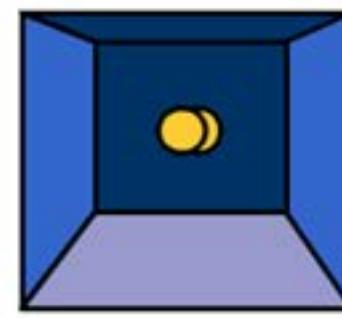
- An other form of energy is the **internal energy (U)**



Translational



Rotational



Vibrational



Chemical, Nuclear
& Electrical

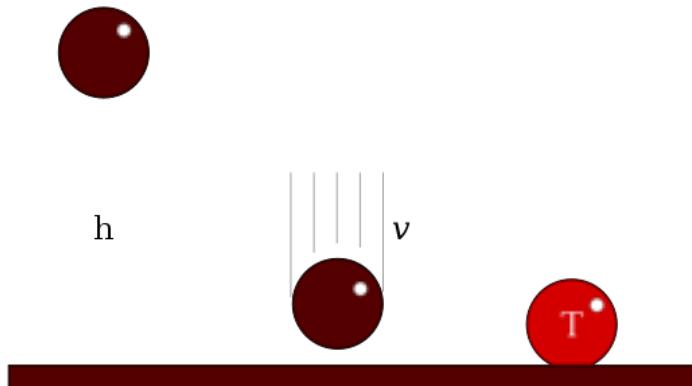
- Internal energy (U):** energy related to matter, including bounding energy and energy related to the movement of the molecules of which the matter exists
- The internal energy is strongly dependent on the temperature
- The internal energy is not related to the outside world and therefore a microscopic form of energy

Energy within a system boundary: U

- The total internal energy (U) of a system is an extensive property, like the total kinetic (KE) and potential energy (PE)
- Total internal energy: U in Joules or kilo Joule [J or kJ]
- Specific internal energy: $u = U/m$ in Joule per kg [J/kg or kJ/kg]
- The internal energy can not be measured directly
- It can be determined but always a reference state should be chosen at which the internal energy is zero (compare this to the potential energy that is zero at $z = 0$)
- The internal energy can often be looked up in tables (class 3)
- In thermodynamics only changes in internal energy are important as we are mainly interested in the effect of the process between two or more different states

Energy within a system boundary: KE, PE & U

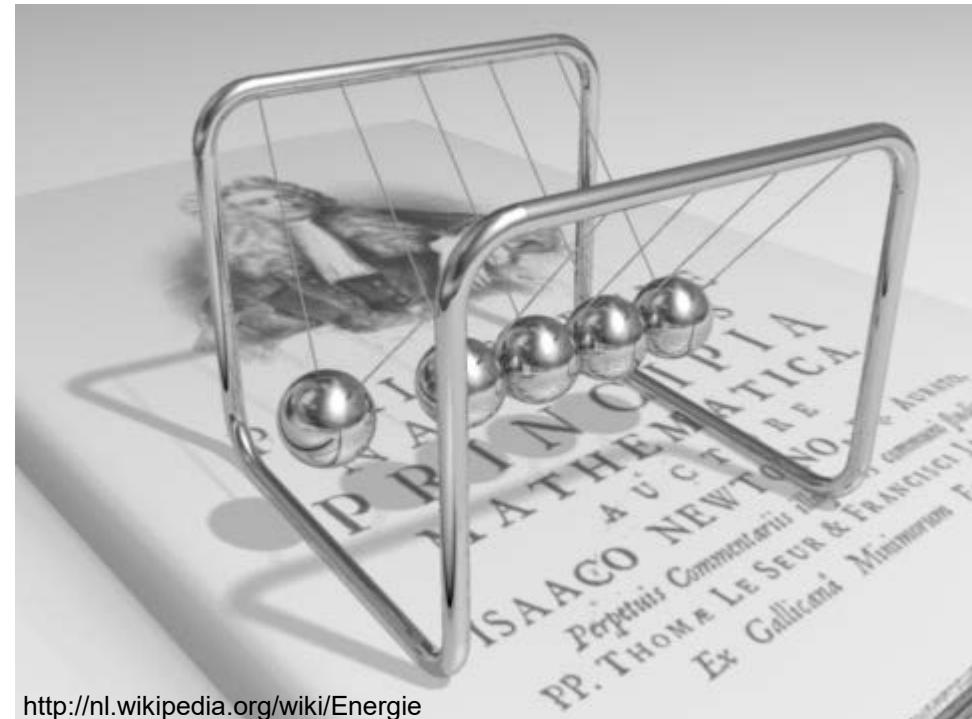
- The various forms of energy (kinetic energy, potential energy, internal energy) can be converted into each other



Three types of energy: potential, kinetic and internal

$$U = KE = PE$$

$$U = \frac{1}{2} m C v^2 = mgh \quad [J]$$



<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

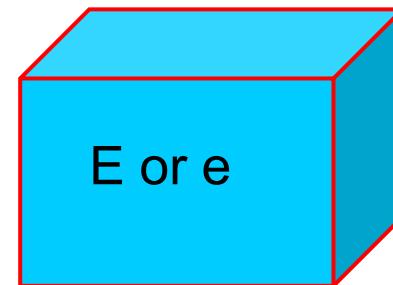
Energy within a system boundary: KE, PE & U

- The **total energy** of a system is the sum of all different forms of energy within the system:

$$E = U + KE + PE \quad [\text{in Joule, J or kJ}]$$

- The **specific energy** of a system is:

$$e = u + ke + pe \quad [\text{in J/kg or kJ/kg}]$$



- The difference between the two is the mass
- The total energy is dependent on the mass while the specific energy is independent of the mass
- Note the total energy is denoted by capitals and the specific energy by small caps (and take care of the difference in units)

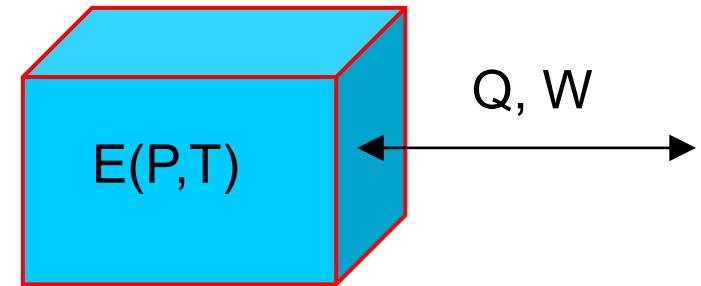
Change of energy of a system

- The energy of a system can change by **transferring energy** across the system boundary
- There are different ways to do this

1. Adding or subtracting work (W)

Different types of work exist

- Compression (PdV)
- Mechanical e.g. shaft
- Electricity

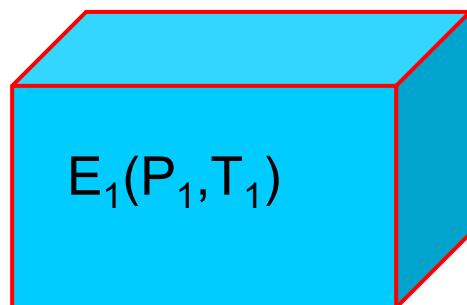


2. Adding or subtracting heat called, heat transfer (Q)

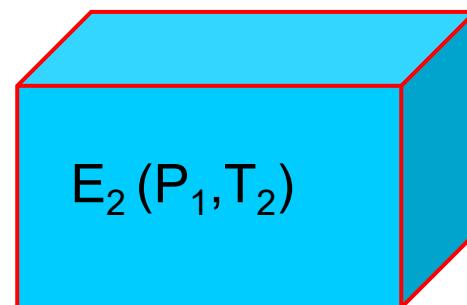
- Work and heat transfer can be total work (W) or heat transfer (Q) with the unit Joule (J)
- They can also be specific (w and q) if they are independent of the mass with the unit Joule per kilogram (J/kg)

State and path functions

- There is a fundamental difference between the energies in the form of potential, kinetic and internal energy which are related to a specific state and work and heat transfer that cross the system boundary
- Potential, kinetic and internal energy (which form the total energy E of a system) are **state functions**, this means that these energies only depend on the state the system is in (e.g. internal energy depends on the temperature of the state and potential energy on the height of the state)
- Between two states of the system an energy difference ΔE can exists (e.g. if the temperature is different), but if the system returns to its original state the energy has not changed

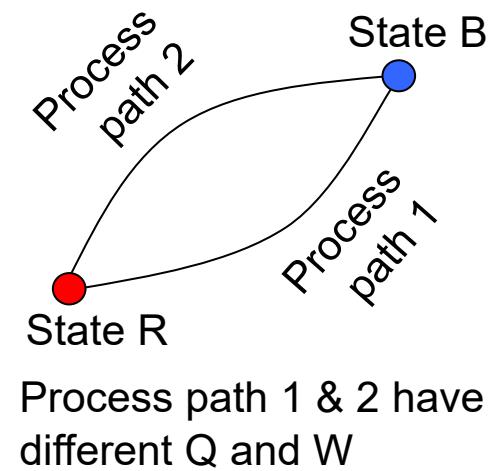
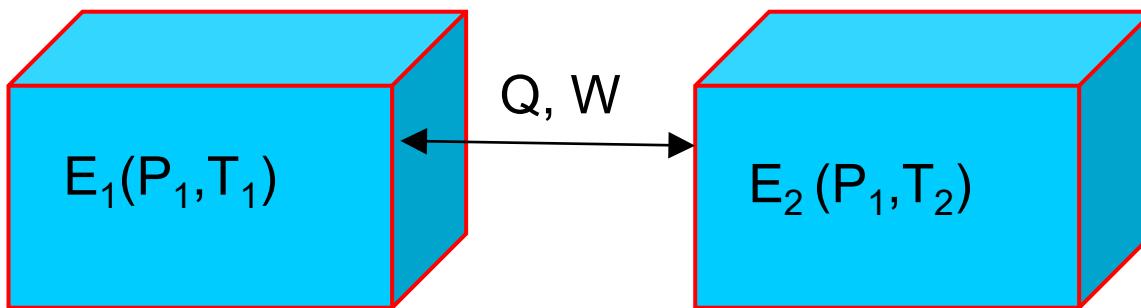


$$\Delta E = E_1 - E_2$$



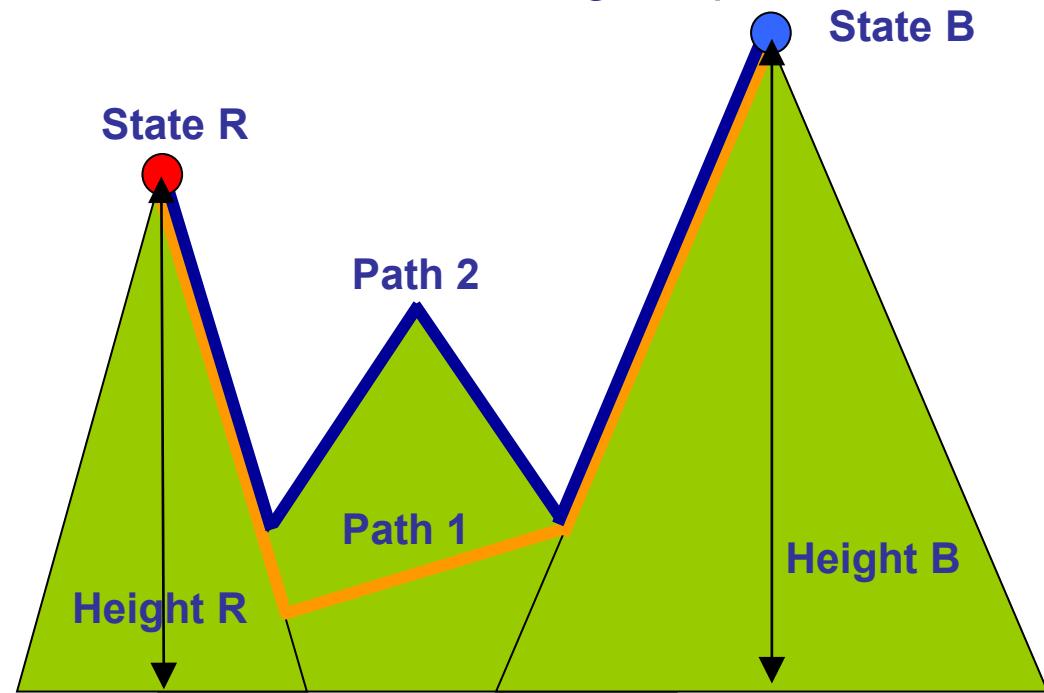
State and path functions

- On the other hand the energies that cross the system boundary, work and heat transfer are **path functions**, this means that the work or heat added or subtracted from a system depends on the path (the process) the system has followed
- Between two different paths/processes a difference in work/heat can exist
- If a system returns to its original state work and/or heat added to or subtracted from the system are not zero
- To go from one to another state a certain amount of work or heat is needed, this is not a difference in work or heat, therefore ΔW and ΔQ do not have a meaning for a single path
- Note: a state does not have work or heat transfer



Path and state functions and hiking

- Energy → height & potential energy (State functions)
- Work and heat → way & distance (Path functions)
- The potential energies of state R and B depend on the height (property) only and are always the same, also the difference is constant
- By travelling from state R to state B and back the potential energy will change during the travel but at the end there is no change in potential energy
- Traveling from R to B can go via different paths, the distance travelled is different, the work performed is different
- Returning to the original state does not mean the distance travelled (the work) is zero however the potential energy is not changed

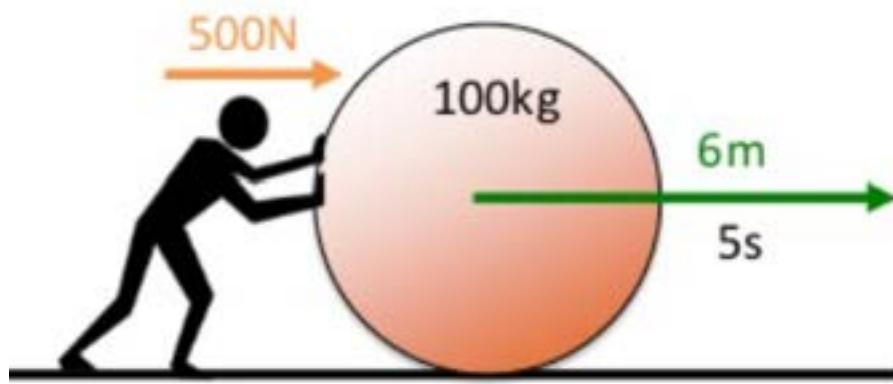


Energy transfer across a boundary: Work

- Energy transfer by work is the application of a force over a distance
- When we push an object and it moves, we do work
- The force is the weight of the object (F) in Newton [N] and the distance is the distance (s) in meter [m] the object moves

$$\delta W = FdS \rightarrow W_{a-b} = \int_a^b FdS = F \Delta S \text{ [J]}$$

- Units: Work, W in [N.m = J]
Specific work, $w = W/m$ in [J/kg]



Total work

$$W = F\Delta S = 500 * 6 \\ = 3000 \text{ Nm} = 3000 \text{ J} = 3 \text{ kJ}$$

Specific work

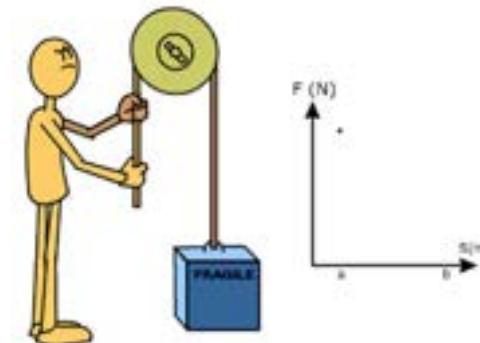
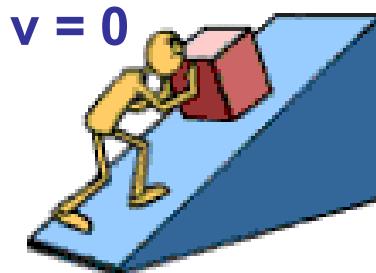
$$w = \frac{W}{m} = \frac{3000}{100} = 30 \text{ J/kg}$$

Power

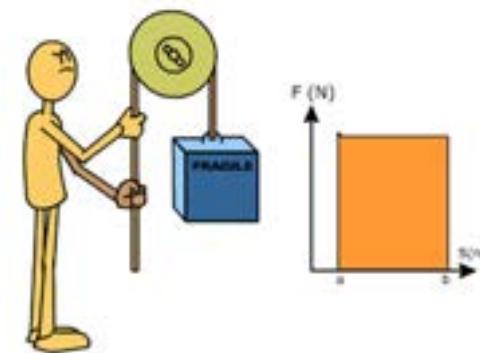
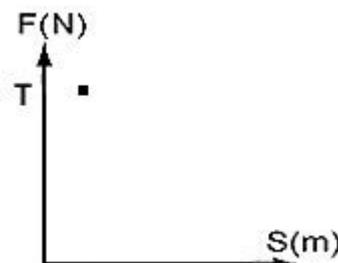
$$\dot{W} = \frac{W}{t} = \frac{3000}{5} = 600 \text{ J/s}$$

Energy transfer across a boundary: Work

- Energy transfer by work:



- Does this man perform work?
 - No work since $dS = 0$
 - No area in FS - diagram

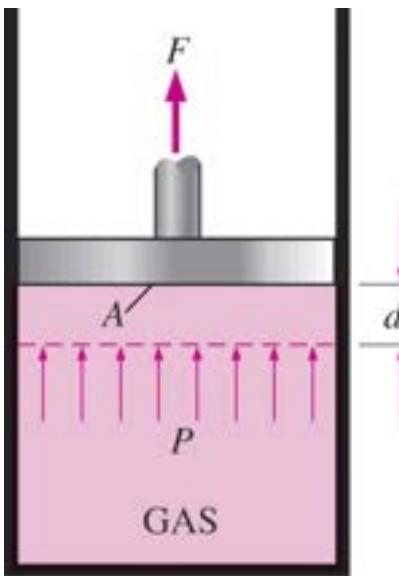


- Does this man perform work?
 - Yes, depends on mass and distance
 - Work = area under FS - diagram

Boundary work (PdV)

- In thermodynamic systems work is often done by piston cylinder device
- The pressure inside the system is related to the force and volume change is related to the distance, and $F \, dS$ can be rewritten to

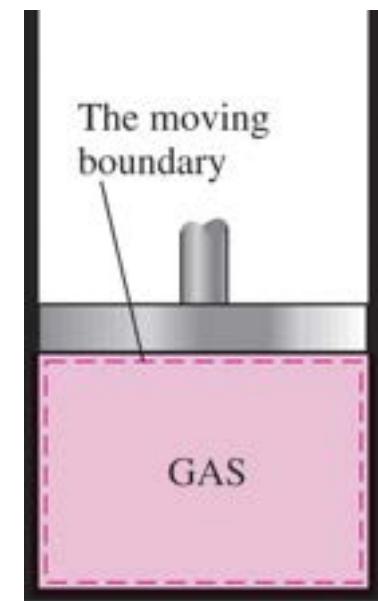
$$W_{a-b} = \int_{S_a}^{S_b} \mathbf{F} \cdot d\mathbf{S} = \int_{S_a}^{S_b} (PA) dS = \int_{S_a}^{S_b} P d(AS) = \int_{V_a}^{V_b} P dV \rightarrow [J]$$



A gas does a differential amount of work δW_b as it forces the piston to move by a differential amount ds .

$$P = \frac{F}{A} \rightarrow F = PA$$

The work associated with a moving boundary is called *boundary work*.



Boundary work (PdV)

- Boundary work is the work needed to change the volume of a compressible substance (e.g. in a piston – cylinder device)

$$W_{a-b} = \int_{S_a}^{S_b} \mathbf{F} \cdot d\mathbf{S} = \int_{S_a}^{S_b} (PA)dS = \int_{S_a}^{S_b} Pd(AS) = \int_{V_a}^{V_b} PdV \rightarrow [J]$$

- Therefore boundary work in thermodynamics is defined as:

Total boundary work: $\delta W = P dV$ [J]

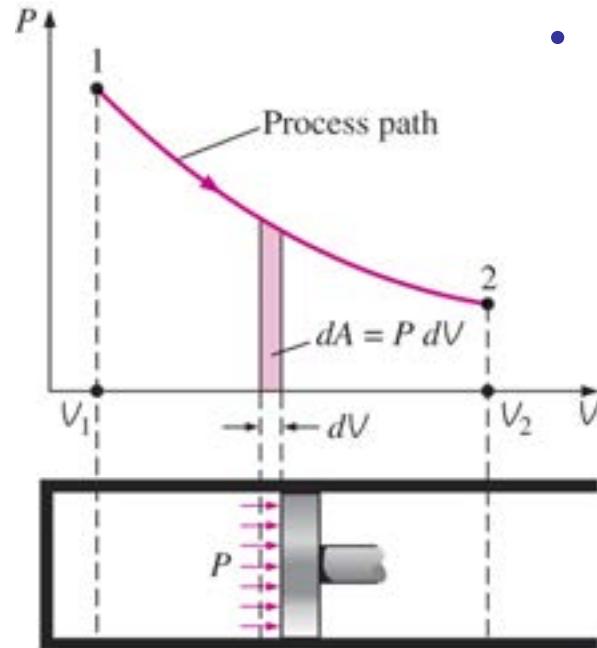
Specific boundary work: $\delta w = P dv$ [J/kg]

- W_{in} : Work added to the system from surroundings
 - Compression $\rightarrow dV$ negative $\rightarrow W_{in} = \text{negative}$
- W_{out} : Work taken from the system to surroundings
 - Expansion $\rightarrow dV$ positive $\rightarrow W_{out} = \text{positive}$

The symbol δ (Greek delta) denotes a small, differential change for a path function, like work or heat transfer it is like the 'd' you now as a small, differential change of a property. Integrating: $\int \delta W = W$ and $\int dV = \Delta V$

Boundary work (PdV)

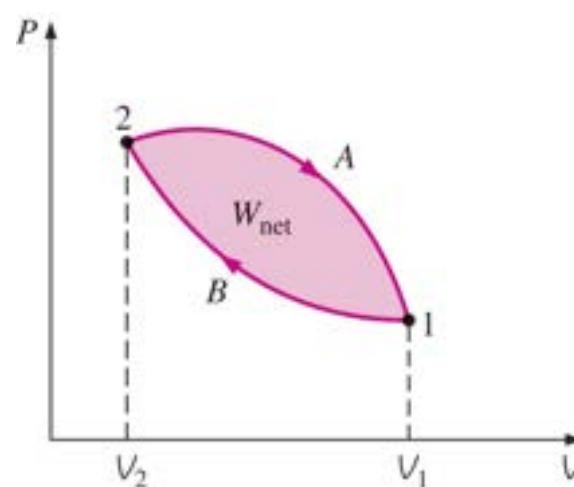
- The work done is represented by the area under the Pv – diagram



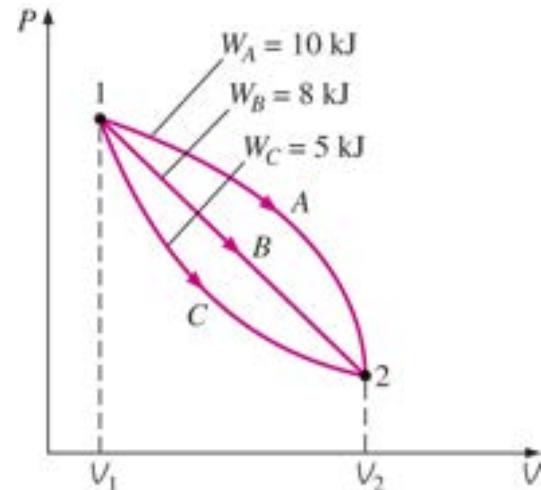
The area under the process curve on a PV - diagram represents the boundary work.

$$\text{Area} = A = \int_1^2 dA = \int_1^2 P dV$$

- The work is different for different paths / processes (work is a path function) and therefore in the end work is done by the system or on the system



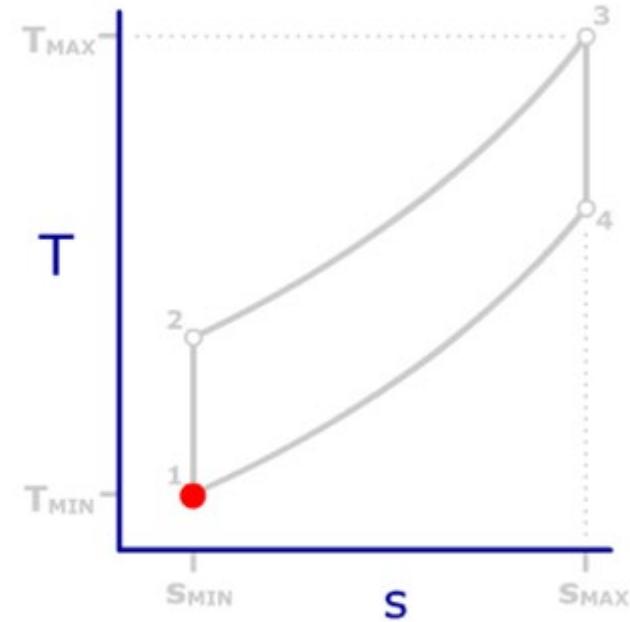
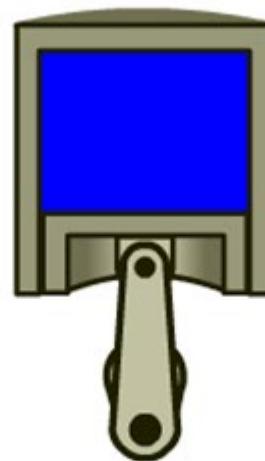
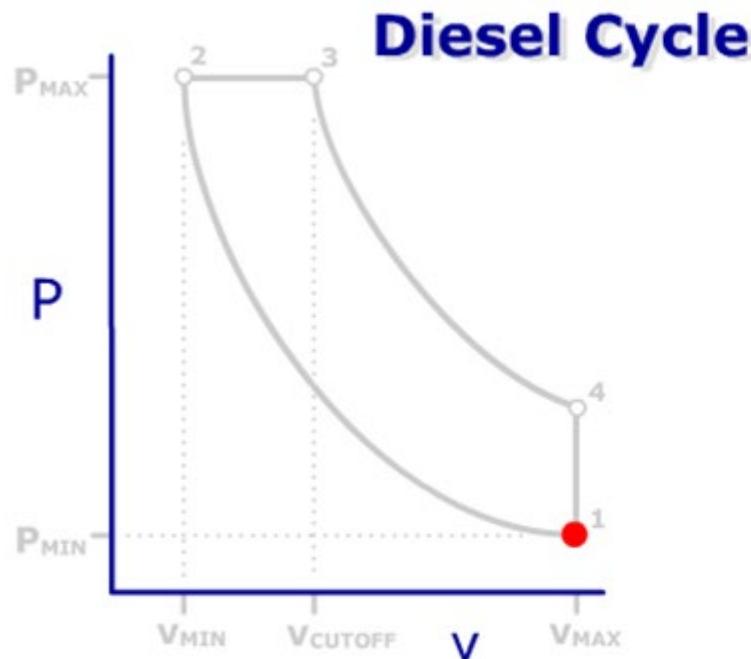
The net work done during a cycle is the difference between the work done by the system and the work done on the system.



The boundary work done during a process depends on the path followed as well as the end states, see example at the end.

Boundary (PdV) work in Diesel engine

- Example of energy transfer by boundary work

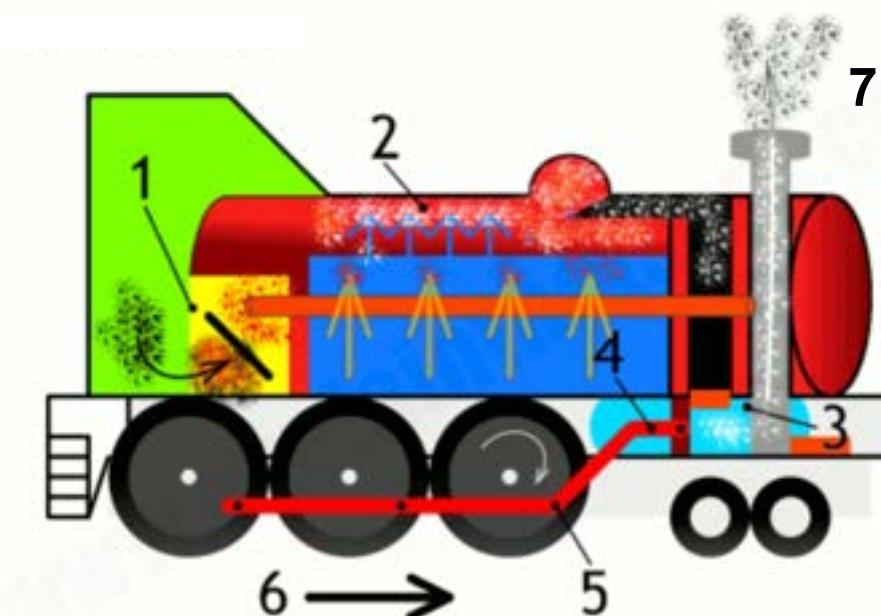


- Step 1 → 2: Boundary work added to the engine
- Step 2 → 3 and step 3 → 4: Boundary work extracted from the engine
- Net work is the area enclosed in the PV diagram by the curve: 1-2-3-4-1

ThermoNet: Wiley

Boundary (PdV) work in a locomotive

- Example of energy transfer by boundary work
- The moving piston delivers to and extracts (boundary) work from the system



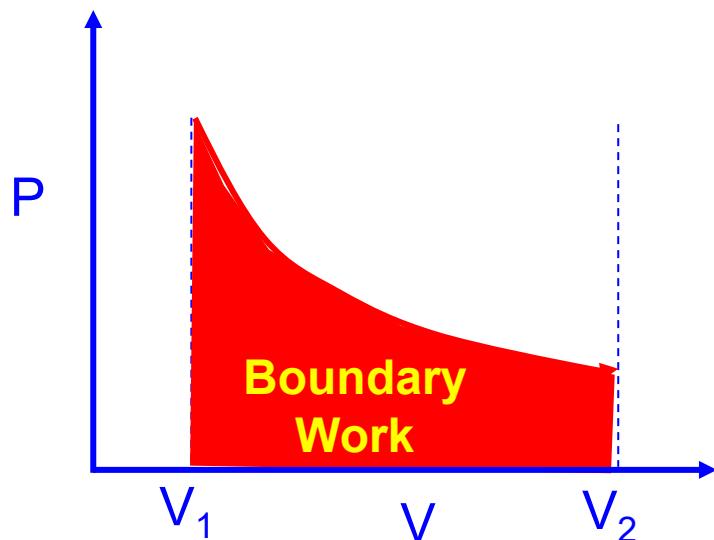
<https://100cia.site/index.php/fisica/item/9638-que-es-exactamente-un-motor-que-tienen-de-malo-los-motores-de-vapor>

Steam engines, like the one in this locomotive, are examples of external combustion engines. The fire that provides the energy by combustion (1) is outside (external) of the cylinder, where the thermal energy is converted into mechanical energy (3). Between the two there is a boiler (2) that converts thermal energy into steam. The steam acts as a heat transfer fluid, pushing a piston (4) that moves the wheels with a crank (5) and propels the train (6). Steam and heat energy is constantly expelled from the chimney (7), which makes this a particularly inefficient and inconvenient way to power a moving machine. But it was fine in the days when coal was plentiful and nobody cared much about damaging the planet.

Example P-V (Indicator) diagram

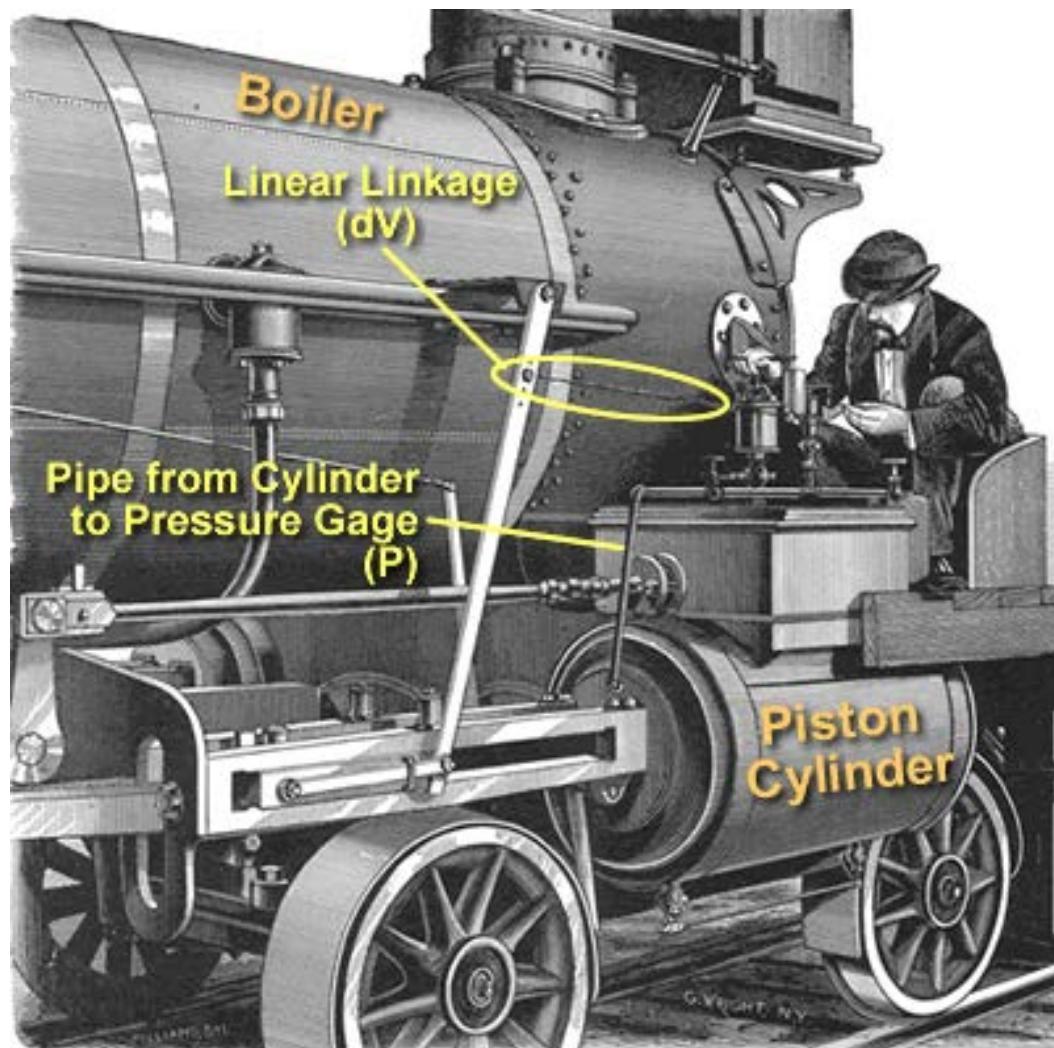
- Old steam engine

Area under P-V diagram
= boundary work added
to the locomotive



- $\delta W = P dV$

$$W_{OUT,1-2} = \int_{V_1}^{V_2} P dV$$



An engineer producing an indicator (P-V) diagram to test a steam engine.

ThermoNet:Wiley

Different types of work

- Three different types of work can be distinguished:
 1. Boundary work (also called volume work) $\rightarrow \delta w = Pdv$
 2. Mechanical work (e.g. shaft work, spring work)
 3. Electrical work
- To identify the presence of shaft work: draw a system boundary around system, if any rotating shafts crosses the system boundary, shaft work is present.
- Shaft work common for:
 - Pumps
 - Compressors
 - Blowers
 - Engines



ThermoNet: John Wiley

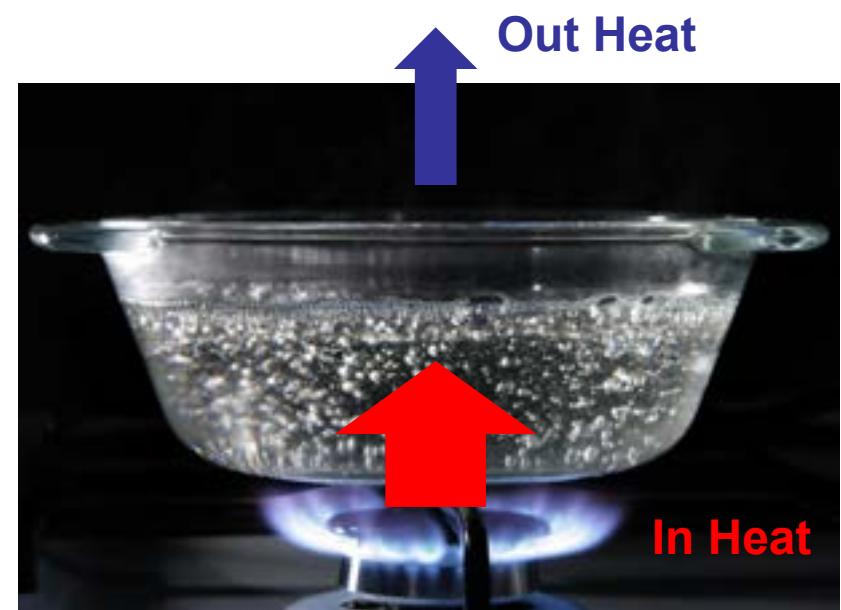
Energy transfer across boundary: Heat Transfer

- Besides by work the energy of a system can change by **transfer of heat** across the boundaries
- **Heat Transfer** is the energy crossing the system boundary because of a temperature difference between the system and the surroundings
- Spontaneously the energy always goes from high to low temperature
- Heat transfer can carry energy into, Q_{in} , or out of, Q_{out} , the system, depending on whether the system has a lower or higher temperature than the surroundings

$$Q_{heat-transfer} = Q_{in} - Q_{out}$$

- Units

- Heat transfer: Q in [J or kJ]
 - Specific heat transfer: [J/kg or kJ/kg]



Modes of Heat Transfer

- Heat transfer can occur by 1: Conduction
2: Convection
3: Radiation
- Note that a detailed study of heat transfer is fairly complex and beyond the scope of thermodynamics classes → next year module 7
- In thermodynamics, we will be concerned with how heat transfer relates to work and energy, and not on the fundamental mechanisms that control heat transfer

Conduction



Courtesy US DOE

A well isolated house losses less heat through conduction through the walls and the glass

Elephants rely on their ears to cool their blood. Heat transfer from their ears to the air occurs by convection. The large size of the ears (large A) serves to increase the heat transfer rate. As the weather gets hotter, the temperature difference between the elephant's ears and the ambient air decreases (smaller T). The elephants compensate by flapping their ears, which increases the velocity of the air passing by their ears (larger h).



CA

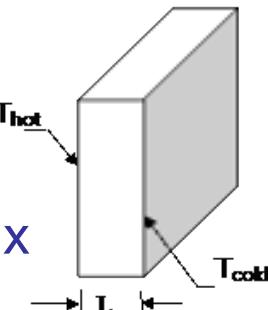
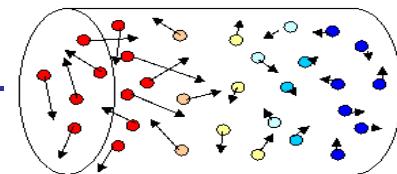
Radiation



Infrared dryer for automotive paint

Heat transfer: Conduction

- **Conduction heat transfer** is heat transfer associated with a random molecular motion and occurs in gases, liquids, and solid
- Joseph **Fourier** first published the phenomenological relationship that governs heat transfer by conduction in 1822
- Fourier found that the rate of heat transfer is proportional to the temperature difference across the material of interest, and is inversely proportional to the thickness of the material
- The constant of proportionality between the heat transfer rate per unit area and the temperature gradient is called the thermal conductivity, k [W/mK]
- In a differential sense, the heat transfer rate divided by the area can be written as:
$$\frac{\dot{Q}}{A} = -k \frac{dT}{dx} \approx -k \frac{\Delta T}{L}$$
- The heat transfer rate per unit area, Q/A , is called the heat flux
- The thermal conductivity is a property of the material and can vary with the local temperature of the material
- In general, for the three phases of matter, gasses have the smallest values of thermal conductivity and solids the largest



(Extra information,
not part of the exam)

Heat transfer: Convection

- Heat transfer from a surface to a moving fluid occurs by **convection**
- The rate at which energy is transferred between a solid object and a flowing fluid is proportional to the temperature difference between the surface and the fluid
- The law governing this transfer process is called **Newton's Law of Cooling**
- The constant of proportionality between the heat flux and the temperature difference is the heat transfer coefficient, h [W/m²K], which is a function of the fluid properties and the flow
- The rate of convection from a surface at temperature, T_s to a fluid at temperature, T_f is governed by the equation $\dot{Q} = hA(T_s - T_f)$
- Liquids tend to have higher heat transfer coefficients than gases and heat transfer coefficients tend to increase with the velocity of the fluid. Elephants rely on their ears, to cool their blood heat transfer from their ears to the air occurs by convection.

(Extra information, not part of the exam)

Heat transfer: Radiation

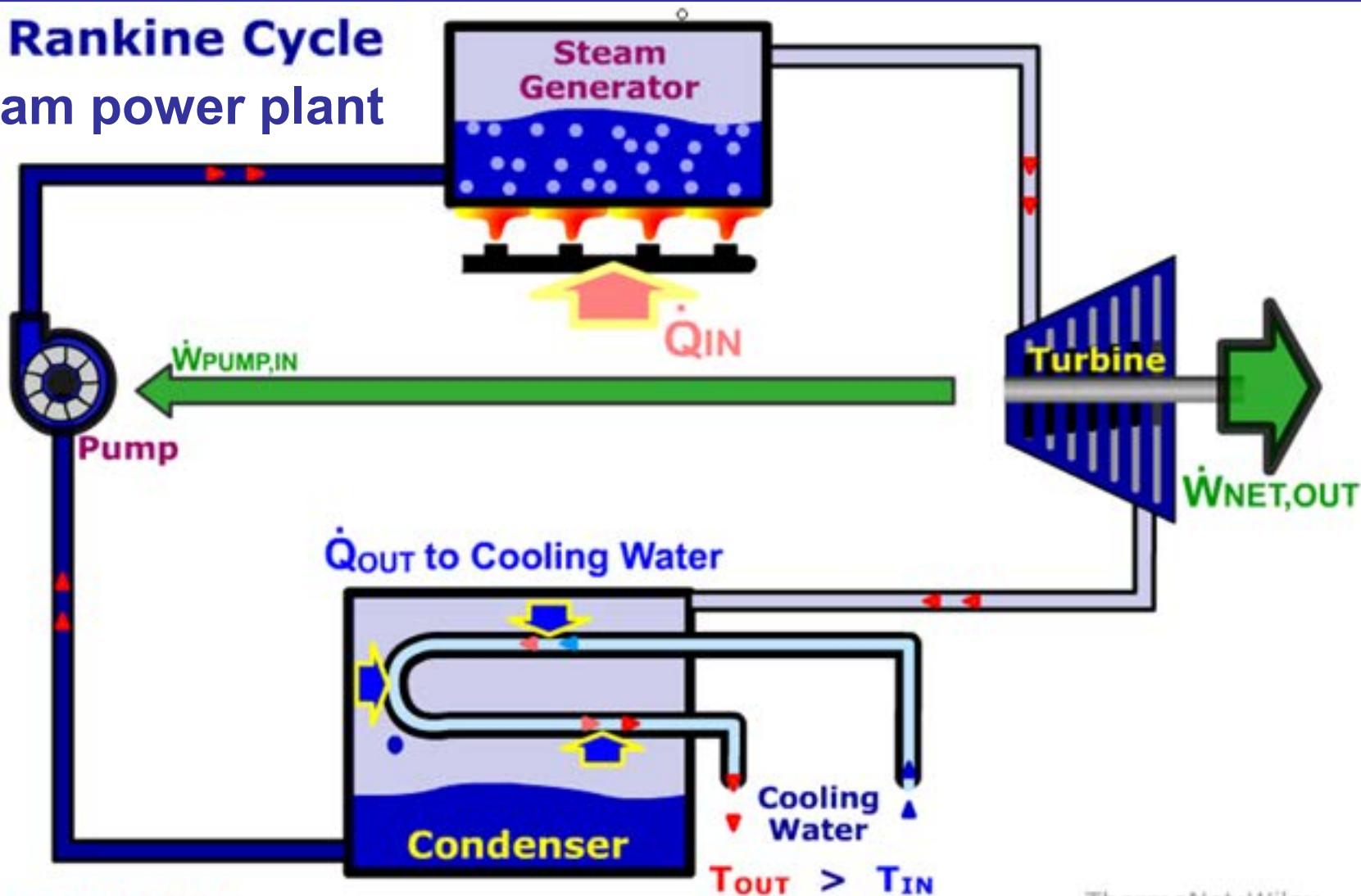
- Heat transfer by electromagnetic waves is called **thermal radiation**
- All substances with a temperature greater than absolute zero emit radiation
- The following equation can be used in many cases as a first approximation to estimate the amount of heat transfer due to radiation

$$\dot{Q} = \epsilon \sigma A (T_1^4 - T_s^4)$$

- Here ϵ is the emissivity of the surface, σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$), A is the surface area of the body, T_1 is the surface temperature of the body, and T_s is the temperature of the surroundings
- Heat transfer due to radiation is often negligible until temperatures much greater than room temperature are reached
- Radiation is the only of the three modes of heat transfer that can occur in a vacuum (i.e., in the absence of matter, such as in space)
- Examples of heat transfer by radiation include all of the energy that reaches the earth from the sun and the majority of the energy that is emitted by a heat lamp
- The emissive power of a blackbody is spread across a spectrum of λ 's
(Extra information, not part of the exam)

Heat transfer and work in a steam power plant

Rankine Cycle Steam power plant



ThermoNet:Wiley

- Example: See the shaft work and heat transfer in the steam power plant

BREAK



<https://www.cafepress.com/+thermodynamics+mugs>

Power: The Rate of Doing Work / Heat Transfer

- Speed determines how quickly we can travel a certain distance → m/s
- Power determines how quickly we can do a certain amount of work or heat transfer → J/s
- **Power = Rate of doing work or heat transfer**

$$\dot{W} = \lim_{\Delta t \rightarrow 0} \frac{W}{\Delta t} = \frac{\delta W}{dt} \rightarrow [\text{in Watt}, W = \frac{J}{s}]$$

- Power is denoted by a dot on the variable, \dot{W} or \dot{Q}
- Lightning has a lot of power; however, it occurs so rapidly (small Δt) that, relative to its power, it cannot do a lot of work:

$$W = \int_{t_1}^{t_2} \dot{W} dt \quad [J] = [Ws]$$

- Also the rate of heat transfer:

$$Q = \int_{t_1}^{t_2} \dot{Q} dt \quad [J] = [Ws]$$



Photo Courtesy US NOAA

Energy Transfer: Work and Heat

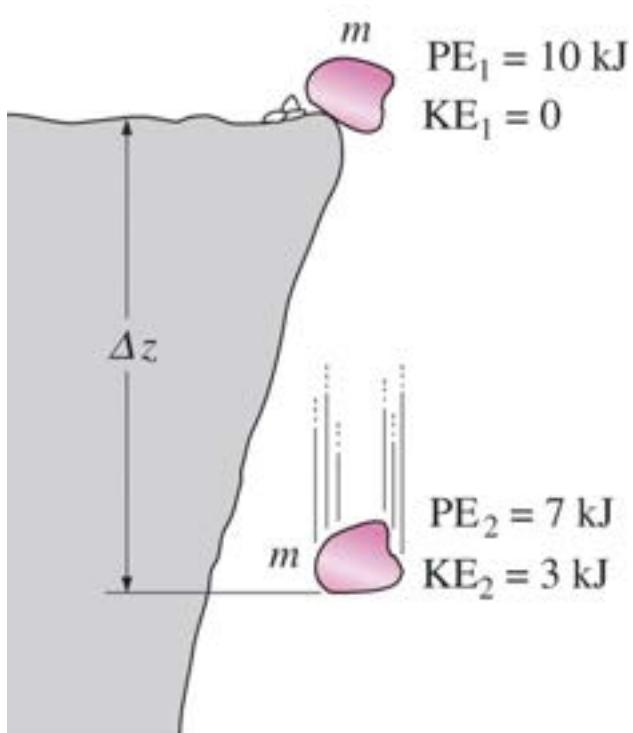
Symbol	Definition	Units
W	Work	kJ
w	Specific work = work per unit mass, $w = W/m$	kJ/kg
\dot{W}	Power = rate of work*	kW (= kJ/s)
Q	Heat transfer	kJ
q	Specific heat transfer = heat transfer per unit mass, $q = Q/m$	kJ/kg
\dot{Q}	Rate of heat transfer*	kW (= kJ/s)

* Note: rates are denoted by a dot on top of the variable

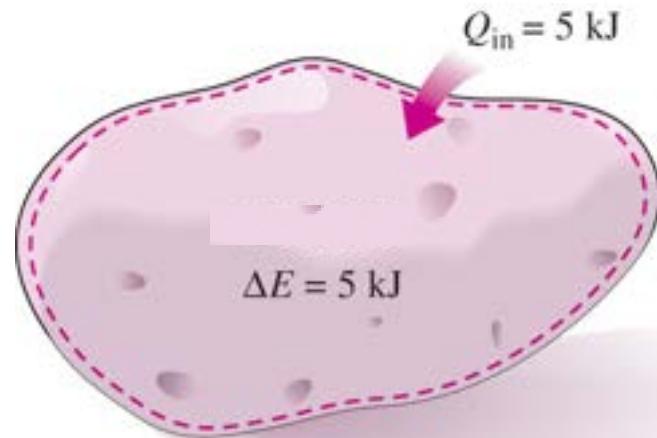
* However, sometimes these dots are hard to see

First law of thermodynamics

- First law of thermodynamics: the total energy is conserved
- Energy can not be destroyed but it can be transformed to a different form of energy (with a different quality)



Energy cannot be created or destroyed; it can only change forms.

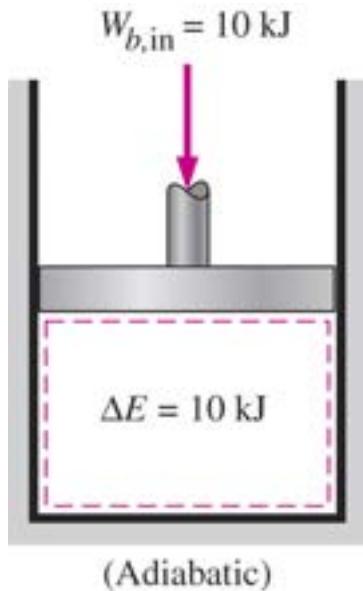


The increase in the energy of a piece of steel in an oven is equal to the amount of heat transferred to it.

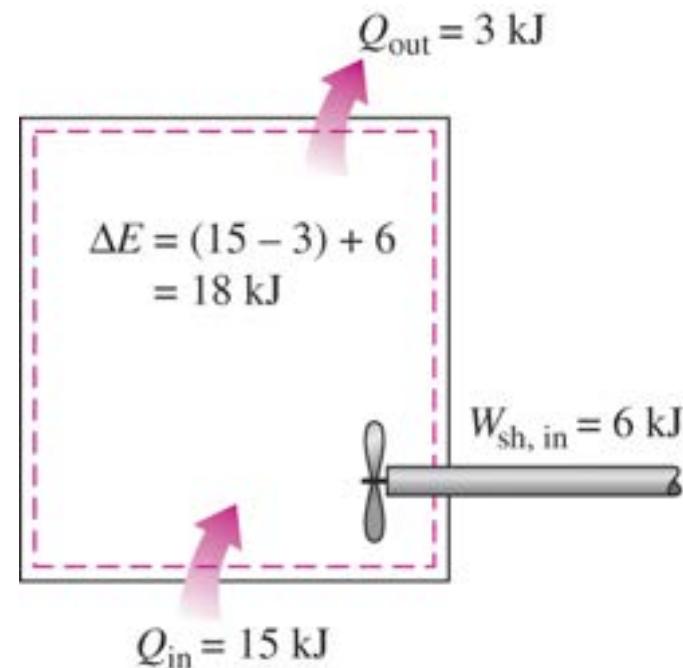
Energy balance

- The net change (increase or decrease) in the total energy of the system during a process is equal to the difference between the total energy entering and the total energy leaving the system during that process:

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



The work (boundary) done on an adiabatic system is equal to the increase in the energy of the system.



The energy change of a system during a process is equal to the *net* work and heat transfer between the system and its surroundings.

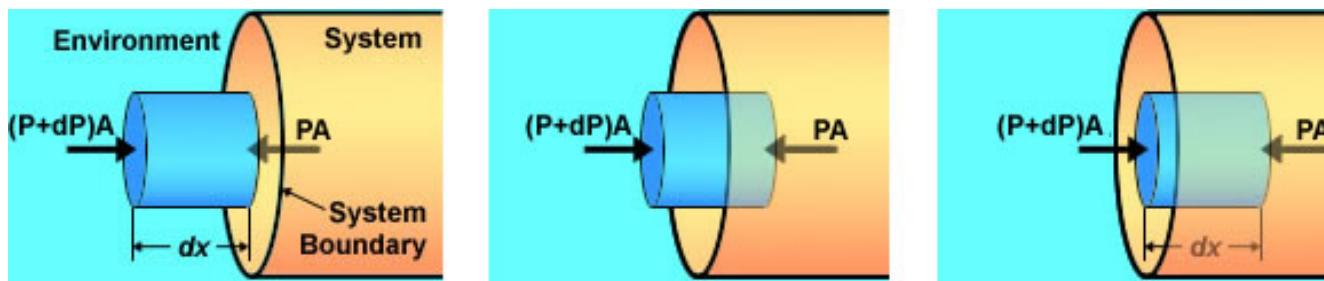
Enthalpy – a combination property

- In the analysis of thermodynamic processes, particularly in open flow processes like, power generation we frequently encounter the combination of properties, $u + Pv$
- This combination is defined as a new property, for the sake of simplicity and convenience
- It is called **enthalpy** and defined as: $h = u + Pv$
 - u = internal energy
 - Pv = flow work (see next slide)
- It was Professor Richard Mollier who recognized the importance of the combination $u + Pv$ in the analysis of steam turbines and in the representation of properties of steam in tables and diagrams
- The famous Mollier diagram, a diagram with h on the y – axis and s on the x – axis is named after him

Energy Transfer by Mass Transport & Enthalpy

- **Flow Work (Pv)**, work required to push mass across the system boundary into the open system

$$\delta W_{\text{flow}} = FdX = PAdX = Pd(AX) = PdV = Pd(v_m) = Pvdm \quad [\text{J or kJ}]$$



- Energy (due to mass) inside system boundary

$$dE_{\text{IN,MASS}} = (u + ke + pe) dm$$

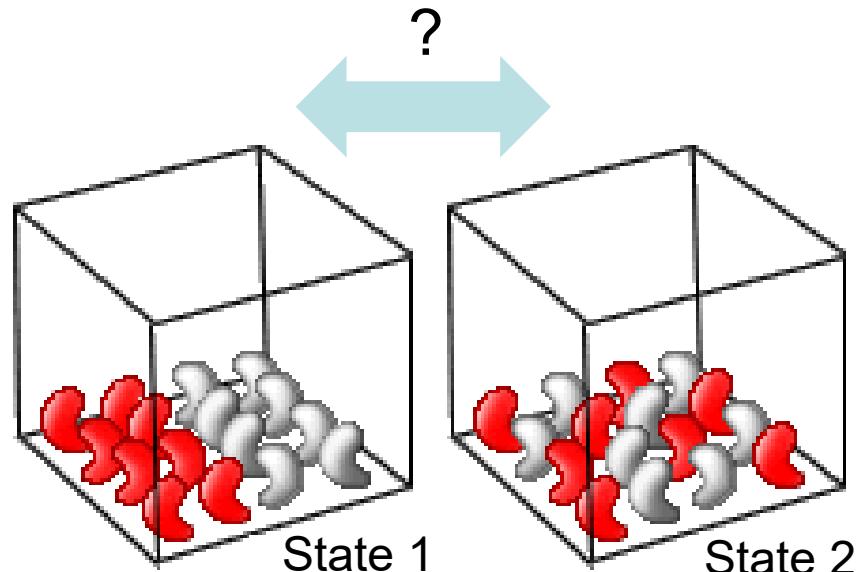
- Energy crossing system boundary with mass transfer (energy inherent to mass + flow work)

$$dE_{\text{IN,TOTAL}} = (u + Pv + ke + pe) dm = (h + ke + pe) dm$$

- **Enthalpy** by definition: $h = u + Pv$ (Units: like energy [J/kg])

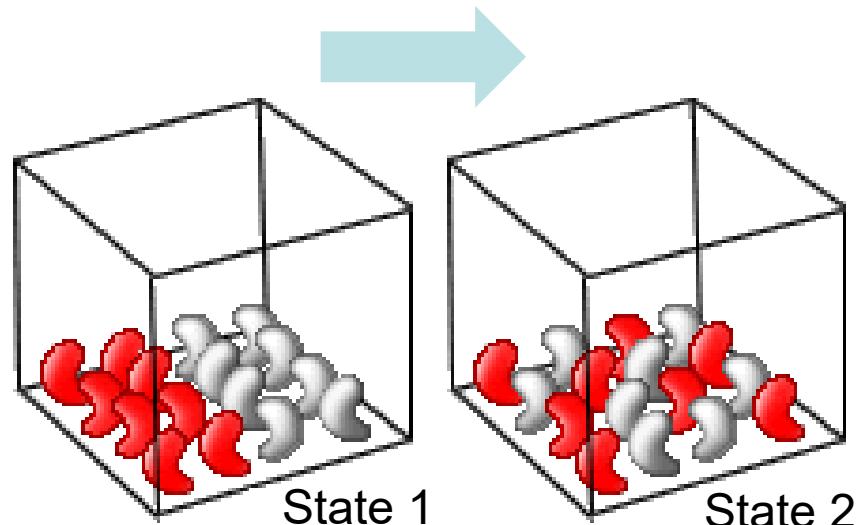
Direction of processes

- What happens spontaneously?
- Which direction will the process go?



Direction of processes

- What happens spontaneously?
- Which direction will the process go?



- Ice cubes will melt, coffee will cool down and state 1 goes to 2
- You know what happens based on your observations in this world
- The reversed process will not take place unless we put effort in it

Direction of processes

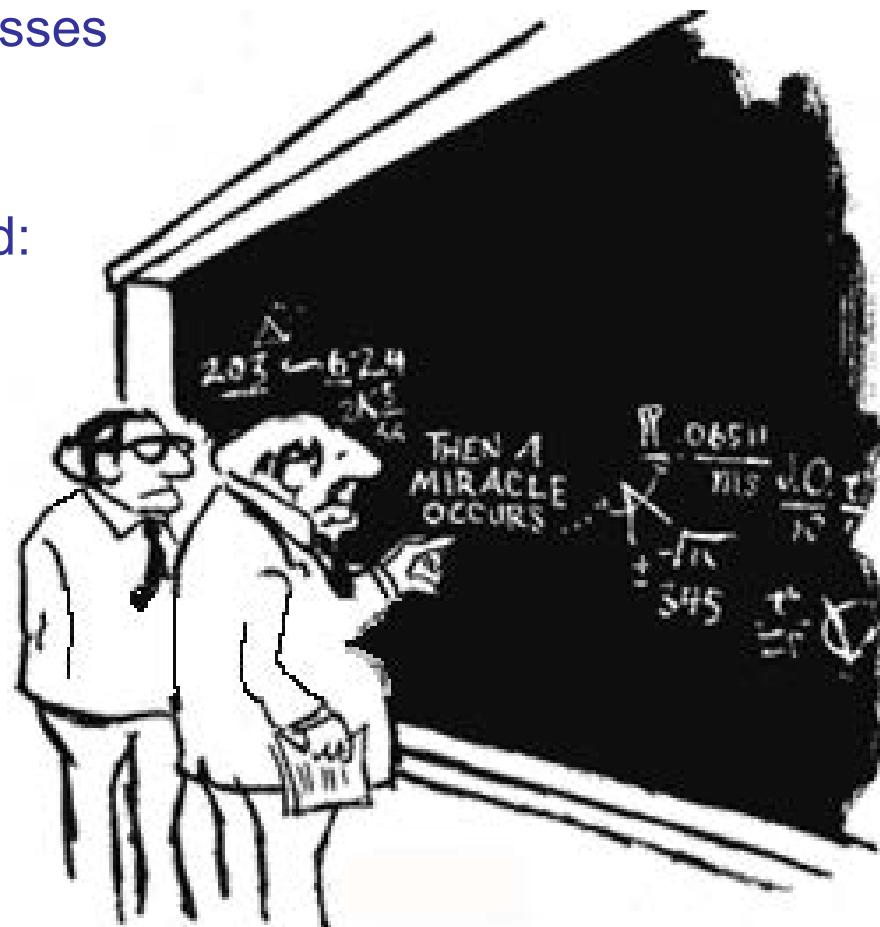
- A spontaneous process always goes in one direction



- A spontaneous process always reaches a state of equilibrium in which 'things' (mass, heat) are distributed more evenly throughout the system
 - Cold ice cubes will melt and get the temperature of the environment
 - Hot coffee will cool down and get the temperature of the environment
- The reversed process does not take place although the energy is still conserved (if we put effort in it, we can reverse the process)
- How to understand and describe this theoretically?

Entropy

- In the 19th century a lot of scientist looked for a property that could be used to describe the direction of processes
- It was Clausius who in 1865 the key concept of thermodynamics discovered: a new thermodynamic property
- The ‘mystery’ property is called **entropy (S)**, [unit J/K]
- Entropy is an extensive property
- It can be made specific: **specific entropy s = S/m** [unit J/kgK]



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

Entropy

- Entropy is an abstract property that is difficult to understand and best understood by its use in engineering processes
- Understanding is mostly intuitively based on expected direction of processes in combination with order and disorder
- Entropy always increases in a spontaneous process and is at a maximum in equilibrium when disorder is at a maximum
- The **second law of thermodynamics** is based on entropy
(Class 5)



Efficiency of energy conversion

- An **efficiency** indicates how well an energy conversion or energy transfer process is accomplished

$$\text{Efficiency} = \frac{\text{What we get out}}{\text{What we put in}} = \frac{\text{Desired outcome}}{\text{Necessary input}}$$



Efficiency of a water heater:
The ratio of the energy delivered to the house by hot water to the energy supplied to the water heater



Efficiency of a power plant: The ratio of the energy (heat), delivered to the plant through burning the fuel over the energy (work / electricity), produced by the plant

Overall efficiency of an energy installation

- The **overall efficiency** of a complete thermal installation is the ratio of the net electrical power output over the rate of fuel energy input

$$\eta_{overall} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net\ electrical}}{\dot{Q}_{in\ fuel}}$$

- In general this efficiency is a combination of the efficiency of different devices and processes of the powerplant:
 - the combustion / burning of the fuel
 - the boiler
 - the thermal power cycle / heat engine
 - the generator
- The overall efficiency** can be calculated by multiplying the individual efficiencies

$$\eta_{overall} = \eta_{combustion} \eta_{boiler} \eta_{thermal_cycle} \eta_{generator}$$



Efficiency of combustion

- The efficiency of the combustion process can be characterized by the **combustion efficiency**

$$\eta_{Combustion} = \frac{Q_{fuel}}{HHV} = \frac{\text{Amount of heat released during combustion}}{\text{Heating value of the burned fuel}}$$

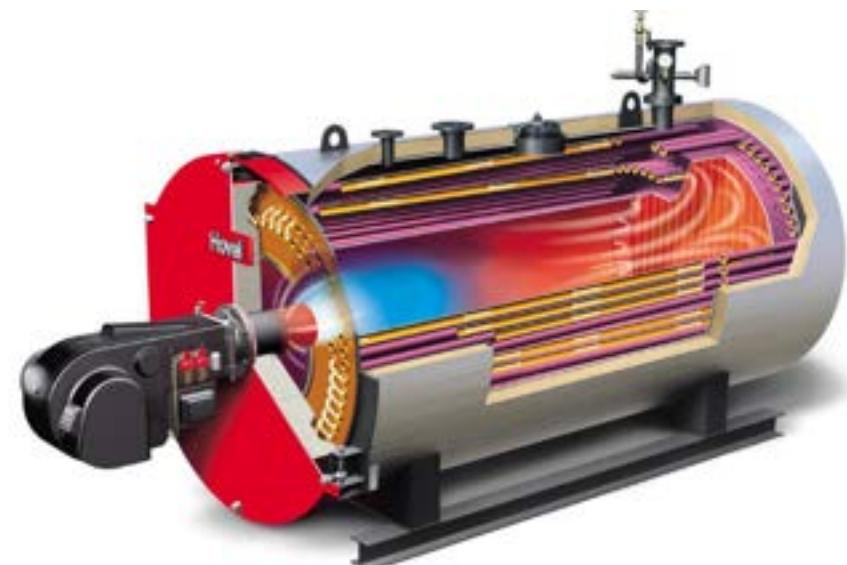
- Heating value of the fuel:** The amount of heat released when a unit amount of fuel at room temperature is completely burned and the combustion products are cooled to the room temperature

1. Lower heating value (LHV):

When the water in the combustion gases leaves as a vapor

2. Higher heating value (HHV):

When the water in the combustion gases is completely condensed and thus the heat of vaporization is also recovered



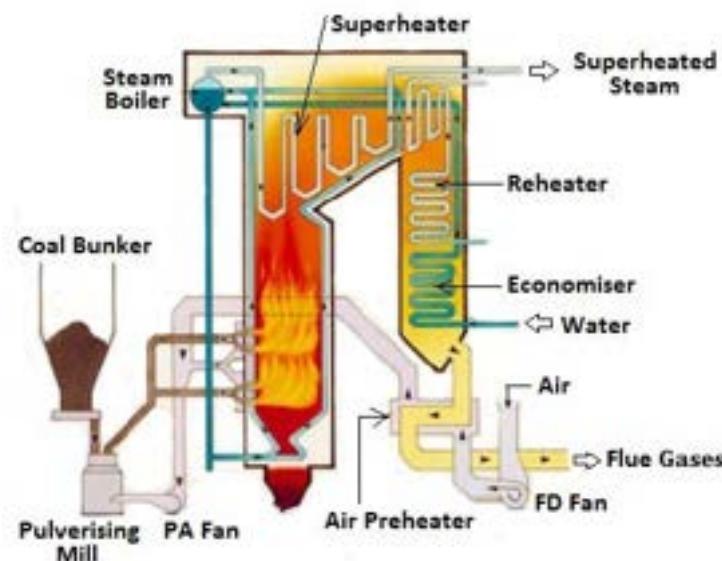
Efficiency of a boiler

- A **boiler** is used to transfer the energy of the burned fuel to the water in the vapor power cycle
- Not all energy is transferred to the water, a part of the energy leaves the boiler through the flue gasses
- The **boiler efficiency** is the ratio of the power released by the fuel over the power (rate of heat) transferred to the thermal vapor power cycle:

$$\eta_{boiler} = \frac{\dot{Q}_{fuel}}{\dot{Q}_{in_cycle}}$$

A boiler of a power plant is a very large structure consisting of different parts right). Pulverized industrial boiler (left)

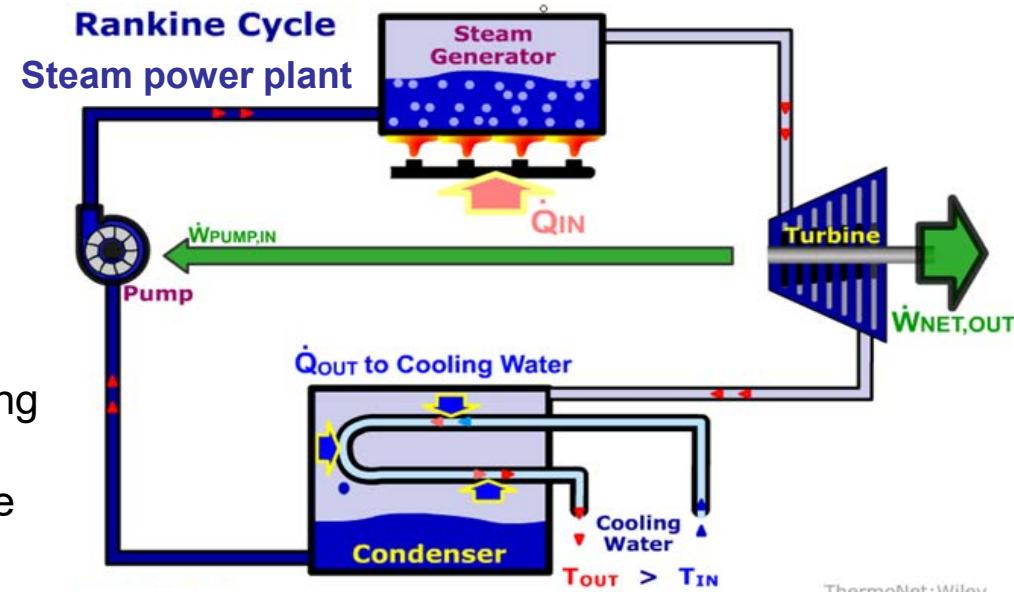
<https://www.coalhandlingplants.com/boiler-in-thermal-power-plant/>



Thermal efficiency of a power cycle

- A thermal power cycle (or heat engine) converts thermal energy (e.g. heat released by fuel) to mechanical energy (e.g. a turning turbine shaft)
- Thermal power cycles include vapor power cycles (Rankine) and gas power cycles (Brayton)
- Note that it is the goal of this course to analyse and design power cycles
- The **thermal efficiency** is the ratio of the power added to the cycle over the power produced by the cycle:

$$\eta_{thermal} = \frac{\dot{W}_{net_out_cycle}}{\dot{Q}_{in_cycle}}$$



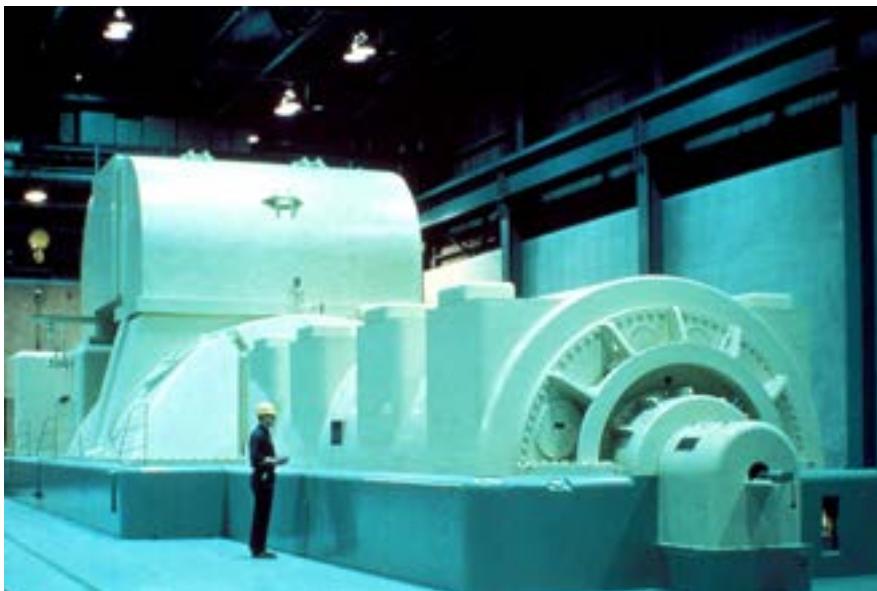
Rankine cycle / steam power cycle converting thermal energy, transferred to the cycle through a boiler, to mechanical energy in the form of a turning turbine shaft

ThermoNet:Wiley

Efficiency of a generator

- A **generator** is a device that converts the mechanical energy of the turbine into electrical energy by electromagnetic induction
- The **generator efficiency** is the ratio of the electrical power output over the mechanical power input of the turbine:

$$\eta_{generator} = \frac{\dot{W}_{net\ electrical}}{\dot{W}_{net\ turbine}}$$



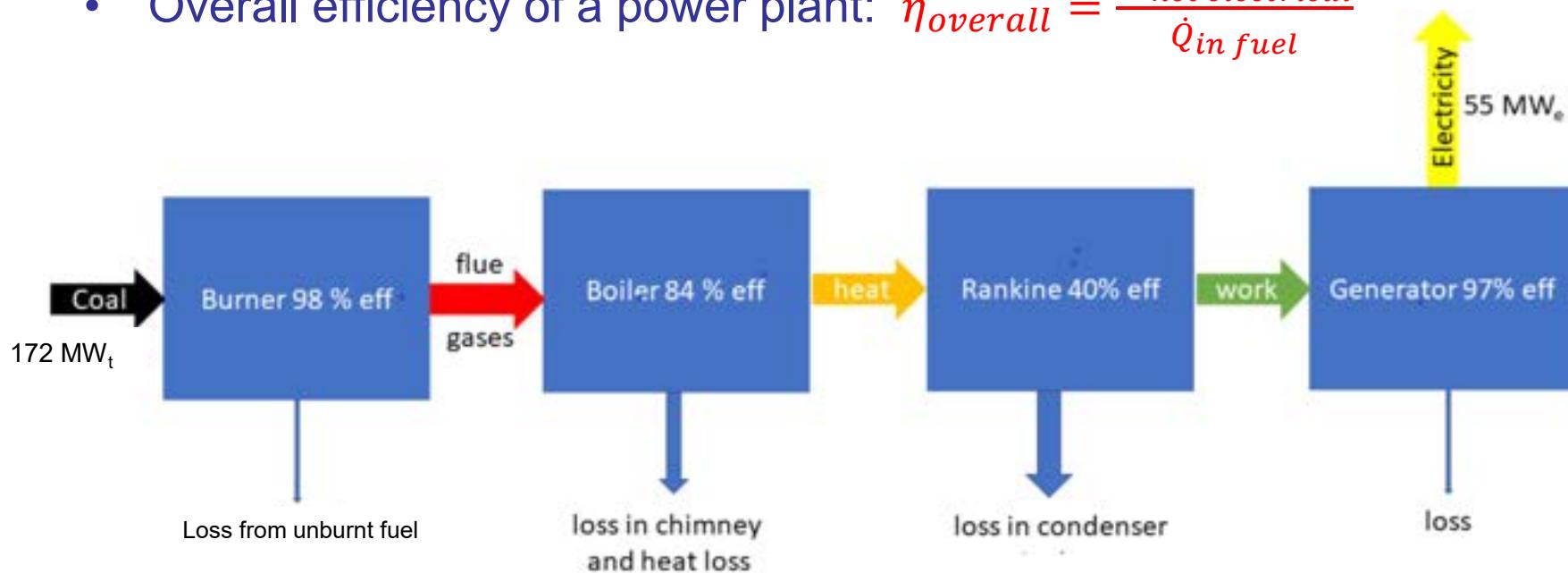
A modern steam turbine generator



A large generator with the rotor removed

Example: efficiency of an energy installation

- Overall efficiency of a power plant: $\eta_{overall} = \frac{\dot{W}_{net\ electrical}}{\dot{Q}_{in\ fuel}}$



$$\eta_{overall} = \frac{\dot{W}_{net\ electrical}}{\dot{Q}_{in\ fuel}} = \frac{55}{172} = 0.32 \text{ (32%)}$$

or multiplying all individual efficiencies

$$\eta_{overall} = \eta_{combustion} \eta_{boiler} \eta_{thermal_cycle} \eta_{generator}$$

$$\eta_{overall} = 0.98 * 0.84 * 0.40 * 0.97 = 0.32 \text{ (32%)}$$

Energy: What is it?

- Energy is a word that is very difficult to grasp into a precise definition, it is hard to describe and understand

Energy is any quantity that changes the state of a closed system when crossing the system boundary



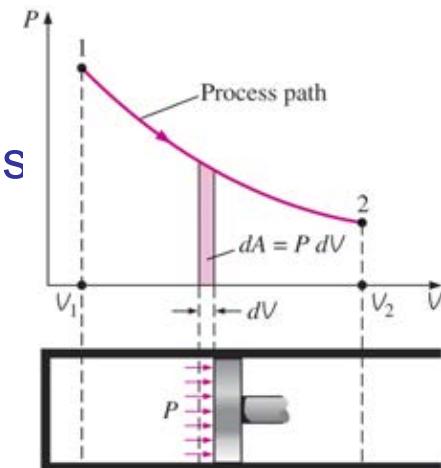
Solar Flare (Photo Courtesy US NOAA)

- For an open system also mass crossing the boundary of the system can change the state of the system

An amount of energy equivalent to 100-megaton hydrogen bombs is released when a solar flare occurs

Recapitulate class 2

- Energy within system boundaries
 - Kinetic / potential / internal energy / total energy
- State and path functions
- Mechanisms of energy transfer across system boundaries
 - Work
 - Boundary work, $\delta W = PdV$ or $\delta w = Pdv$
 - P-v diagrams (compare to F-s diagram)
 - Mechanical work
 - Heat transfer, due to a temperature difference
 - Flow work (Pv), energy transfer due to mass transport across the boundaries of an open system
- The rate of doing work (power) / heat transfer / mass
- First law of thermodynamics (conservation of energy)
- Energy balances, $E_{in} - E_{out} = \Delta E_{system}$
- New properties
 - Enthalpy, $h = u + Pv$, open systems
 - Entropy
- Efficiencies of energy conversion processes

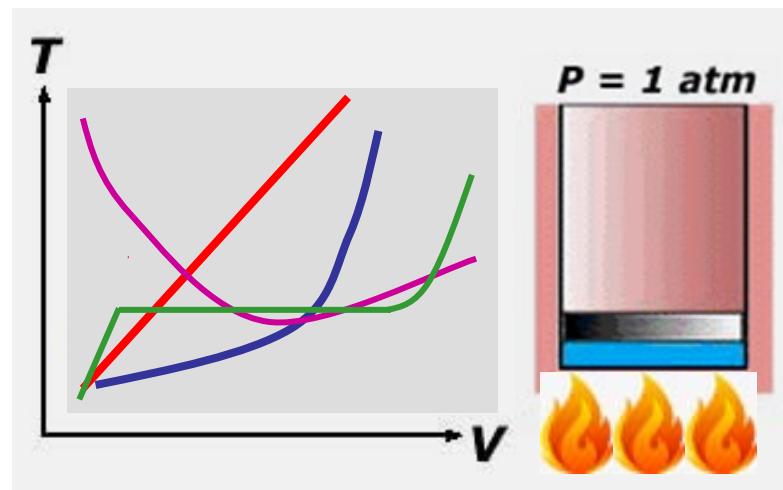


Next Class 3: Phase-change processes: Water

- How can we get values for properties of water?
- Pure substances
- Physics of phase change processes
- Phase change and P - v - T surface (diagrams)
- Liquid - steam - mixture
- Saturation and quality
- Tables / diagrams to obtain thermodynamica properties of water
- Specific heat of water

Heating water at a constant pressure of 1 atm. Which of the lines displays the correct process?

How works a natural geyser?



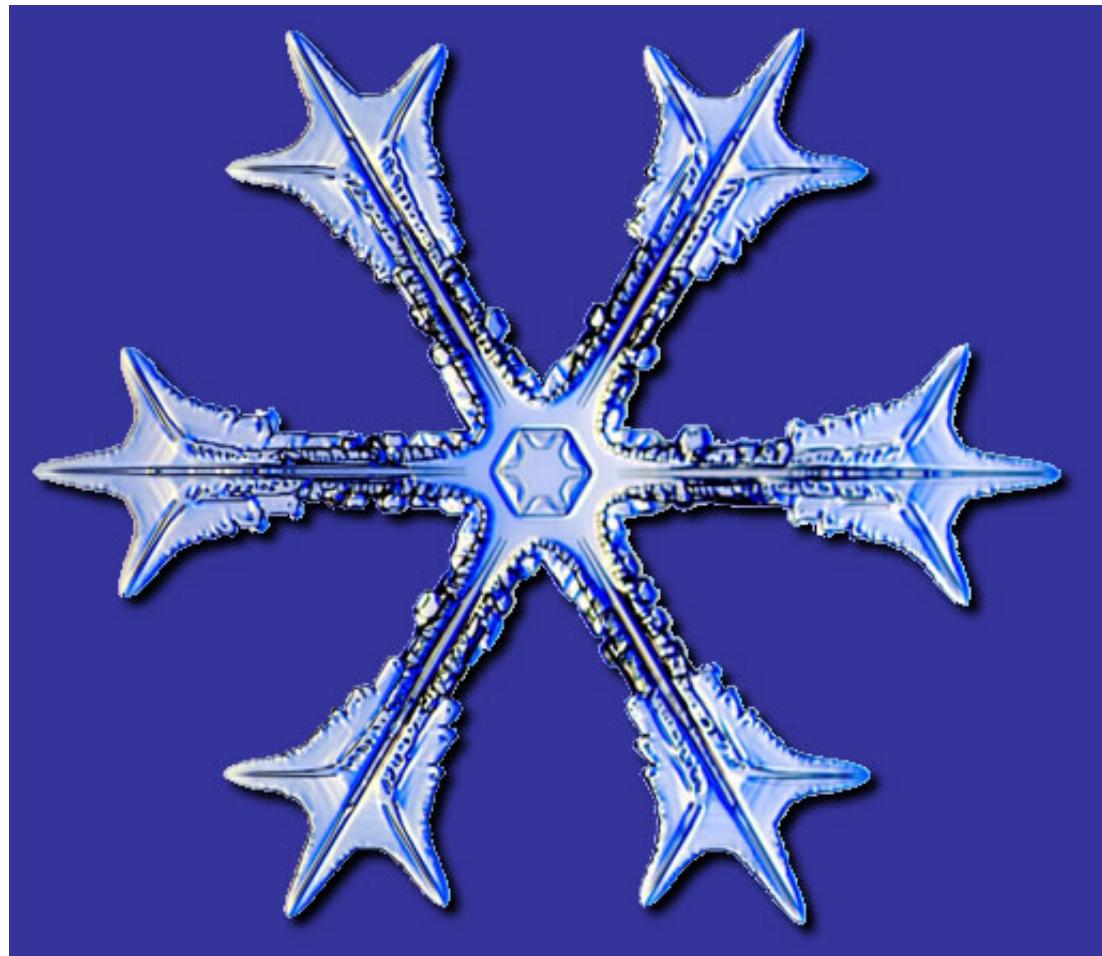
Keep in mind: Important formulas

- 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 (and not velocity!)
- Conservation of energy (first law) $E_{in} - E_{out} = \Delta E_{system}$
- Efficiency $\eta_{thermal} = \frac{Net\ electrical\ power\ output}{Rate\ of\ fuel\ energy\ input} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$

Class 3: Thermodynamic Properties of Pure Substances: Water

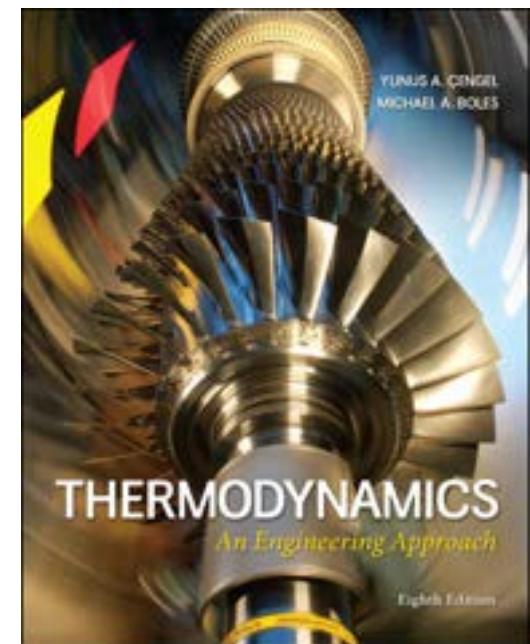
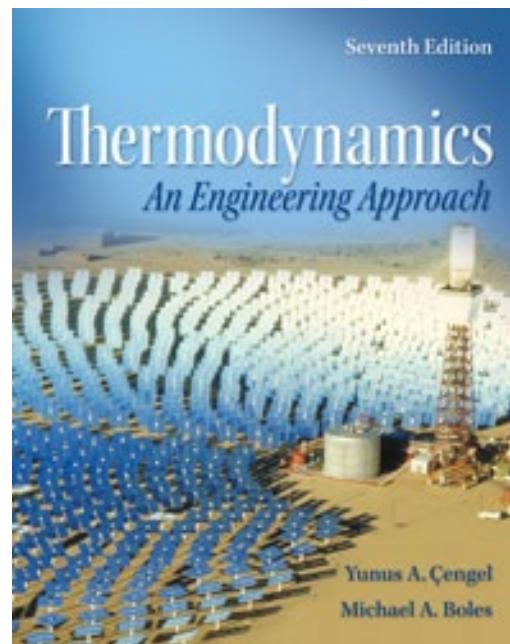
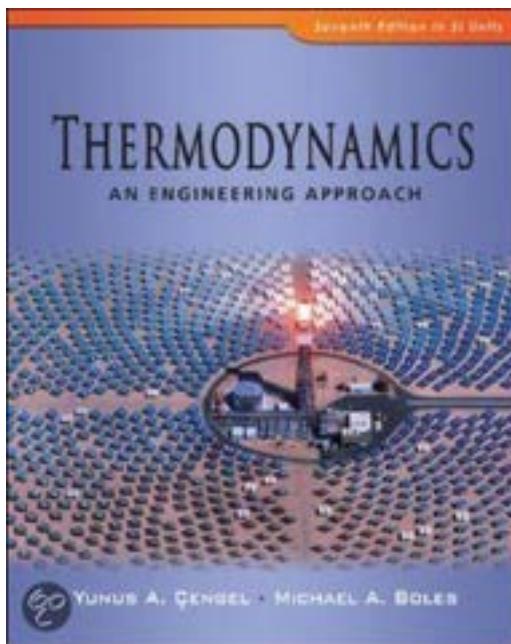
A snowflake at high magnification. The solid phase of water in one of its forms.

(Courtesy of Kenneth G.
Libbrecht, Cal Tech)



Announcement

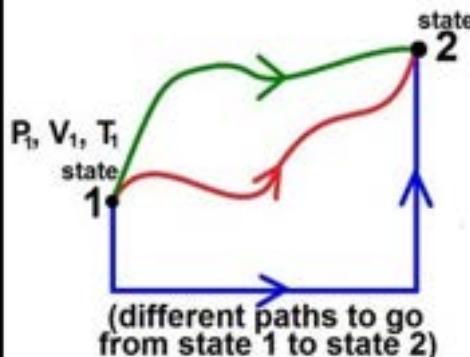
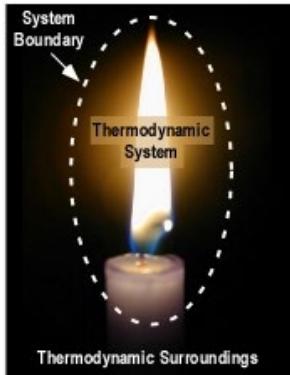
- Take the book to the next on campus tutorial
- Tables are needed for determining the thermodynamic properties of substances



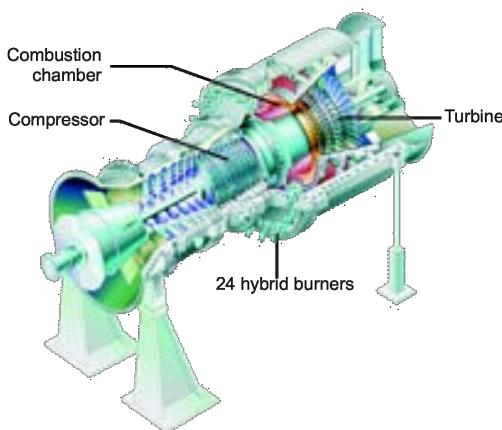
- Open book exam, practice using the book

Roadmap Engineering Thermodynamics

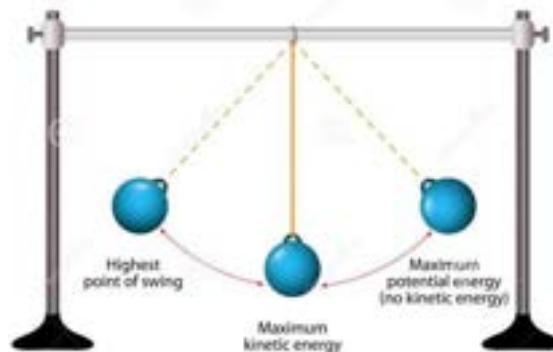
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) ➔ Various forms of energy (Class 2)



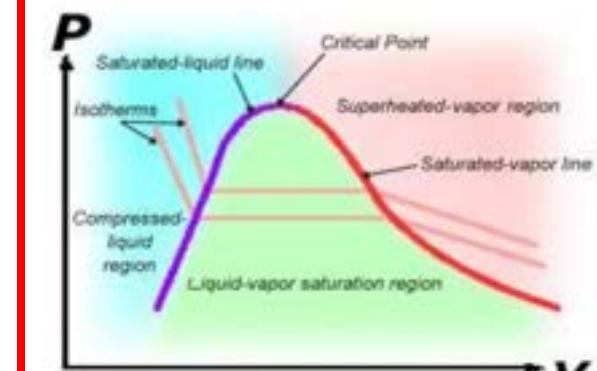
- Power cycles
(Class 6 – 11)



- Laws of Thermo
(Class 4 and 5)

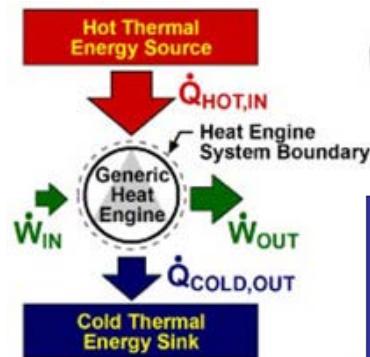


- Properties of Substances
(Class 3, 9)

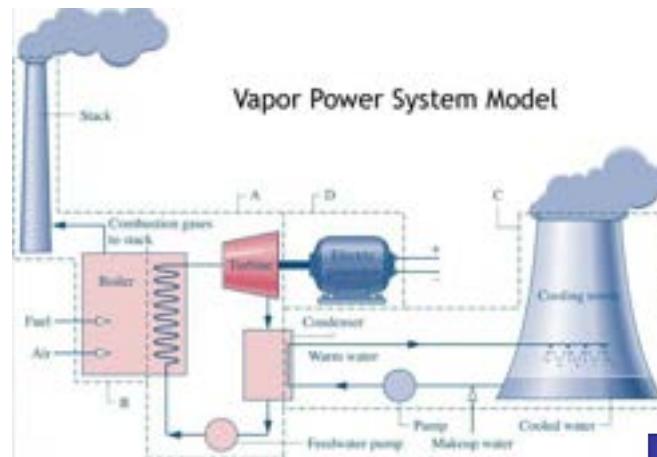


Roadmap Engineering Thermodynamics

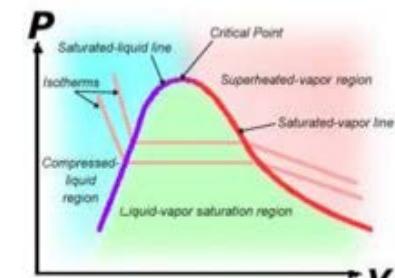
Thermodynamic cycles (Class 6)



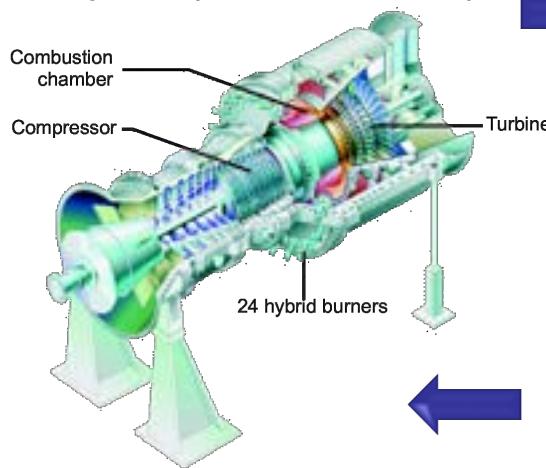
Vapor power cycles –
Rankine cycle (Class 7, 8)



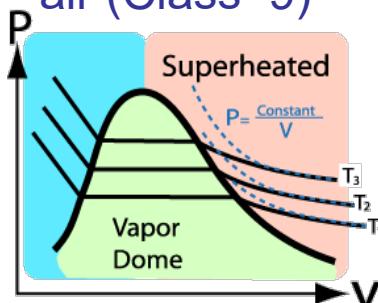
Properties of
water (Class 3)



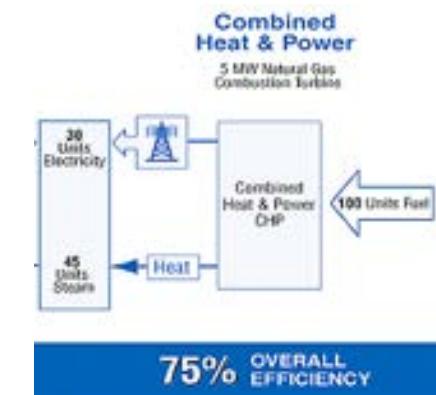
Gas power cycles – Brayton
cycle (Class 10, 11)



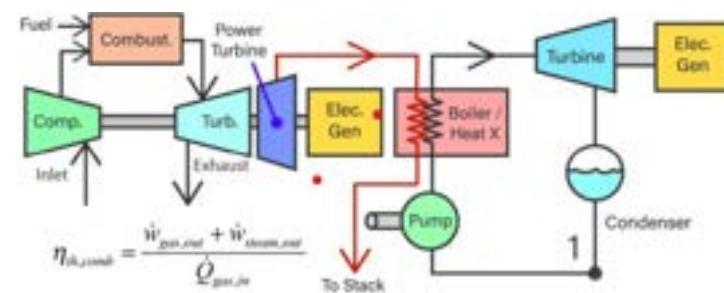
Properties of
air (Class 9)



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

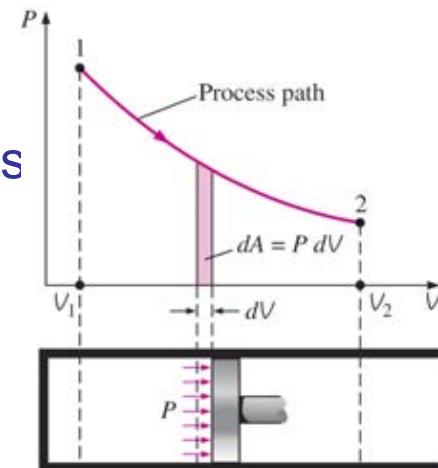


75% OVERALL EFFICIENCY



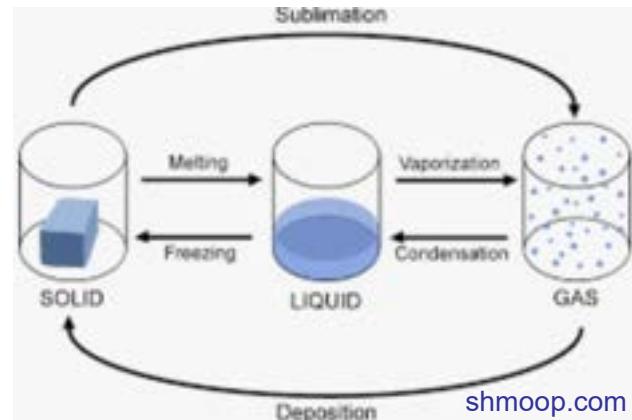
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- Efficiencies of energy conversion processes



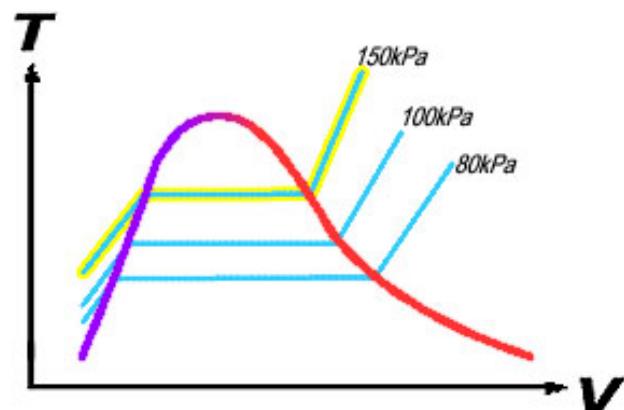
Content Class 3

- **Thermodynamic properties of pure substances: water**
- Pure substances
- Physics of phase change processes
- Phase P-v-T surface, diagrams
- Liquid - steam - mixture
- Saturation - quality
- Diagrams and tables to obtain thermodynamic properties of water
- Specific heat of water
- **Learning goal:** declare and explain the behavior of fluids at different temperatures and pressures and draw and interpret phase diagrams



Properties of Saturated Water - Press. Table (SI)

P kPa	T °C	Specific Volume, m ³ /kg		
		v _L	v _{LV}	v _V
80	93.511	0.001038	2.0866	2.0876
100	99.632	0.001043	1.6933	1.6943
150	111.38	0.001053	1.1584	1.1595



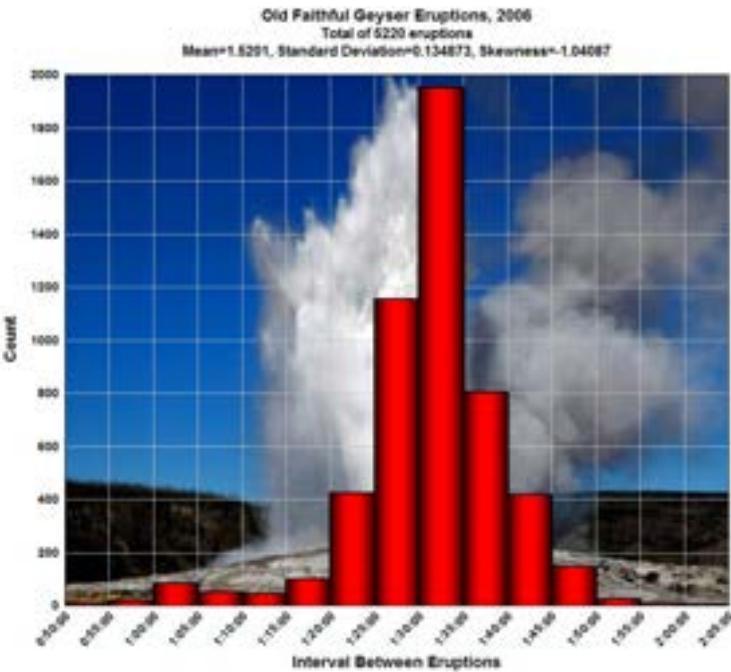
Old Faithful Geyser (Yellowstone Nat. Park)



Old Faithfull eruption

http://www.youtube.com/watch_popup?v=tShhZvvIM84&vq=medium#t=32

How does it work?



Geyser

- How can the working of a natural geyser be explained?



http://www.youtube.com/watch_popup?v=X4zA_YPCyHs&vq=medium#t=32

State Postulate

- From class 1 the state postulate is known

Sate postulate: The state of a simple compressible system is completely specified by two independent, intensive properties

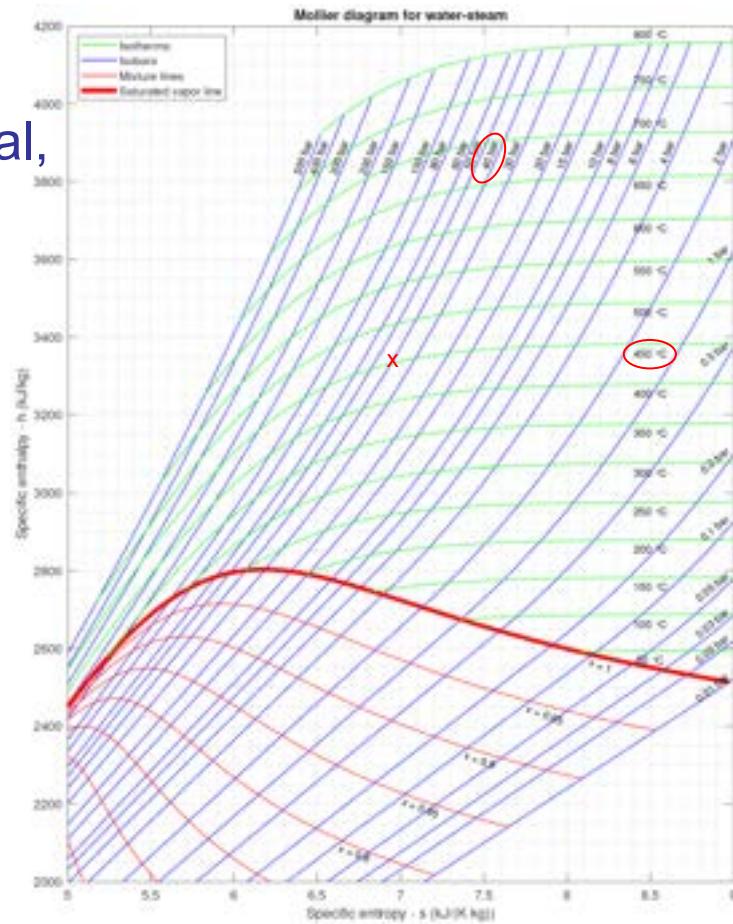
- Simple compressible system: If a system involves no electrical, magnetic, gravitational, motion and surface tension effects

Table of Steam Properties

P (kPa)	T (°C)	v (m³/kg)
100	100	1.696
100	120	1.793
100	160	1.984

ThermoNet: John Wiley Publishers

- A postulate is not proven, but accepted as a basic theorem, which is never contradicted by observations



Pure Substances

- **Pure substances** are composed of a single chemical species (e.g. either O₂ or CO₂ but not a mixture of O₂ and CO₂).
- However pure substances may exist in more than one phase (e.g. solid and liquid or liquid and vapor)

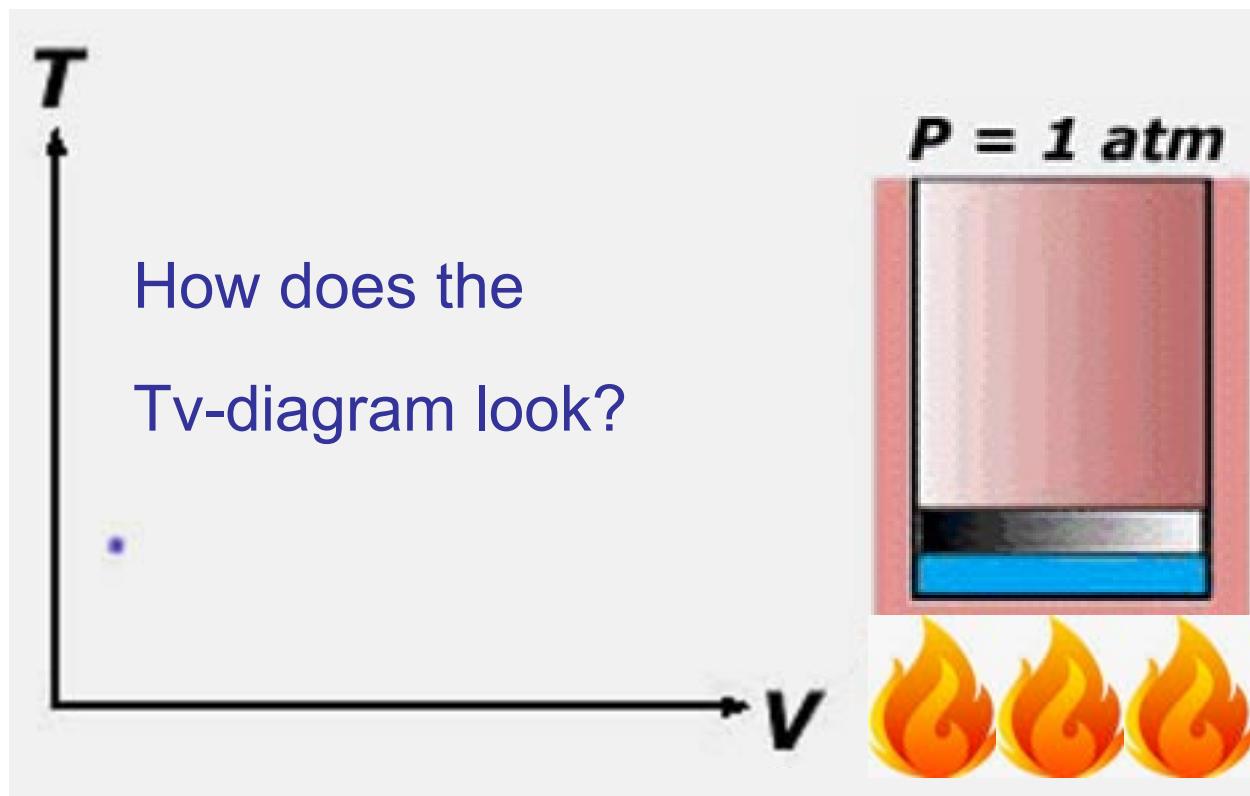
A mixture of
snow, ice, liquid
water
and water vapor
is a
pure substance



- **Mixtures of substances** are treated in chapter 14 (not in this course)

Phase Change and T_v - Diagram

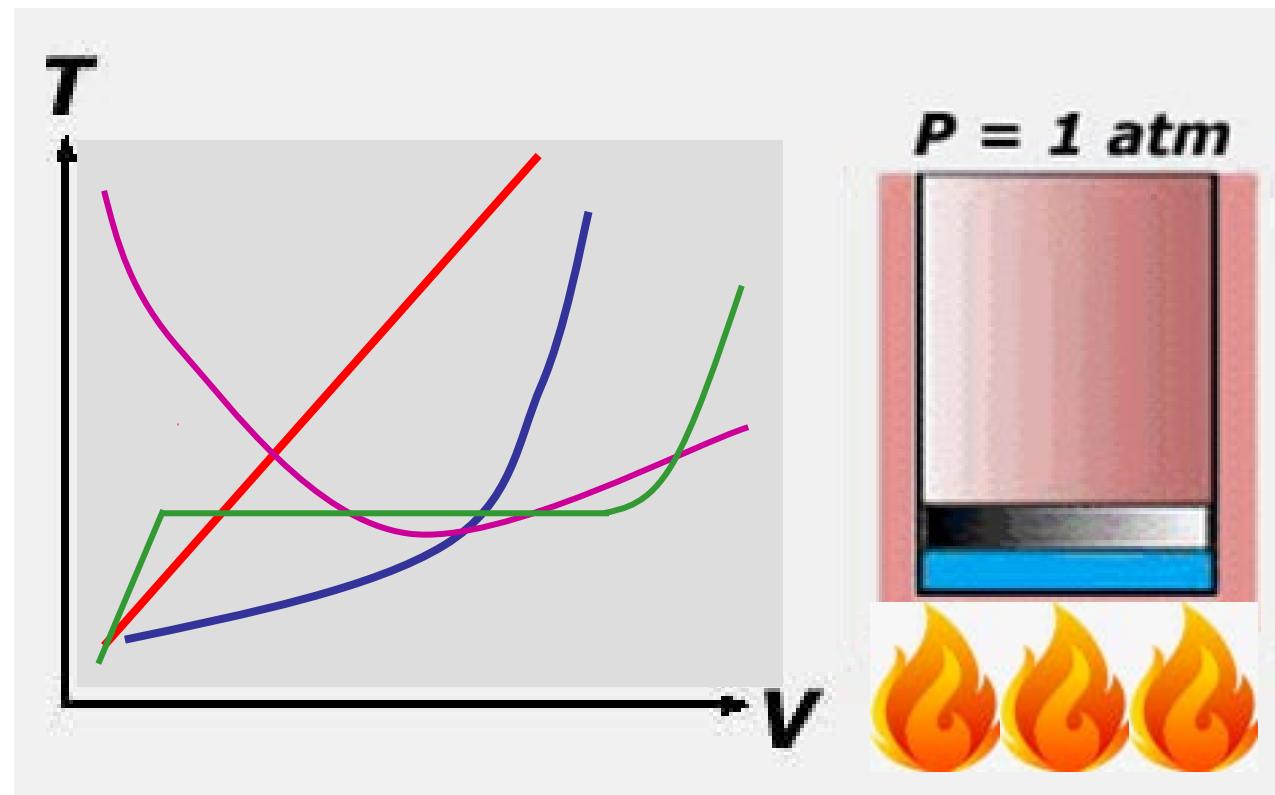
- Everyday example: Heat a pan of water on the furnace
- Heat added at constant pressure to the water, what happens?
- In thermodynamic terms you can translate this problem to
Constant pressure heating in piston-cylinder at $P = 1 \text{ atm}$



Phase Change and T_v - Diagram

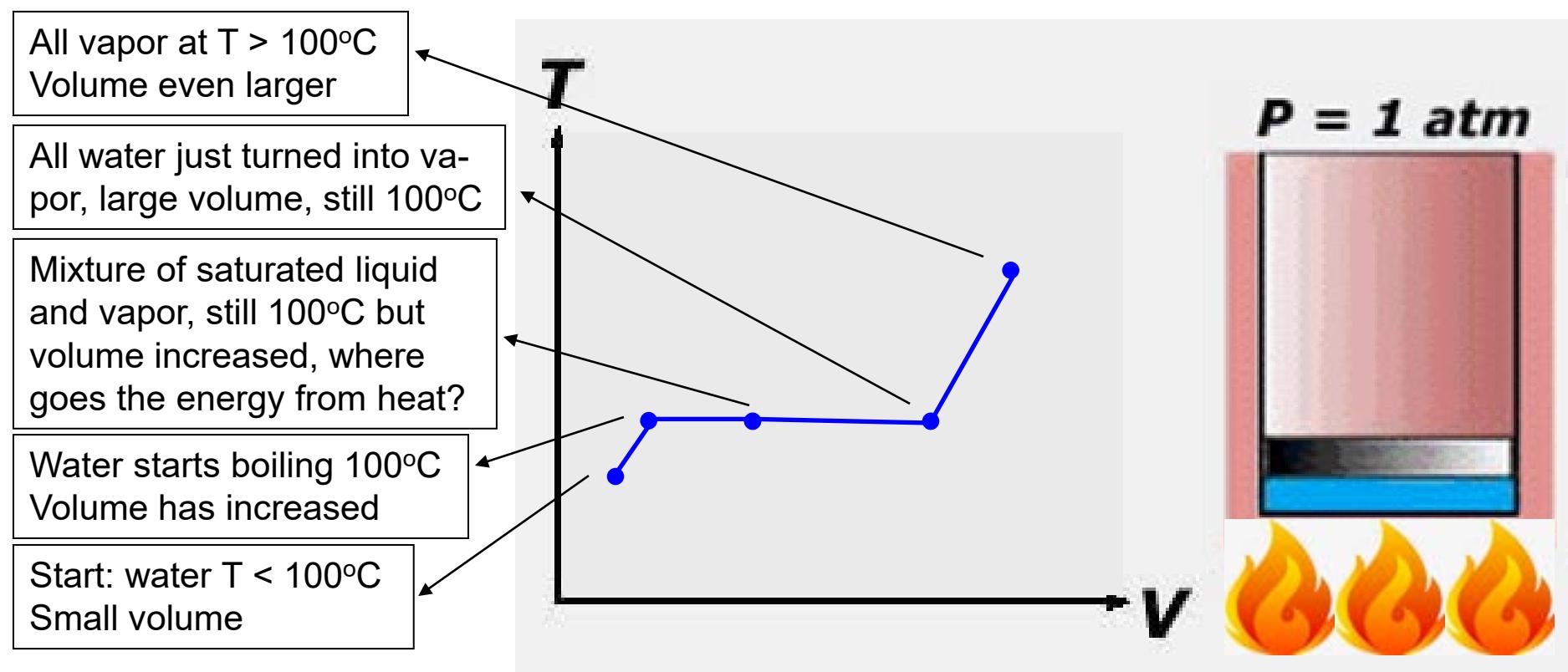
- Everyday example: Heat a pan of water on the furnace
- Heat added at constant pressure to the water, what happens?
- In thermodynamic terms you can translate this problem to
Constant pressure heating in piston-cylinder at $P = 1 \text{ atm}$

- Which line is correct?
 - Red
 - Blue
 - Green
 - Purple
 - No one



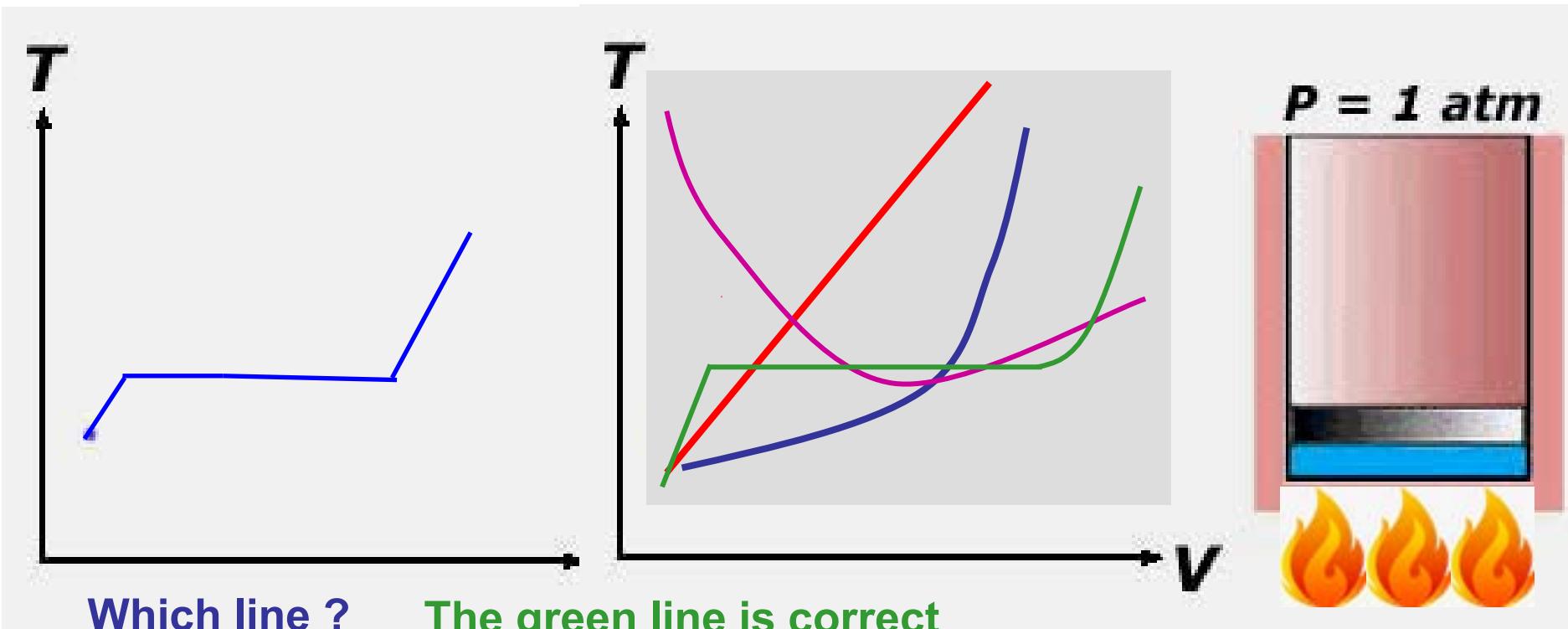
Phase Change and T_v - Diagram

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- In thermodynamic terms you can translate this problem to
Constant pressure heating in piston-cylinder at $P = 1 \text{ atm}$



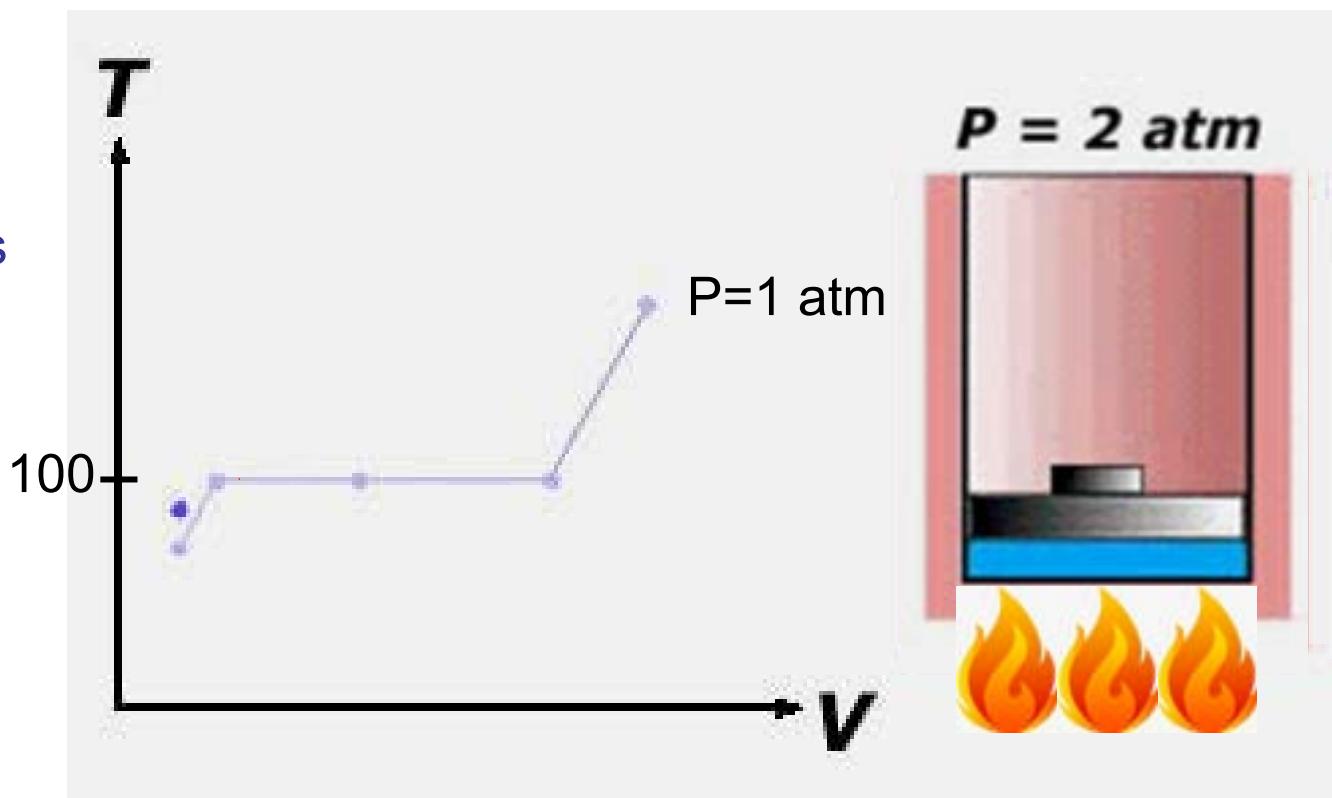
Phase Change and T_v - Diagram

- Everyday example: Heat a pan of water on the furnace
- Heat added at constant pressure to the water, what happens?
- In thermodynamic terms you can translate this problem to
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Phase Change and T_v - Diagram

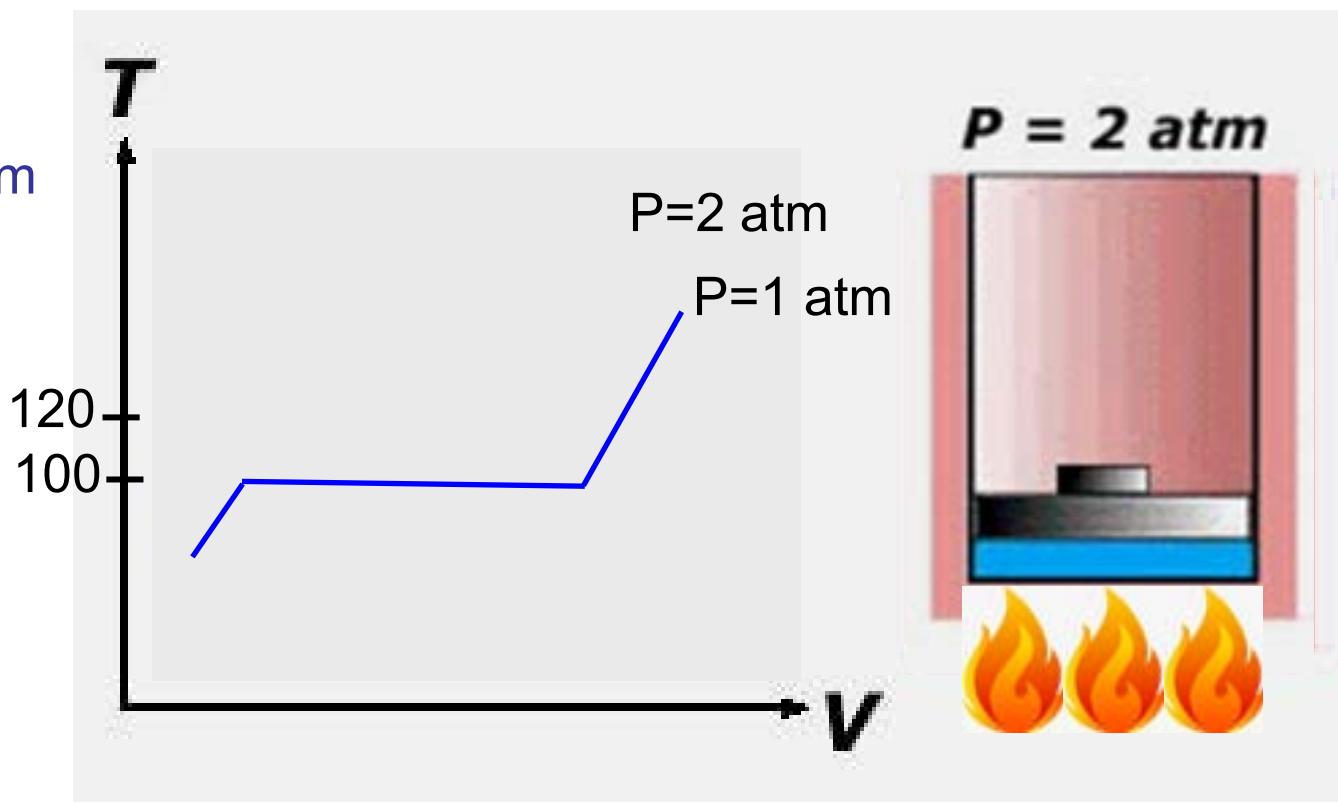
- Replace the pan by a high pressure one ($P = 2 \text{ atm}$)
- Again add heat at constant pressure, what is the difference with 1 atm ?
- In thermodynamic terms you can translate this problem to
Constant pressure heating in piston-cylinder at $P = 2 \text{ atm}$
- **What happens ?**
- How will the diagram look in this case compared to the line at 1 atm?



Phase Change and T_v - Diagram

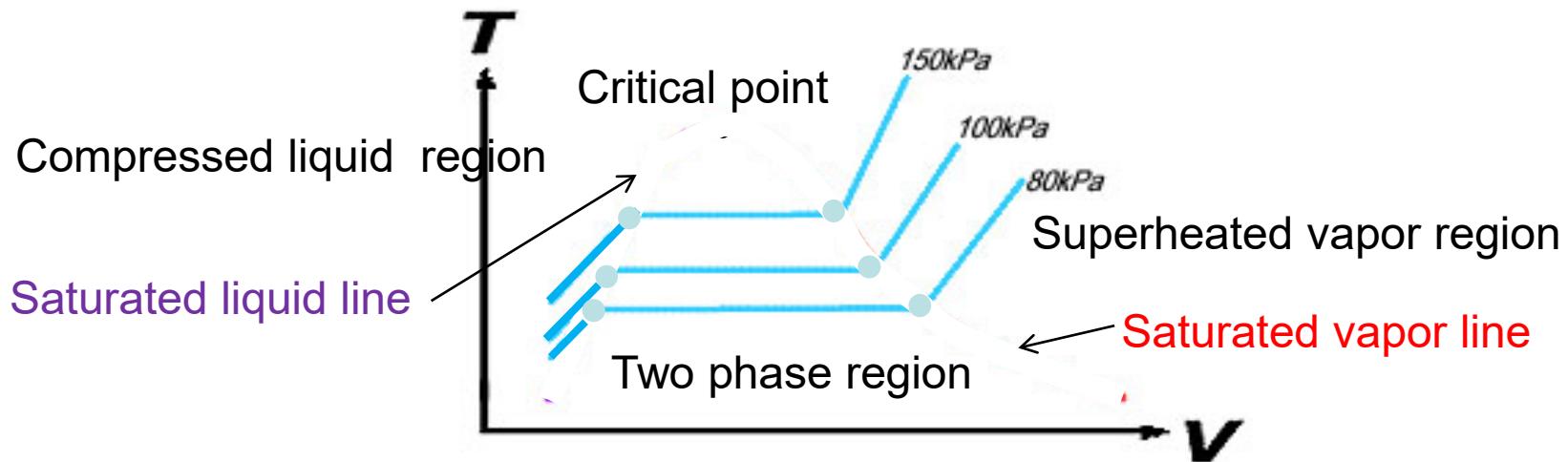
- Replace the pan by a high pressure one ($P = 2 \text{ atm}$)
- Again add heat at constant pressure, what is the difference with 1 atm ?
- In thermodynamic terms you can translate this problem to
Constant pressure heating in piston-cylinder at $P = 2 \text{ atm}$

- **What happens?**
- Actually the same happens as at 1 atm
- However the temperatures and volumes are different
- At **every** pressure same behavior but at different combinations of volume-pressure-temperature



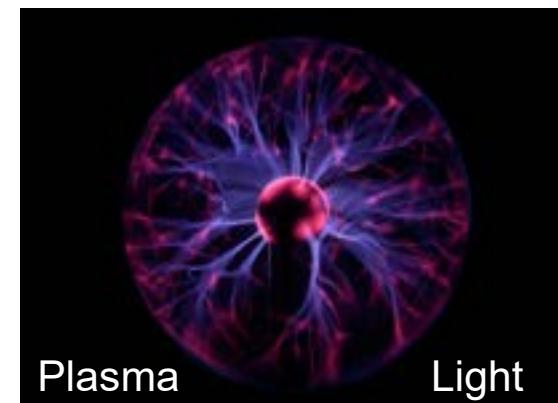
Phase Change and T-v - Diagram

- Repeating this process with different pressures results in the horizontal line to become a point, **critical point** (above this point the fluid is supercritical)
- A dome can be drawn around the vertical lines, this **saturation dome (or vapor dome)** divides the T-v diagram into different regions
 - Region under the dome: **liquid-vapor region or two phase region**
 - Region left of the dome: **compressed liquid region**
 - Region right of the dome: **superheated vapor region**
- The dome consists of two lines
 - **Saturated liquid line** (between the compressed liquid and two phase region)
 - **Saturated vapor line** (between the two phase region & the superheated vapor)



Supercritical Fluid versus Plasma

- A **supercritical fluid** is any substance at a temperature and pressure above its critical point.
 - Diffuse through solids like a gas, and dissolve materials like a liquid.
 - Close to the critical point , small changes in pressure or temperature result in large changes in density: properties of a supercritical fluid to be "fine-tuned".
 - Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes.
 - CO₂ and water are the most commonly used supercritical fluids, being used for decaffeination and power generation.
- In physics and chemistry, **plasma** is a gas in which a certain portion of the particles are ionized.
 - It responds strongly to electromagnetic fields.
 - Plasma therefore has properties quite unlike those of solids, liquids, or gases and is sometimes considered to be a distinct state of matter.
 - The transition from gas to plasma is continuous while there is a sharp distinction between the solid, liquid and gas phase.



Plasma

Light

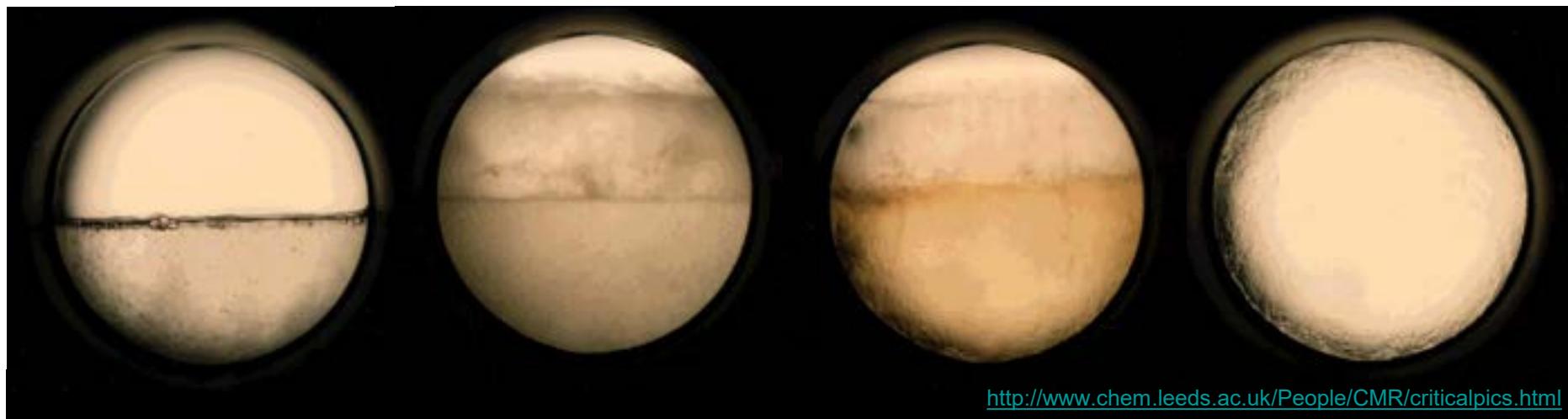
Plasma Globe,

<http://en.wikipedia.org/wiki/Plasma>

(Extra information, not part of the exam)

Supercritical Carbon Dioxide

The process of carbon dioxide undergoing a phase transition to form a supercritical fluid



1. Here we can see the separate phases of carbon dioxide (fluid at the bottom and gas above). The meniscus is easily observed.
2. With an increase in temperature the meniscus begins to diminish.
3. Increasing the temperature further causes the gas and liquid densities to become more similar. The meniscus is less easily observed but still evident.
4. Once the critical temperature and pressure have been reached the two distinct phases of liquid and gas are no longer visible. The meniscus can no longer be seen. One homogeneous phase called the "supercritical fluid" phase occurs which shows properties of both liquids and gases.

(Extra information, not part of the exam)

A movie of SF₆: <http://www.rsc.org/suppdata/jm/b3/b315262f-e/>

Example: Supercritical fluid extraction

The use of classic organic solvents in the food industry entails environmental and health risks. That is why it has been studied for years which mild solvents can be used in extraction processes to replace these organic solvents. CO₂ is such a solvent.

A substance is called supercritical when the phase transition between liquid and gaseous is no longer perceptible. This phenomenon occurs above a specific pressure and temperature and depends on the substance. In supercritical extraction - supercritical fluid extraction (SFE) in English - specific components are extracted from the starting material using a supercritical solvent.

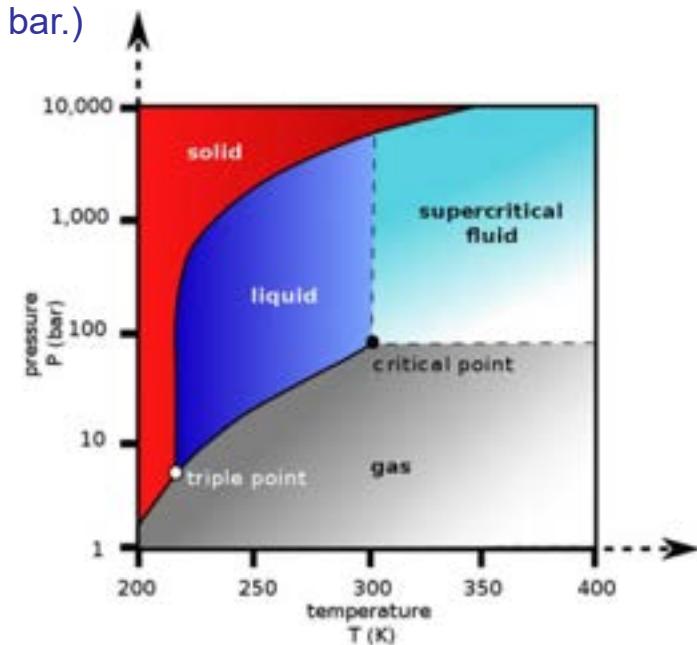
Various solvents can be used for this, but CO₂ is generally used. Water is also easily soluble in supercritical CO₂. As a result, the technology also has the potential to be used as a drying technique = specific extraction of water as an alternative to freeze drying.

The critical temperature of CO₂ is 31.3 °C at a critical pressure of 72.9 bar, see Figure 1. (For comparison: for water the critical temperature is 374.4 °C at a critical pressure of 226.8 bar.)

Physico-chemical properties can change significantly when a substance becomes supercritical. In this state, the physicochemical properties of CO₂ resemble those of liquid CO₂ in some cases and gaseous CO₂ in other cases. For example, supercritical CO₂ (abbreviated as scCO₂) has the physical properties of gaseous CO₂ (high diffusivity, low viscosity, no surface tension) and the chemical properties of liquid CO₂ (high density and high dissolving power).

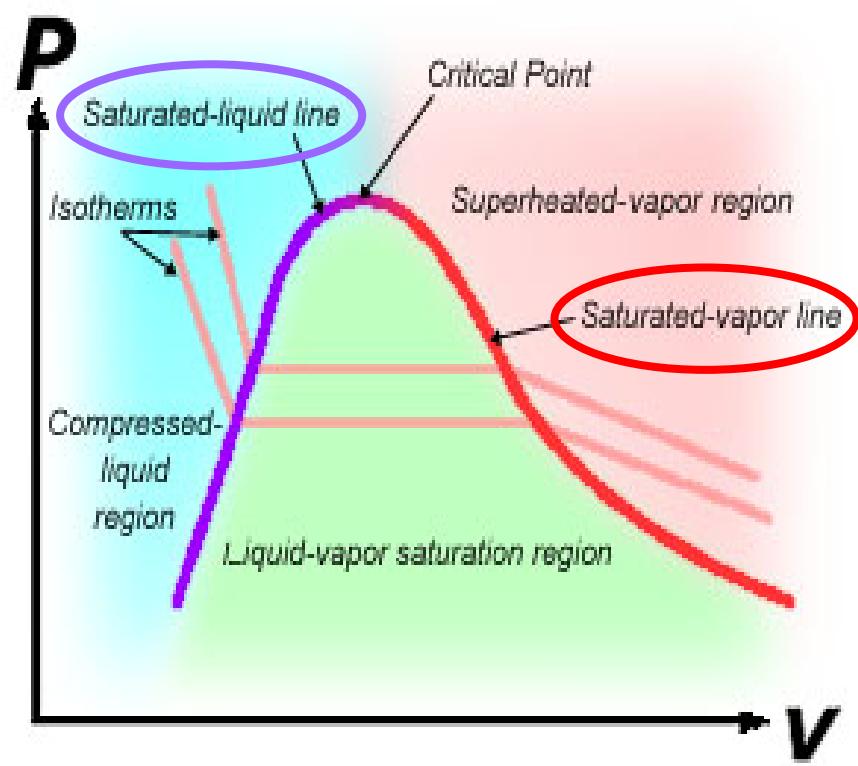
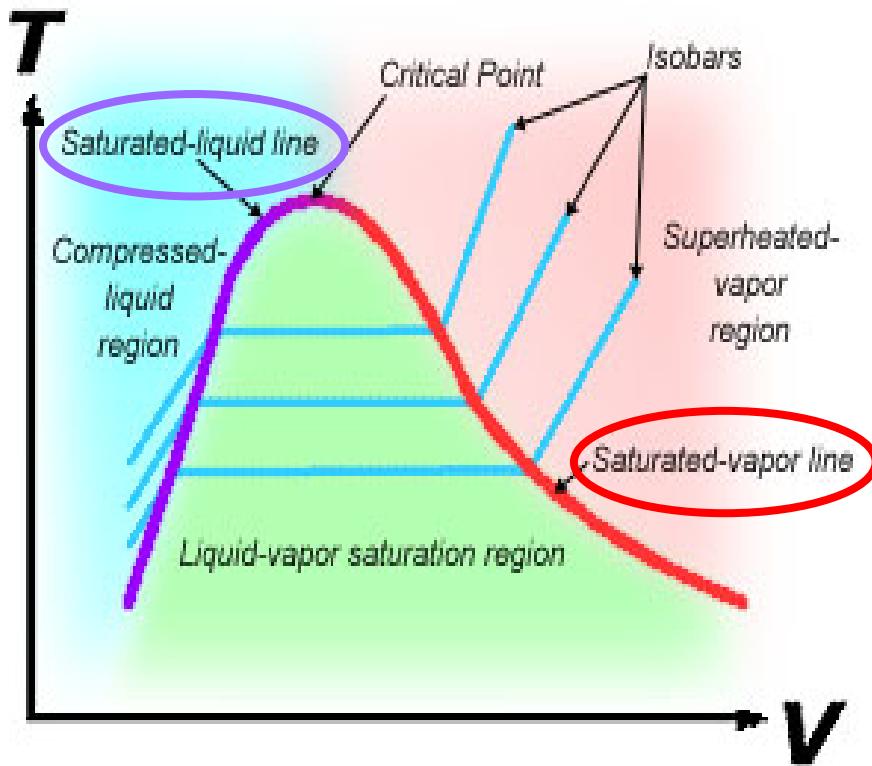
These physicochemical properties can be changed quite significantly by adjusting pressure and / or temperature. In other words, it is possible to adapt the properties of scCO₂ to the specific application, so that scCO₂ can be used in many processes.

(Extra information, not part of the exam)



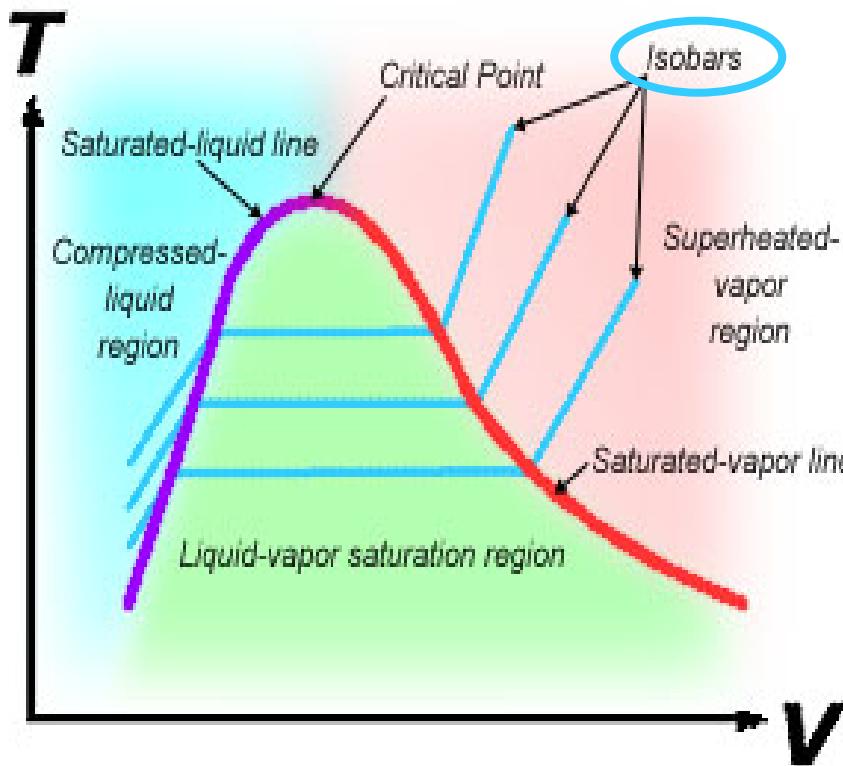
Phase Change and PvT - Surface

- Regions on T-v diagram
- Note saturation lines, **saturated liquid** and **saturated vapor**
- Regions on P-v diagram
- Note saturation lines, **saturated liquid** and **saturated vapor**

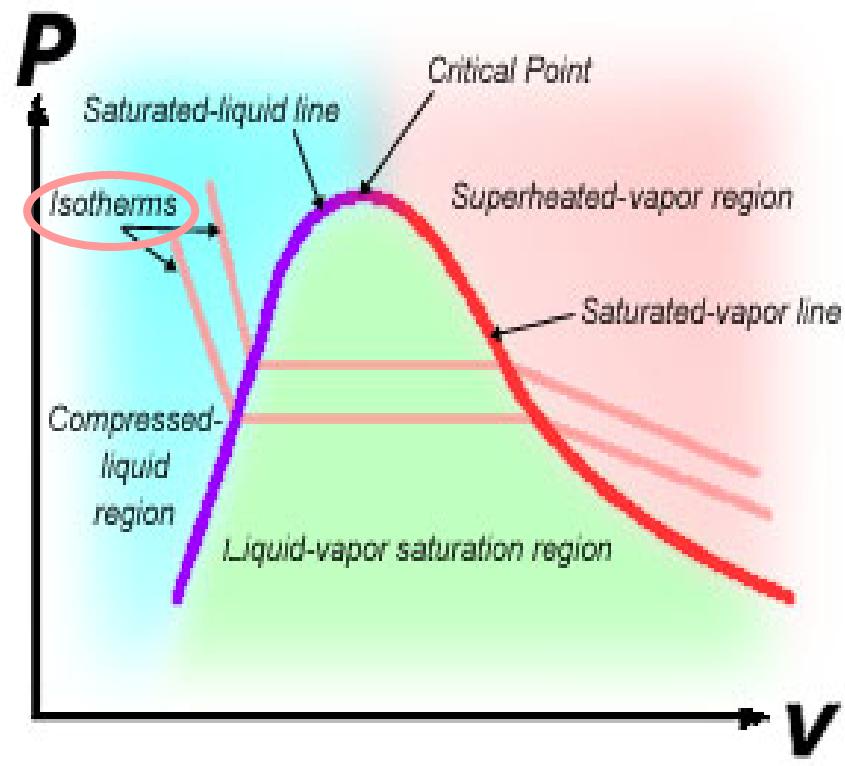


Phase Change and PvT - Surface

- Regions on T-v diagram
- Note directions of **isobars** (constant pressure lines) horizontal inside the dome
- Rising slope outside



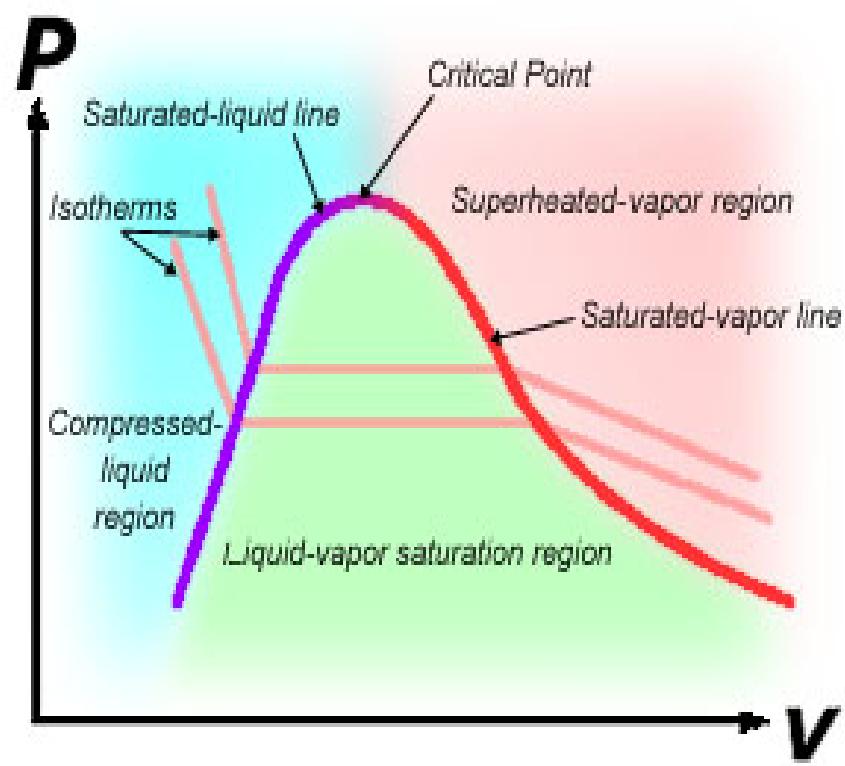
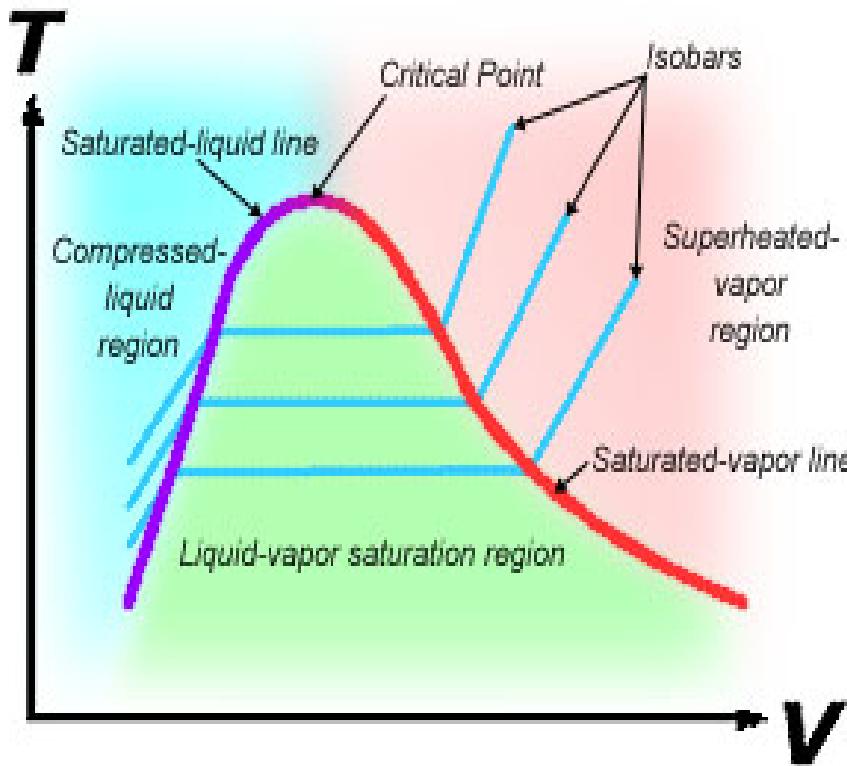
- Regions on P-v diagram
- Note directions of **isotherms** (constant temperature lines) horizontal inside the dome
- Decreasing slope outside



Phase Change and PvT - Surface

Some questions arise from the diagrams

1. Why is the pressure for boiling higher for higher temperatures?
2. Why are the lines in the vapor dome on the T_v and P_v - diagram horizontal, i.e. why does the temperature or pressure not increase inside the dome?

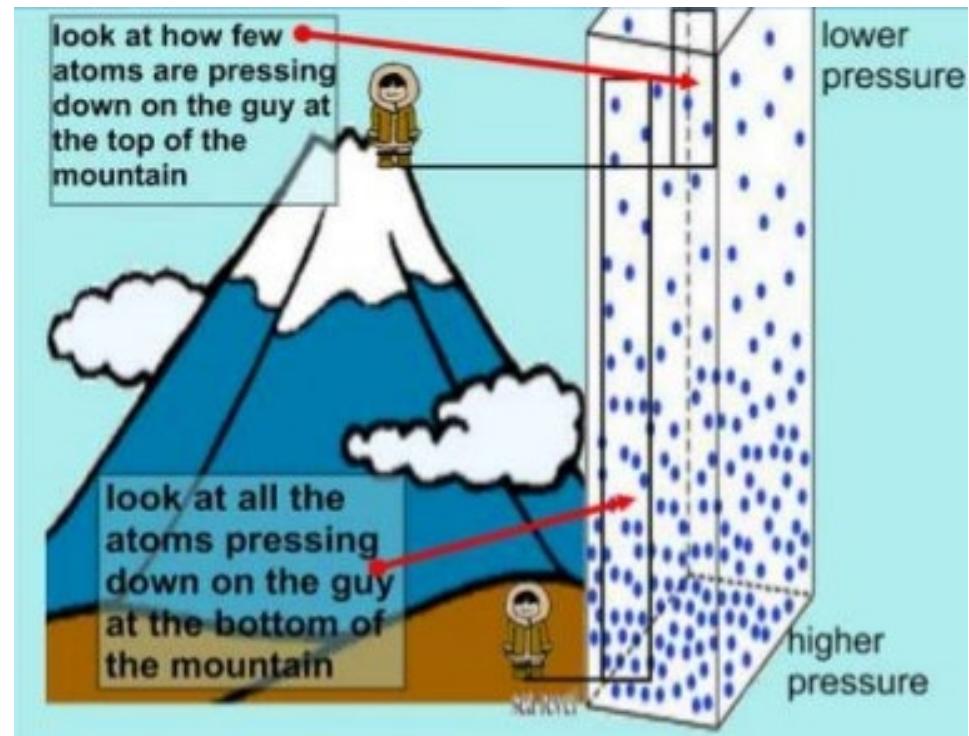


Saturation Temperature and Pressure

Some questions arise from the diagrams

1. Why is the pressure for boiling higher for higher temperatures?

- The temperature at which a liquid starts to boil depends on the pressure
- The higher the pressure the higher the temperature at which the water boils
- At higher pressure, the molecules need more energy (higher velocity) to escape the against the higher pressure
- High in the mountains at lower pressure, water boils at lower temperature



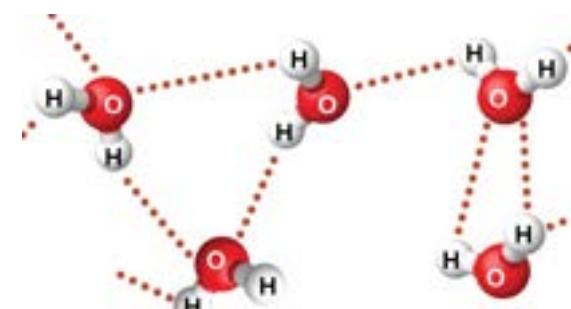
Saturation Temperature and Pressure

Some questions arise from the diagrams

2. Why are the lines in the vapor dome on the T_v and P_v - diagram horizontal, i.e. why does the temperature or pressure not increase inside the dome?

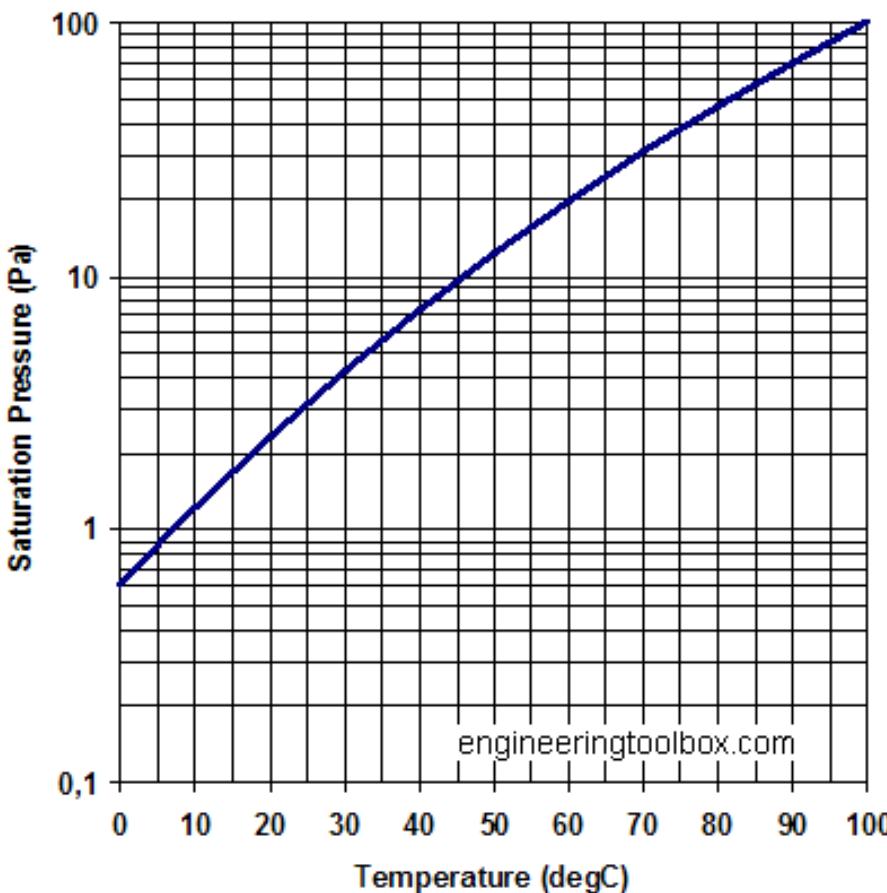
In the saturated liquid - vapor region pressure and temperature are dependent properties and do not increase because

- When a fluid is boiling the added heat is used to destroy the bonding's of the liquid molecules to turn them into vapor, once all liquid is vaporized the heat can be used to heat the vapor and the temperature of the vapor rises again
- It takes a large amount of energy to vaporize a liquid, the same amount of energy is released if vapor is condensed, this is called **latent heat**
- During a phase change process pressure and temperature are dependent properties $T_{sat} = f(P_{sat})$ (we need another second property !)
 - In the two-phase region → **saturated pressure P_{sat} and temperature T_{sat}**



Saturation Temperature and Pressure

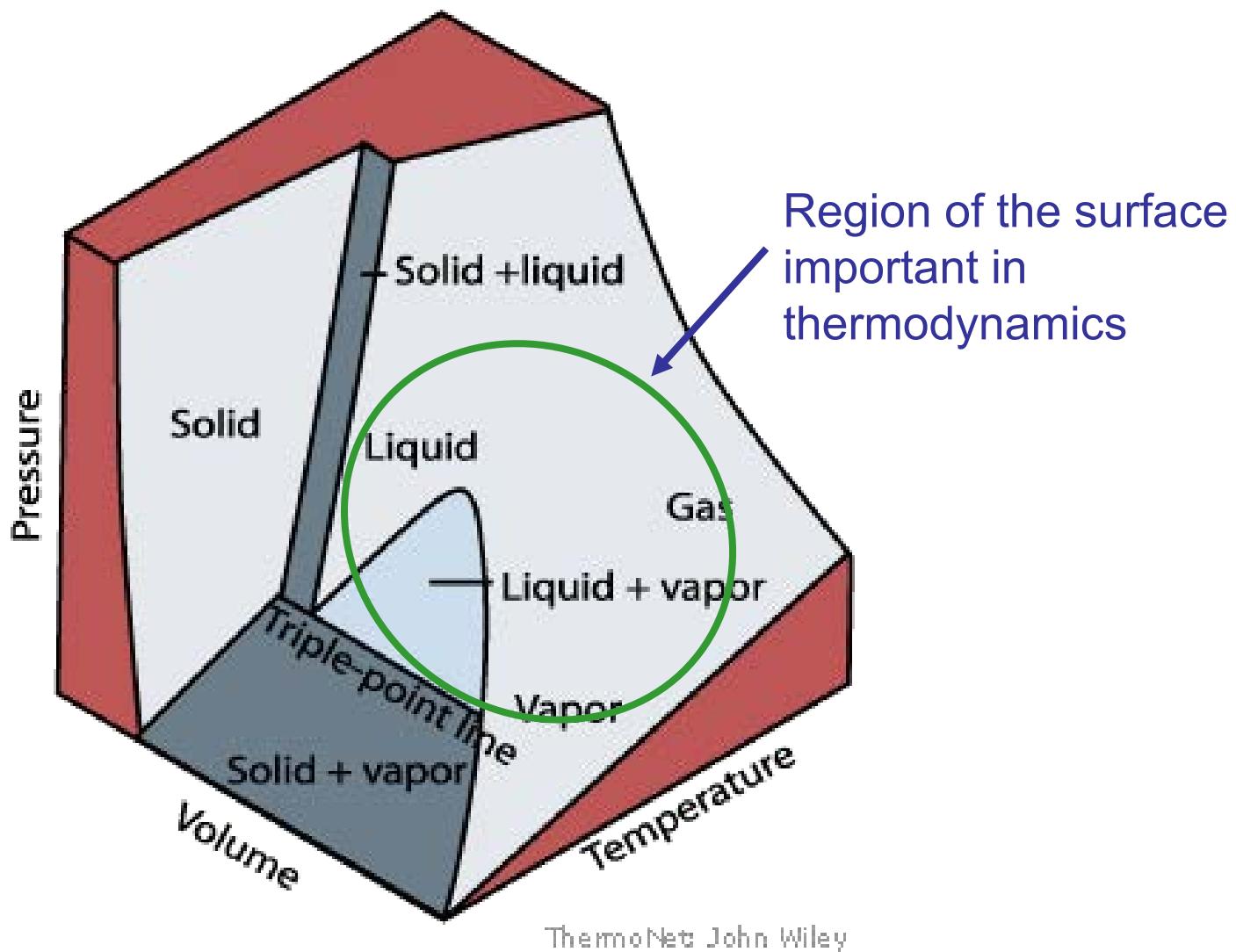
- During a phase change process pressure and temperature are dependent properties $T_{\text{sat}} = f(P_{\text{sat}})$
 - In the two-phase region: saturated pressure P_{sat} and temperature T_{sat}



Temperature - t - ($^{\circ}\text{C}$)	Absolute Vapor Pressure $p_v - (10^3 \text{ Pa}, \text{ N/m}^2)$
0	0.6105
5	0.8722
10	1.228
20	2.338
30	4.243
40	7.376
50	12.33
60	19.92
70	31.16
80	47.34
90	70.10
100	101.3

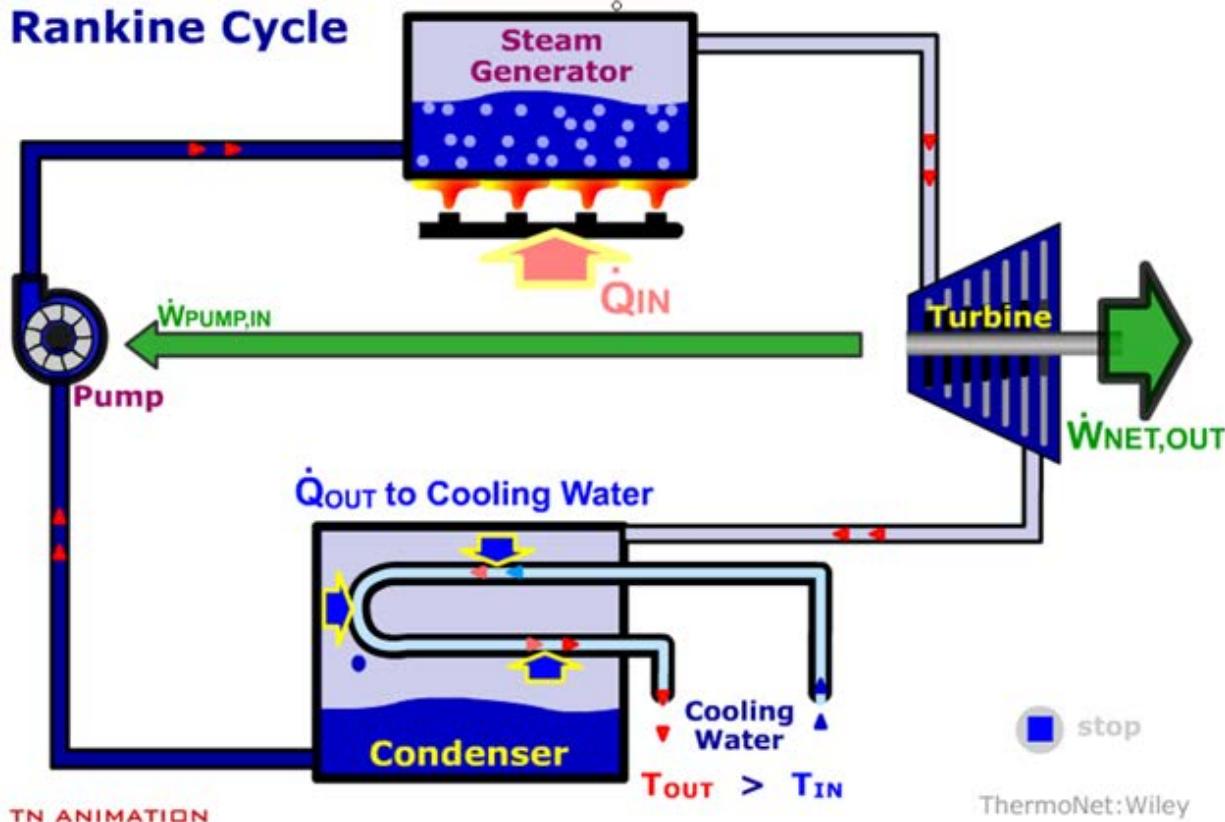
Phase Change and P-v-T Surface

- Three-dimensional P-v-T surface



Example: Steam Cycle

Rankine Cycle



- Energy change steam generator
- $Q_{in} = E_{out} - E_{in}$
- Similar for the condenser
- $Q_{out} = E_{in} - E_{out}$
- E_{out} and E_{in} of the water and vapor depend on the temperature and pressure of the water and vapor

- In a steam cycle two times phase transitions occur
 1. From liquid to vapor in the steam generator
 2. From vapor to liquid in the condenser
- To analyze the system knowledge about the energy of water / vapor at different temperatures and pressures is necessary

Liquid-Vapor Tables

- To analyse a thermodynamic systems we need to know the energy values for water (or air) as a function of temperature and pressure
- Ideal would be to have simple equations to describe the relationships between properties (Equations of State)
 - For ideal gases very simple and accurate relation exist: $Pv = RT$, $du = c_v dT$, $dh = c_p dT$ (class 9)
 - For liquids, saturated liquid & vapor, vapor mixtures or superheated vapors such (simple) relations do not exist
 - Typically superheated vapors do not obey the ideal gas law
- Tables or diagrams are needed to find energy values
- Which tables and how to do that?

Table of Steam Properties		
P (kPa)	T (°C)	v (m³/kg)
100	100	1.696
100	120	1.793
100	160	1.984

ThermoNet: John Wiley Publishers

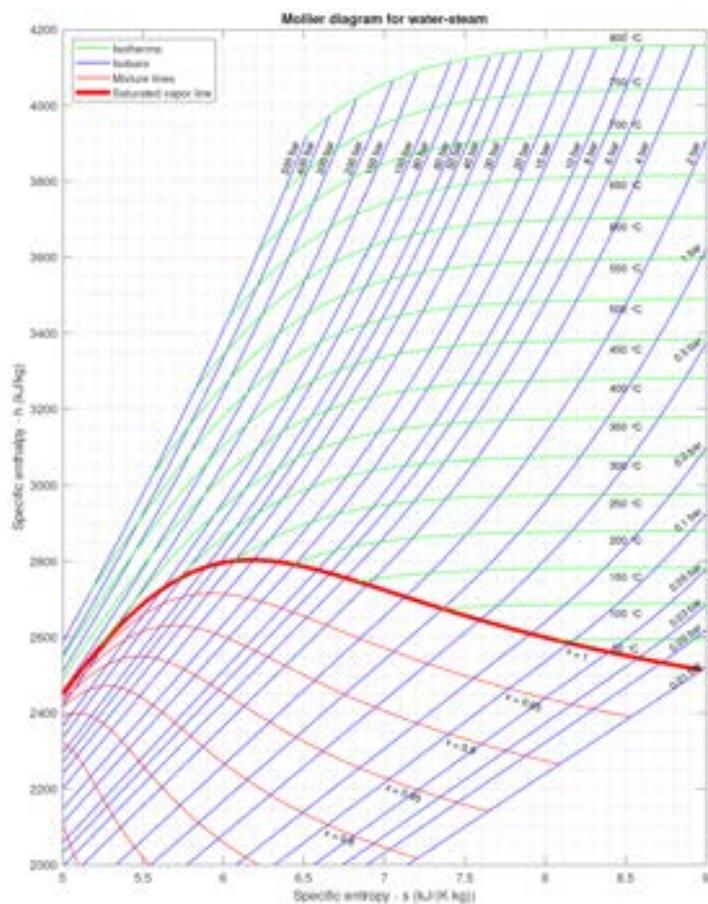
Liquid-Vapor Tables

- Tables
 - Saturated liquid-vapor tables (A4 & A5)
 - Superheated vapor tables (A6)
 - Compressed liquid tables (A7)
- Matlab (MopPro 2)
 - Xsteam.m, returns steam and water properties based on tabulated data



Example: XSteam('h_pt',1,20) returns the enthalpy of water at 1 bar and 20 degC → 84.0118 kJ/kg

- Diagram
 - Mixture (partly)
 - Superheated vapor



BREAK



<https://www.cafepress.com/+thermodynamics+mugs>

Saturated Liquid and Saturated Vapor Lines

- For **saturated values** use tables A4 and A5
- On the **saturated liquid and saturated vapor lines**
 - **Saturated liquid** denoted by **L** (e.g. v_L and u_L) (also f (fluid) is used)
 - **Saturated vapor** denoted by **V** (e.g. v_V and u_V) (also g (gas) is used)
 - **LV** = difference between saturated vapor and liquid values ($v_{LV} = v_V - v_L$)
- Under the dome in the **saturated liquid vapor region**
 - **Saturated mixture** denoted by **SAT** (T_{SAT} and P_{SAT})

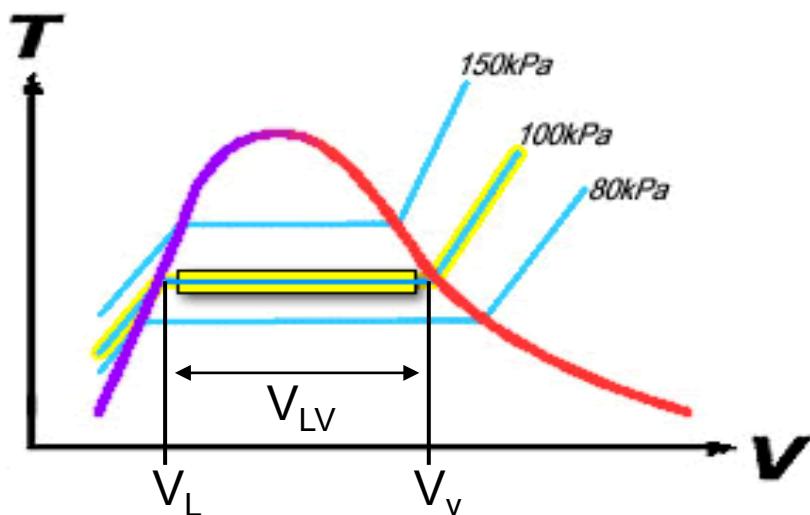


Table A5

Properties of Saturated Water - Press. Table (SI)

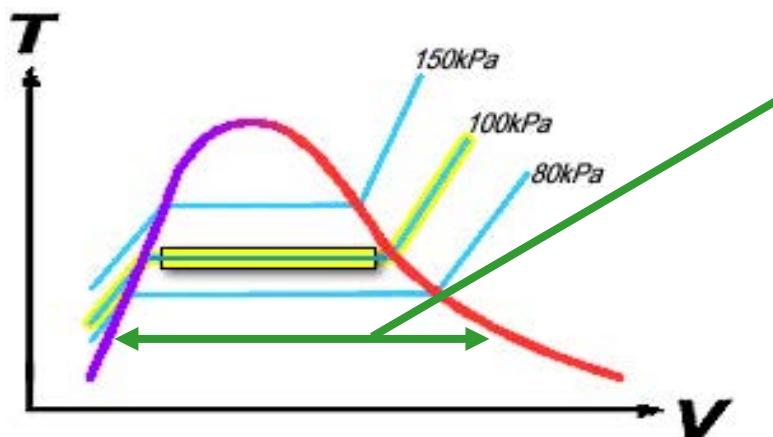
P kPa	T °C	Specific Volume, m ³ /kg		
		v _L	v _{LV}	v _V
80	93.511	0.001038	2.0866	2.0876
100	99.632	0.001043	1.6933	1.6943
150	111.38	0.001053	1.1584	1.1595

$$v_{LV} = v_V - v_L$$

Known P (for known T table A4)

Saturation and Quality

- Saturated liquid vapor region, this is under the vapor dome \rightarrow liquid and vapor in equilibrium
- P and T are coupled (dependent) \rightarrow extra parameter needed



Saturated mixture, T & P coupled \rightarrow extra parameter needed $\rightarrow x$

- Total mass = mass liquid +
mass vapor

$$m = m_l + m_v$$

- The ratio between mass of the vapor, m_v and total mass, m is denoted by the **quality (x)**: Mass fraction of saturated vapor

$$x = \text{Mass fraction of vapor} = \frac{\text{Mass of vapor}}{\text{Total mass of mixture}} = \frac{m_v}{m}$$

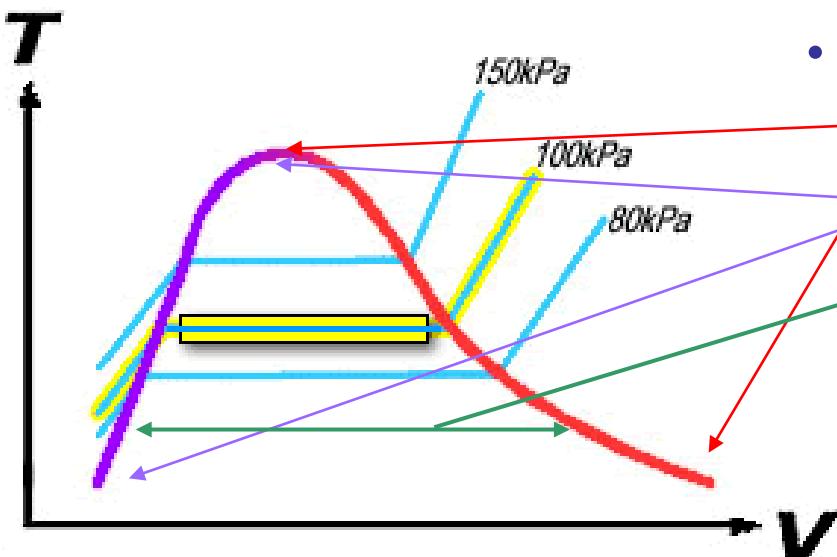
$$1-x = \text{Mass fraction of liquid} = \frac{\text{Mass of liquid}}{\text{Total mass of mixture}} = \frac{m_l}{m}$$

Saturation and Quality

- Saturated mixture → extra parameter needed
- The ratio between the mass of the vapor and the total mass is denoted by the **quality (x)**: Mass fraction of saturated vapor

$$x = \text{Mass fraction of vapor} = \frac{\text{Mass of vapor}}{\text{Total mass of mixture}} = \frac{m_v}{m}$$

$$1-x = \text{Mass fraction of liquid} = \frac{\text{Mass of liquid}}{\text{Total mass of mixture}} = \frac{m_l}{m}$$



- Quality (x) of a saturated mixture
 - Saturated vapor line $x = 1$
 - Saturated liquid line $x = 0$
 - In between, a saturated mixture $0 < x < 1$
- Outside the saturation area x is not defined! x is never negative or > 1

Saturation and Quality

- Specific volume, v , of saturated liquid vapor mixture with quality, x :

$$v = v_L + xv_{LV} \quad \text{or specific enthalpy: } h = h_L + xh_{LV}$$

- Quality of saturated liquid vapor mixture with specific volume, v

$$x = \frac{v - v_L}{v_v - v_L} = \frac{v - v_L}{v_{LV}} \quad \text{or with enthalpy, } h \quad x = \frac{h - h_L}{h_v - h_L} = \frac{h - h_L}{h_{LV}}$$

- These relations also hold for specific internal energy u (and entropy, s)

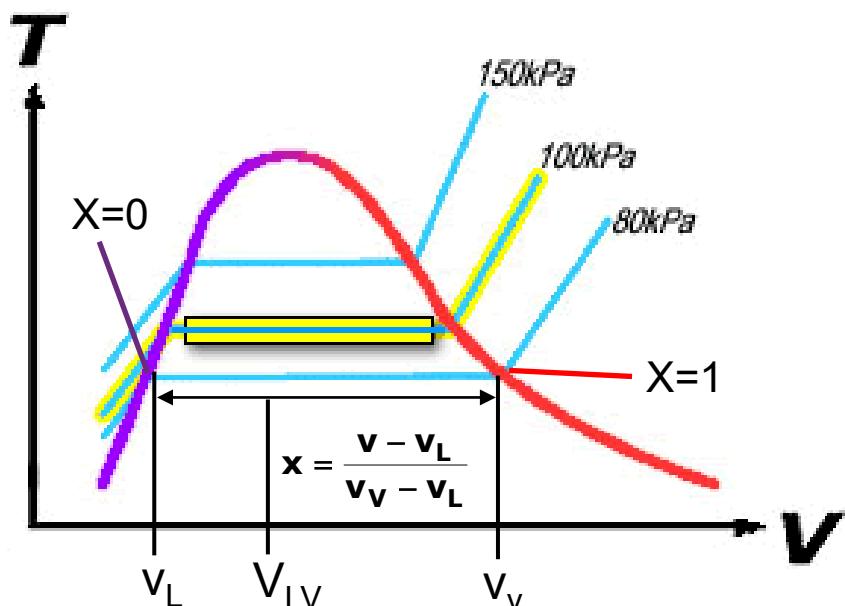


Table A5

Properties of Saturated Water - Press. Table (SI)

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		v_L	v_{LV}	v_V
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100	99.632	0.001043	1.6933	1.6943
150	111.38	0.001053	1.1584	1.1595

Example: Saturation and Quality

- Determine phase if:
 - $P = 100 \text{ kPa}$ and $v = 0.001000 \text{ m}^3/\text{kg}$
 - $P = 100 \text{ kPa}$ and $T = 100^\circ\text{C}$
 - $P = 100 \text{ kPa}$ and $v = 1.0000 \text{ m}^3/\text{kg}$
- $v < v_L$, liquid phase
- $T > T_{\text{sat}}$, vapor phase
- $v_L < v < v_v$, saturated mixture

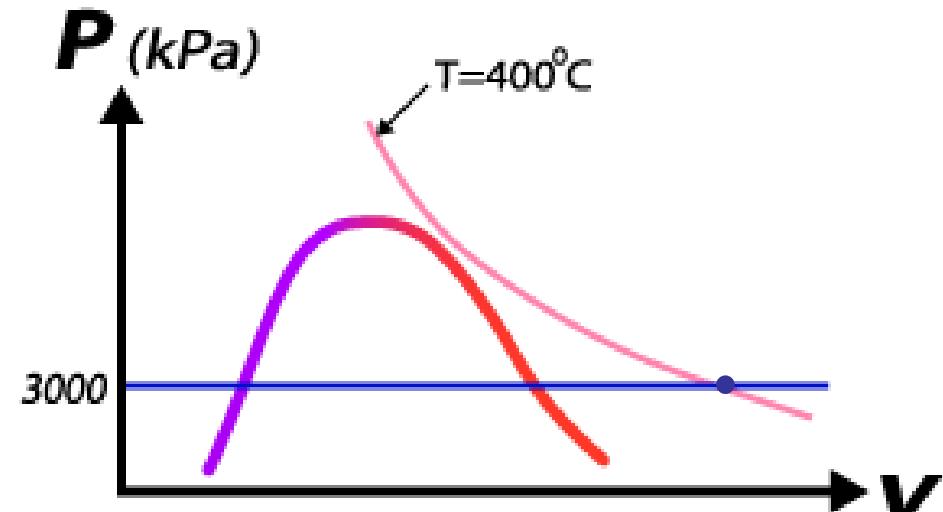
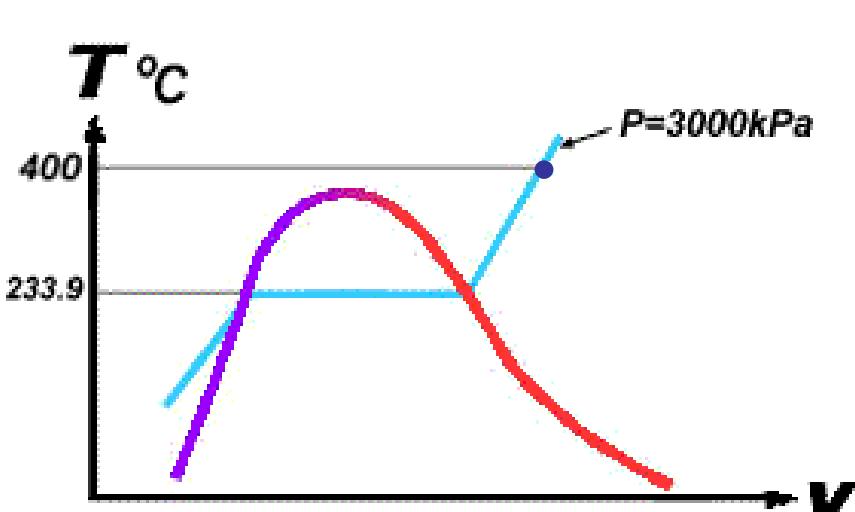
Table A5

Properties of Saturated Water - Press. Table (SI)

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		v_L	v_{LV}	v_v
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100	99.632	0.001043	1.6933	1.6943
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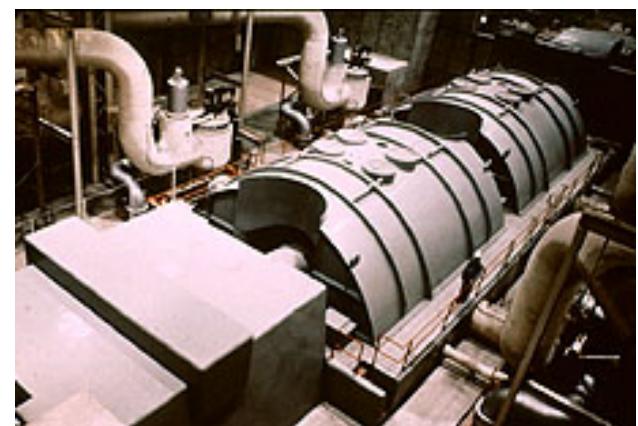
Superheated Vapor

- For superheated vapor values use table A6
 - Superheated vapor denoted by **SV**, (e.g. v_{SV} and u_{SV})



Steam entering the turbine is at
 $T = 400^{\circ}\text{C}$ & $P = 3000 \text{ kPa}$
 $T_{\text{SAT}@3000 \text{ kPa}} = 233.9^{\circ}\text{C}$

Since $T > T_{\text{SAT}}(P) \rightarrow \text{Superheated Vapor}$



Superheated Vapor

- Superheated vapor with: $P = 300 \text{ kPa}$ and $T = 200^\circ\text{C}$

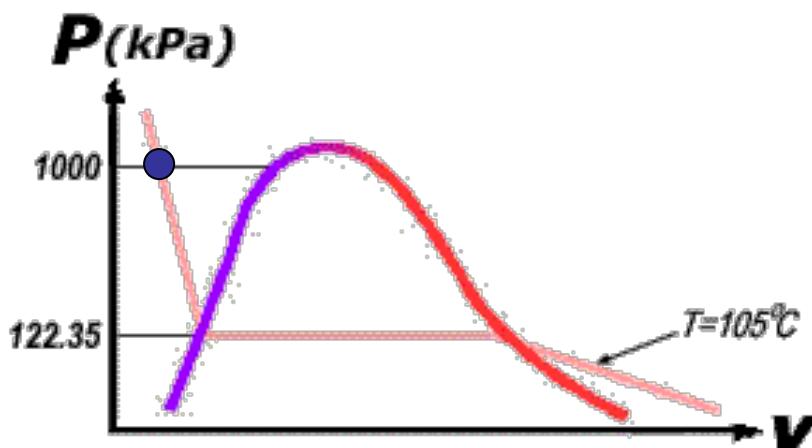
Table A6

Properties of Water in the Superheated Vapor State (SI)

P kPa	T °C	v m^3/kg	u kJ/kg	h kJ/kg	s $\text{kJ/(kg}\cdot\text{K)}$
200	(120.24)	(0.8859)	(2529.4)	(2706.5)	(7.1272)
	150	0.9597	2576.7	2768.6	7.2793
	200	1.0803	2653.9	2870.0	7.5059
	250	1.1988	2730.8	2970.5	7.7078
300	(133.56)	(0.6059)	(2543.5)	(2725.3)	(6.9921)
	150	0.6339	2570.7	2760.9	7.0779
	200	0.7163	2650.2	2865.1	7.3108
	250	0.7963	2728.2	2967.1	7.5157

Compressed (Subcooled) Liquids

- For compressed liquid values use table A7
 - Compressed liquid denoted by CL, (e.g. v_{CL} and u_{CL})

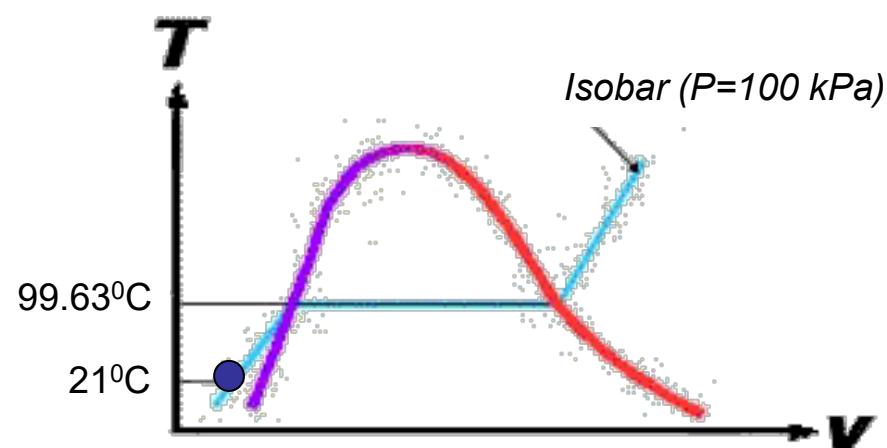


$$P = 1000 \text{ kPa} \text{ & } T = 105^\circ\text{C}$$

$$P_{SAT@105^\circ\text{C}} = 122.35 \text{ kPa}$$

Since $P > P_{SAT}(T)$

→ Compressed Liquid



$$T = 21^\circ\text{C} \text{ & } P = 100 \text{ kPa}$$

$$T_{SAT@100\text{kPa}} = 99.63^\circ\text{C}$$

Since $T < T_{SAT}(P)$

→ Subcooled Liquid

Incompressible Liquid Approx (ICL)

- Table A7 is only given for pressures above 5 MPa
- What to do for lower pressures?
- Use incompressible liquid approximation

Table A7

Properties of Water in the Compressed Liquid State (SI)					
P	T	v	u	h	s
kPa	°C	m³/kg	kJ/kg	kJ/kg	kJ/(kg·K)
5,000					
	50	0.001010	208.58	213.63	0.7014
	70	0.001020	291.97	297.07	0.9520

ThermoNet/Wiley

Table A4

		Properties of Saturated Water (SI)			Internal Energy, kJ/kg			
T	P	Specific Volume, m³/kg			Internal Energy, kJ/kg			
°C	kPa	v _L	v _{LV}	v _V	u _L	u _{LV}	u _V	
70	31.18	0.00102	5.0437	5.045	292.98	2175.8	2468.8	
:	:	:	:	:	:	:	:	:

Table A5

Properties of Saturated Water (SI)								
T	P	Specific Volume, m³/kg			Internal Energy, kJ/kg			
°C	kPa	v _L	v _{LV}	v _V	u _L	u _{LV}	u _V	
264	5000	0.00129	0.03815	0.039	1147.8	1448.7	2596.5	
:	:	:	:	:	:	:	:	:

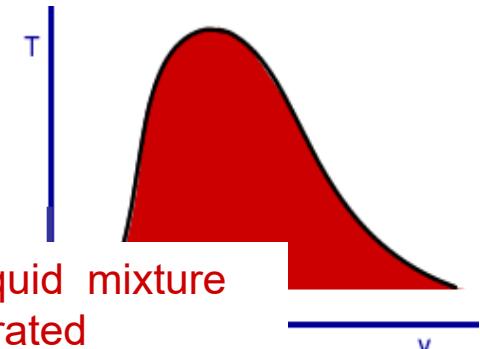
ThermoNet/Wiley

Incompressible Liquid Approx (ICL)

- $v_{CL}(T,P) \approx v_L(T)$
- **For all other properties**
- $u_{CL}(T,P) \approx u_L(T)$
- $h_{CL}(T,P) \approx h_L(T) + v_L(T) [P - P_{SAT}(T)]$
 - Recall $h = u + Pv \rightarrow h$ sensitive to P
 - If $P \approx P_{SAT}(T)$
 - $\rightarrow h_L(T) \gg v_L(T) [P - P_{SAT}(T)]$
 - $\rightarrow h_{CL}(T,P) \approx h_L(T)$
- **In conclusion:** in order to find a property in the compressed liquid region (with too low pressure for the compressed liquid tables) use the value of the saturated liquid at **the right temperature**
(Note: this is often forgotten)

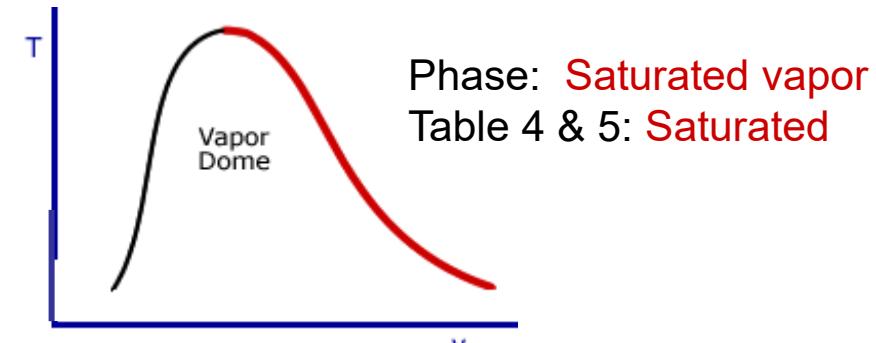
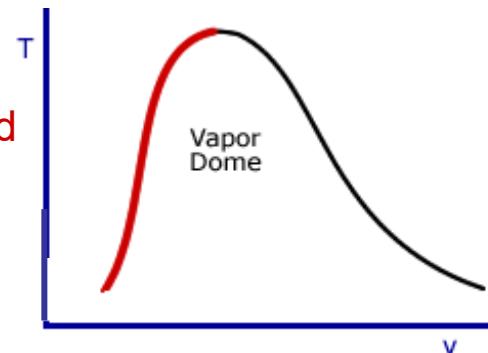
Overview Liquid-Vapor Diagram & Tables

- Regions in T-v diagrams and data tabulated
 - Saturated liquid-vapor
 - Compressed liquid
 - Superheated vapor
- Which region, which table?



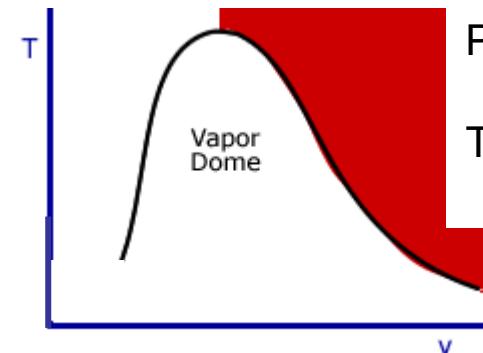
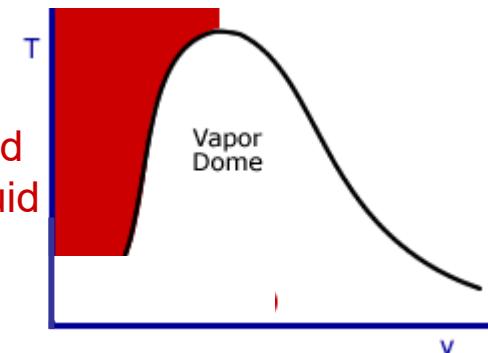
Phase: Saturated liquid mixture
Table 4 and 5: Saturated

Phase: Saturated liquid
Table 4 & 5: Saturated



Phase: Saturated vapor
Table 4 & 5: Saturated

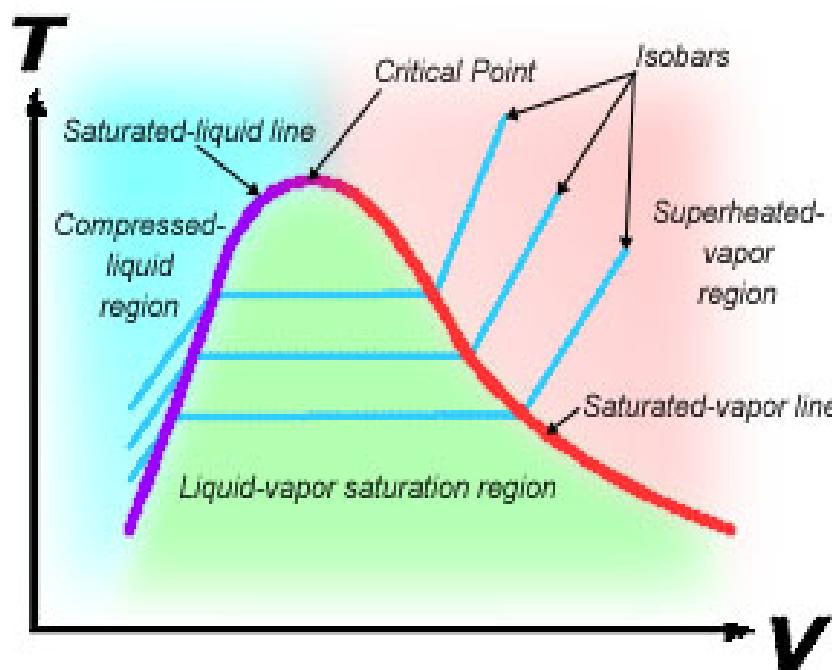
Phase: Compressed liquid
Table 7: Compressed liquid
(if not available use table
4 / 5 and ICL)



Phase: Superheated vapor
Table 6: Superheated vapor

Overview Liquid-Vapor Diagram & Tables

Region	Table nr refers to tables in Çengel and Boles
Compressed liquid	Properties of compressed liquid water (A7)
Saturated liquid line	Properties of saturated water: temperature table (A4)
Saturated vapor line	Properties of saturated water: pressure table (A5)
Saturated mixture	Quality x
Superheated vapor	Properties of superheated water (A6)



XSteam → ModPro2

Examples: Liquid-Vapor Diagram & Tables

- Water at 150 °C has a specific volume of 0.3928 m³/kg
- Find the pressure and specific enthalpy
- Properties of saturated water: temperature table

Temp (°C)	Pres (Bar)	Specific volume (m ³ /kg)		Internal Ener- gy (kJ/kg)		Enthalpy (kJ/kg)			Entropy (kJ/kgK)	
T	P	v _L × 10 ³	v _v	u _L	u _v	h _L	h _{lv}	h _v	s _L	s _v
120	1.985	1.0603	0.8919	503.50	2529.3	503.71	2202.6	2706.3	1.5276	7.1296
130	2.701	1.0697	0.6685	546.02	2539.9	546.31	2174.2	2720.5	1.6344	7.0269
140	3.613	1.0797	0.5089	588.74	2550.0	589.13	2144.7	2733.9	1.7391	6.9299
150	4.758	1.0905	0.3928	631.68	2559.5	632.20	2114.3	2746.5	1.8418	6.8379
160	6.178	1.1020	0.3071	674.86	2568.4	675.55	2082.6	2758.1	1.9427	6.7502
170	7.917	1.1143	0.2428	718.33	2576.5	719.21	2049.5	2768.7	2.0419	6.6663
180	10.02	1.1274	0.1941	762.09	2583.7	763.22	2015.0	2778.2	2.1396	6.5857

- Answer: P = 4.758 Bar, h = 2746.5 kJ/kg

Examples: Liquid-Vapor Diagram & Tables

- Water at 150 °C has a specific enthalpy (h) of 2800 kJ/kg.
- Find the pressure and specific volume.
- Properties of saturated water: temperature table

Temp (°C)	Pres (Bar)	Specific volume (m ³ /kg)		Internal Ener- gy (kJ/kg)		Enthalpy (kJ/kg)			Entropy (kJ/kgK)	
T	P	$v_L \times 10^3$	v_v	u_L	u_v	h_L	h_{lv}	h_v	s_L	s_v
120	1.985	1.0603	0.8919	503.50	2529.3	503.71	2202.6	2706.3	1.5276	7.1296
130	2.701	1.0697	0.6685	546.02	2539.9	546.31	2174.2	2720.5	1.6344	7.0269
140	3.613	1.0797	0.5089	588.74	2550.0	589.13	2144.7	2733.9	1.7391	6.9299
150	4.758	1.0905	0.3928	631.68	2559.5	632.20	2114.3	2746.5	1.8418	6.8379
160	6.178	1.1020	0.3071	674.86	2568.4	675.55	2082.6	2758.1	1.9427	6.7502
170	7.917	1.1143	0.2428	718.33	2576.5	719.21	2049.5	2768.7	2.0419	6.6663
180	10.02	1.1274	0.1941	762.09	2583.7	763.22	2015.0	2778.2	2.1396	6.5857

- Answer: P and v cannot be found from this table.
- $h = 2800 \text{ kJ/kg} > h_{v@150^\circ\text{C}} = 2746.6 \text{ kJ/kg}$, therefore this is a superheated vapor; to find P and v we need the superheated vapor table

Examples: Liquid-Vapor Diagram & Tables

- Water at 15 MPa has a specific volume of 0.001006 m³/kg. Find the temperature and enthalpy of the water.

• **Solution:**

1. Determine the phase

P is given, table A5

(properties of saturated water – pressure)

Examples: Liquid-Vapor Diagram & Tables

Water

$$P = 15 \text{ MPa}$$

$$v = 0.001006 \text{ m}^3$$

Table A5
(properties
of saturated
water – pressure

$$v_L @ 15000 \text{ kPa} =$$

$$0.001657 \text{ m}^3/\text{kg}$$

TABLE A1 Properties of Saturated Water — Pressure Table (SI) (continued)

P kPa	T °C	T °F	SPECIFIC VOLUME, m^3/kg			INTERNAL ENERGY, kJ/kg			ENTHALPY, kJ/kg			ENTROPY, $\text{kJ}/(\text{kg} \cdot \text{K})$		
			v_L	V_l	v_{LV}	u_L	u_{LV}	u_V	h_L	h_{LV}	h_V	s_L	s_{LV}	s_V
1400	195.08	195.08	0.001149	0.1397	0.1408	828.67	1763.6	2592.3	830.28	1959.1	2789.4	2.2842	4.1841	6.4683
1500	198.33	198.33	0.001154	0.1305	0.1317	843.12	1750.8	2593.9	844.85	1946.7	2791.5	2.3150	4.1288	6.4438
1600	201.41	201.41	0.001159	0.1225	0.1237	856.88	1738.4	2595.3	858.73	1934.6	2793.3	2.3441	4.0766	6.4207
1700	204.35	204.35	0.001163	0.1155	0.1167	870.02	1726.6	2596.6	872.00	1923.0	2795.0	2.3717	4.0272	6.3989
1800	207.15	207.15	0.001168	0.1092	0.1104	882.61	1715.1	2597.7	884.71	1911.7	2796.4	2.3980	3.9801	6.3781
1900	209.84	209.84	0.001172	0.1035	0.1047	894.70	1704.0	2598.7	896.92	1900.7	2797.6	2.4231	3.9353	6.3584
2000	212.42	212.42	0.001177	0.09841	0.09959	906.33	1693.2	2599.5	908.69	1890.0	2798.7	2.4471	3.8925	6.3396
2250	218.45	218.45	0.001187	0.08753	0.08872	933.70	1667.5	2601.2	936.37	1864.4	2800.8	2.5032	3.7926	6.2958
2500	223.99	223.99	0.001197	0.07875	0.07995	958.98	1643.3	2602.3	961.97	1840.2	2802.2	2.5544	3.7016	6.2560
2750	229.11	229.11	0.001207	0.07151	0.07272	982.53	1620.5	2603.0	985.85	1817.2	2803.0	2.6016	3.6178	6.2194
3000	233.89	233.89	0.001217	0.06544	0.06666	1004.6	1598.7	2603.3	1008.3	1795.0	2803.3	2.6454	3.5401	6.1855
3250	238.37	238.37	0.001226	0.06027	0.06150	1025.5	1577.7	2603.2	1029.5	1773.6	2803.1	2.6865	3.4673	6.1538
3500	242.60	242.60	0.001235	0.05582	0.05705	1045.3	1557.6	2602.9	1049.6	1753.0	2802.6	2.7251	3.3989	6.1240
3750	246.59	246.59	0.001244	0.05194	0.05318	1064.2	1538.1	2602.3	1068.8	1732.9	2801.7	2.7616	3.3341	6.0957
4000	250.39	250.39	0.001252	0.04852	0.04977	1082.2	1519.3	2601.5	1087.2	1713.4	2800.6	2.7962	3.2727	6.0689
5000	263.98	263.98	0.001286	0.03815	0.03944	1147.8	1448.7	2596.5	1154.2	1639.5	2793.7	2.9201	3.0524	5.9725
6000	275.62	275.62	0.001319	0.03112	0.03244	1205.4	1383.9	2589.3	1213.3	1570.6	2783.9	3.0266	2.8620	5.8886
7000	285.86	285.86	0.001352	0.02602	0.02737	1257.5	1322.7	2580.2	1267.0	1504.8	2771.8	3.1211	2.6919	5.8130
8000	295.04	295.04	0.001384	0.02214	0.02352	1305.5	1264.1	2569.6	1316.6	1441.2	2757.8	3.2066	2.5365	5.7431
9000	303.38	303.38	0.001418	0.01906	0.02048	1350.3	1207.3	2557.6	1363.1	1378.9	2742.0	3.2855	2.3916	5.6771
10,000	311.03	311.03	0.001452	0.01658	0.01803	1392.8	1151.4	2544.2	1407.3	1317.2	2724.5	3.3591	2.2548	5.6139
11,000	318.11	318.11	0.001488	0.01450	0.01599	1433.3	1096.2	2529.5	1449.7	1255.7	2705.4	3.4287	2.1238	5.5525
12,000	324.71	324.71	0.001526	0.01273	0.01426	1472.4	1041.0	2513.4	1490.7	1193.8	2684.5	3.4953	1.9968	5.4921
13,000	330.89	330.89	0.001566	0.01121	0.01278	1510.5	985.20	2495.7	1530.9	1130.9	2661.8	3.5595	1.8723	5.4318
14,000	336.70	336.70	0.001610	0.009870	0.01148	1547.9	928.40	2476.3	1570.4	1066.7	2637.1	3.6220	1.7491	5.3711
15,000	342.19	342.19	0.001657	0.008683	0.01034	1585.0	870.00	2455.0	1609.8	1000.3	2610.1	3.6837	1.6255	5.3092
16,000	347.39	347.39	0.001710	0.007600	0.009310	1622.1	809.20	2431.3	1649.5	930.80	2580.3	3.7452	1.4999	5.2451
17,000	352.34	352.34	0.001770	0.006603	0.008373	1659.9	744.90	2404.8	1690.0	857.10	2547.1	3.8073	1.3704	5.1777
18,000	357.04	357.04	0.001840	0.005665	0.007505	1698.9	675.70	2374.6	1732.0	777.70	2509.7	3.8714	1.2340	5.1054

→ $v < v_L \rightarrow$ compressed liquid ($T_{sat@15000\text{kPa}} = 342.19^\circ\text{C}$)

Examples: Liquid-Vapor Diagram & Tables

Up to now we know:

- Water
- Compressed liquid
- $P = 15 \text{ MPa} = 15000 \text{ kPa}$
- $v = 0.001006 \text{ m}^3/\text{kg}$
- Compressed liquid table A7
- At 15000 kPa look for the volume and see:

$$T = 50^\circ\text{C} \text{ and } h = 222.22 \text{ kJ/kg}$$

TABLE 13S Properties of Water in the Compressed Liquid State (SI)

P kPa	P	T $^\circ\text{C}$	T	v m^3/kg	u kJ/kg	h kJ/kg	h	s $\text{kJ/(kg} \cdot \text{K)}$
5,000								
	10	0.000998		41.860		46.850		0.1505
	30	0.001002		125.21		130.22		0.4350
	50	0.001010		208.58		213.63		0.7014
	70	0.001020		291.97		297.07		0.9520
	90	0.001034		375.59		380.75		1.1890
	110	0.001049		459.63		464.88		1.4145
	130	0.001067		544.28		549.61		1.6301
	150	0.001087		629.68		635.12		1.8371
	170	0.001111		716.04		721.59		2.0367
	190	0.001138		803.64		809.33		2.2304
	210	0.001169		892.89		898.74		2.4193
	230	0.001206		984.40		990.43		2.6053
	250	0.001250		1079.0		1085.3		2.7901
10,000								
	10	0.000996		41.729		51.685		0.1500
	30	0.001000		124.75		134.75		0.4334
	50	0.001008		207.85		217.93		0.6991
	70	0.001018		290.98		301.16		0.9491
	90	0.001031		374.32		384.63		1.1855
	110	0.001046		458.07		468.53		1.4104
	130	0.001064		542.38		553.02		1.6253
	150	0.001084		627.41		638.25		1.8316
	170	0.001107		713.31		724.39		2.0305
	190	0.001133		800.37		811.70		2.2232
	210	0.001164		888.94		900.57		2.4111
	230	0.001199		979.55		991.54		2.5955
	250	0.001241		1073.0		1085.4		2.7784
	270	0.001292		1170.3		1183.2		2.9619
	290	0.001357		1273.5		1287.1		3.1497
15,000								
	10	0.000993		41.593		56.493		0.1494
	30	0.000998		124.30		139.27		0.4319
	50	0.001006		207.13		222.22		0.6968
	70	0.001016		290.01		305.25		0.9461
	90	0.001029		373.08		388.51		1.1820
	110	0.001044		456.54		472.20		1.4063
	130	0.001061		540.53		556.45		1.6206
	150	0.001081		625.19		641.41		1.8263
	170	0.001104		710.67		727.22		2.0244
	190	0.001129		797.20		814.14		2.2163

Examples: Liquid-Vapor Diagram & Tables

- Water at 15 MPa has a specific volume of 0.001006 m³ /kg.
- Find the temperature and enthalpy of the water
- **Solution:**

1. Determine the phase

P is given, table A5 (properties of saturated water – pressure) gives:

$$v_L@15000\text{kPa} = 0.001657\text{m}^3/\text{kg}$$

$$v < v_L \rightarrow \text{compressed liquid} \quad (T_{\text{sat}@15000\text{kPa}} = 342.19^\circ\text{C})$$

2. Compressed liquid table A7, 15000 kPa and $v = 0.001006 \text{ m}^3/\text{kg}$

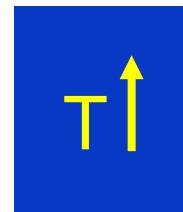
$$T = 50^\circ\text{C} \text{ and } h = 222.22 \text{ kJ/kg}$$

3. The water is in the compressed liquid phase, the temperature is 50°Celsius which is indeed lower than the 342.19°C which is the saturation temperature of water at 15 MPa

Specific heat

- **Specific heat, c [kJ/kgK]:** the amount of energy required to raise the temperature of a unit mass of a substance by one degree in a specified way

- Approximately specific is defined as: $c \approx \frac{de}{dT}$

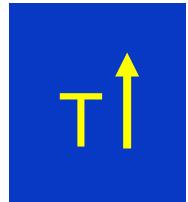


- **The specific heat depends on:**
 - The substance (water, oil, air, helium, steel, wood,...)
 - The temperature
 - The process (constant pressure or constant volume)



Specific heat

- Depending on the **process** different forms of heat capacity are defined (more about this when gases are studied in class 9)



- Specific heat at constant volume, c_v :** The energy required to raise the temperature of a unit mass of a substance by one degree as the volume is maintained constant
- Specific heat at constant pressure, c_p :** The energy required to raise the temperature of a unit mass of a substance by one degree as the pressure is maintained constant

Specific heat

- Depending on the process different forms of heat capacity are defined c_v (**constant volume**) and c_p (**constant pressure**)
- **Solids and liquids are incompressible**, volume does not change, therefore $v = \text{constant}$, no difference between specific heat for constant pressure and constant volume
- For solids and liquids: $c_p = c_v$ (sometimes denoted as c)

$$\Delta e \approx \Delta u \approx \Delta h = \int_{T_1}^{T_2} c \, dT$$

- Values of c_p and c_v can be found in tables
- Tables A2 (gasses), A3 (liquids / solids) and A27 (fuels and hydrocarbons)
- Note: for gases c_p and c_v have different values, we will treat this later in class 9

Old Faithful Geyser (Yellowstone Nat. Park)

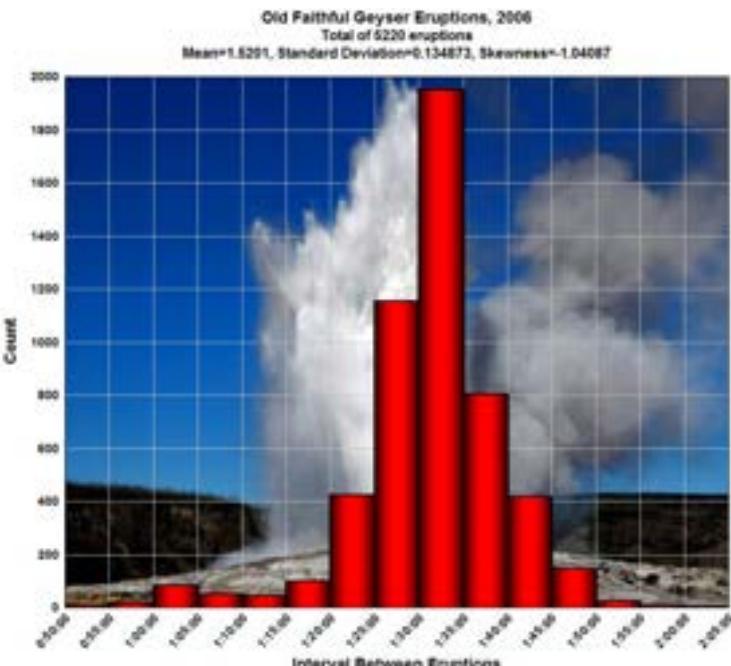


Old Faithfull eruption

http://www.youtube.com/watch_popup?v=tShhZvvIM84&vq=medium#t=32

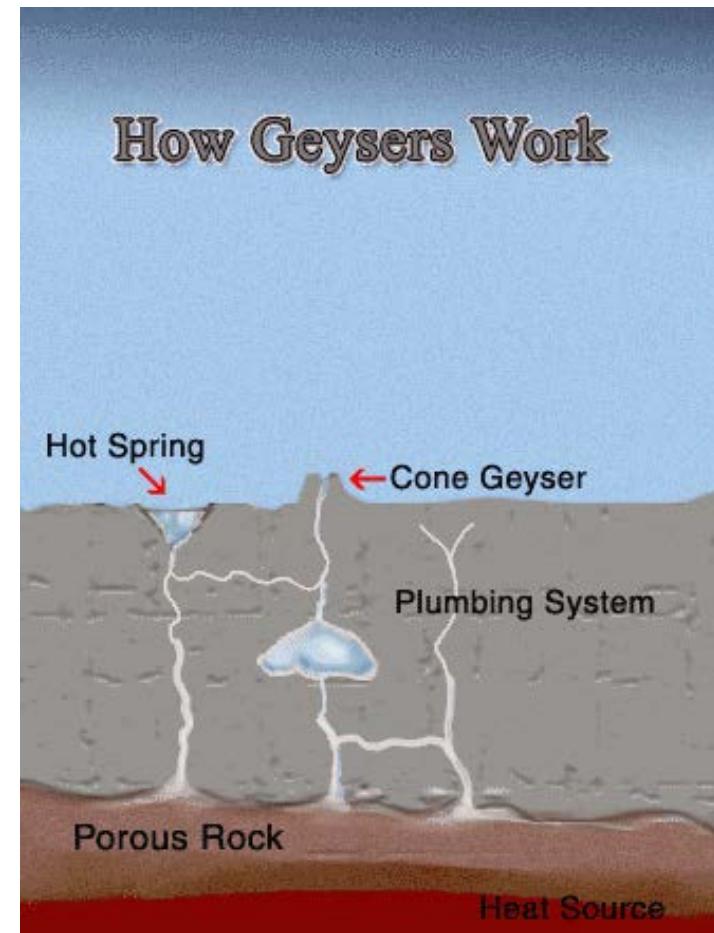
How does it work?

http://www.youtube.com/watch_popup?v=X4zA_YPCyHs&vq=medium#t=32



How works a hot water geyser?

- For geyser to occur there must be heat, water, and a plumbing system. A magma chamber provides the heat, which radiates into surrounding rock. Water from rain and snow works its way underground through fractures in the rock.
- As the water reaches hot rock it begins to rise back to the surface, passing through rhyolite, which is former volcanic ash or lava rich in silica. The hot water dissolves the silica and carries it upward to line rock crevices. This forms a constriction that holds in the mounting pressure, creating a geyser's plumbing system.
- As superheated water nears the surface, its pressure drops, and the water flashes into steam as a geyser. Hot springs have unconstricted plumbing systems.

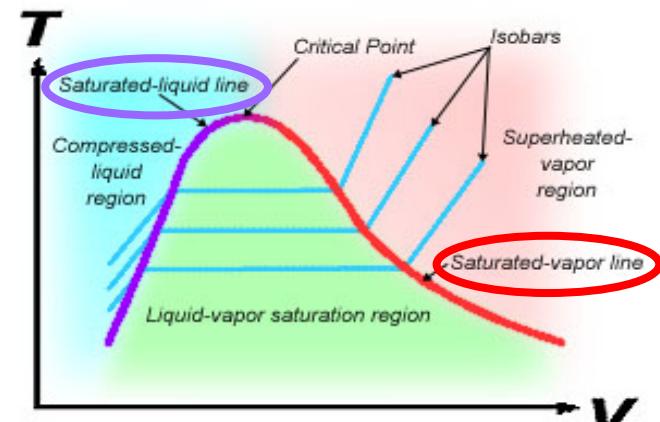


(Extra information, not part of the exam)

https://www.youtube.com/watch?v=x9UEKCYIM-I&feature=emb_rel_pause

Recapitulate class 3

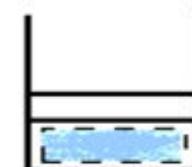
- Pure substances change phases
 - Solid, liquid, gas phase
 - Saturated mixtures of them
- Different regions P – v – T diagram
 - Vapor dome, critical point
 - Saturated liquid and saturated vapor line
 - Liquid-vapor saturated region
 - Saturated mixture, constant dependent P_{sat} and T_{sat} in the mixture region
 - Quality of the mixture: $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
 - Compressed liquid region
 - Superheated vapor region
- Tables to find values of v , u , s and h
- Specific heat of a liquid



T-v diagram of water showing the vapor dome and the different regions

Next Class 4: First law of Thermodynamics

- Energy balance of closed systems
- Conservation of mass and mass balances
- Flow work
- Total energy of a flowing fluid
- Energy balance of steady flow systems
- Applications of the first law of thermodynamics to
 - Turbines
 - Compressors
 - Pumps, blowers
 - Nozzles and diffusers
 - Throttling valves
 - Heat exchangers
 - Mixing device



Air being heated inside the cylinder shows energy transfer in a closed system

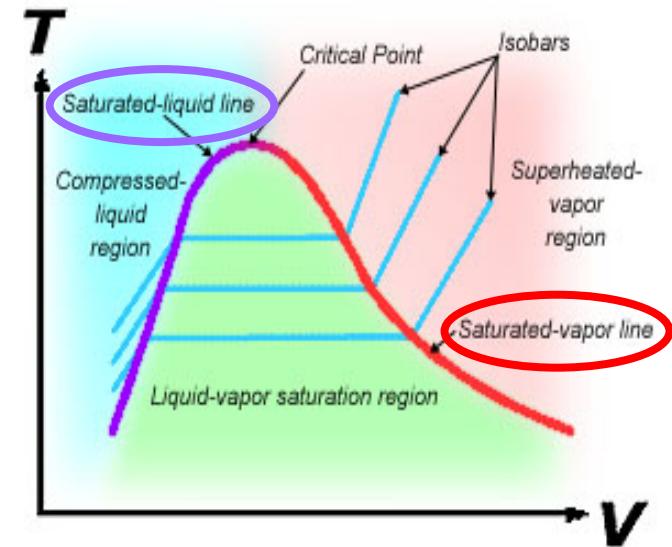


A rocket demonstrates some of the energy flows that can occur in an open system

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 (and not velocity!)
- Conservation of energy (first law) $E_{in} - E_{out} = \Delta E_{system}$
- Efficiency $\eta_{thermal} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Different phases in phase diagrams
- Mixture fraction

$$x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$$



Class 4

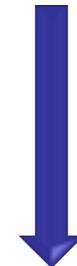
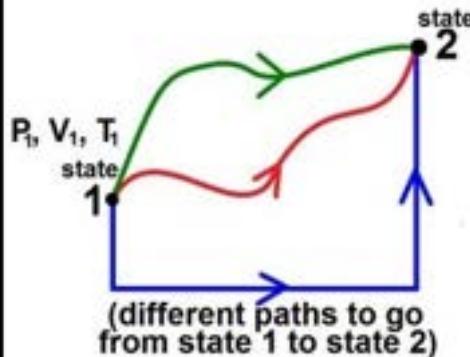
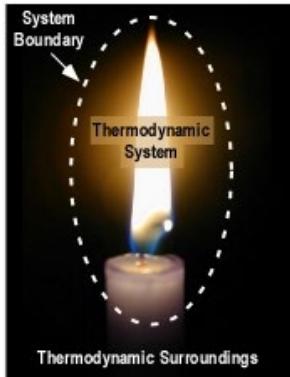
The first law of thermodynamics

Steam power
trains are still in
use on touristic
railways
(Simpelveld)

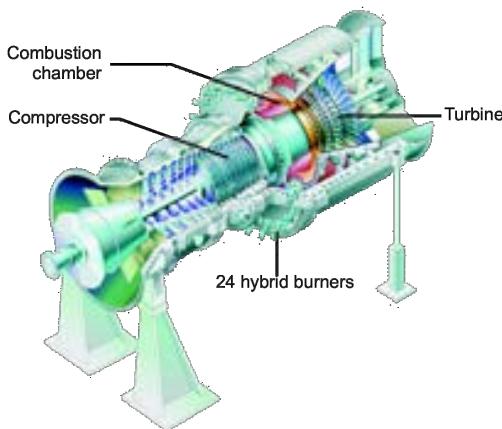


Roadmap Engineering Thermodynamics

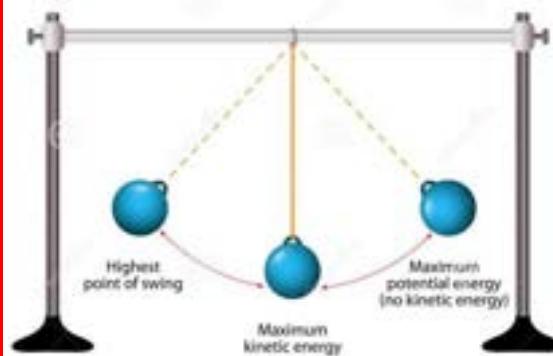
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



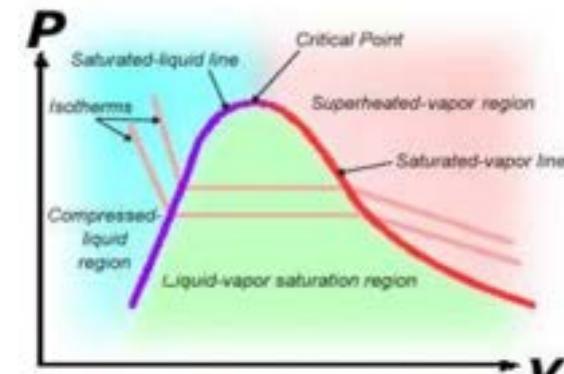
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

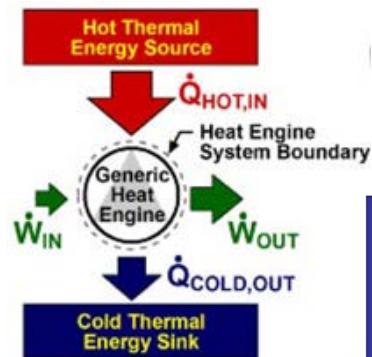


- Properties of Substances (Class 3, 9)

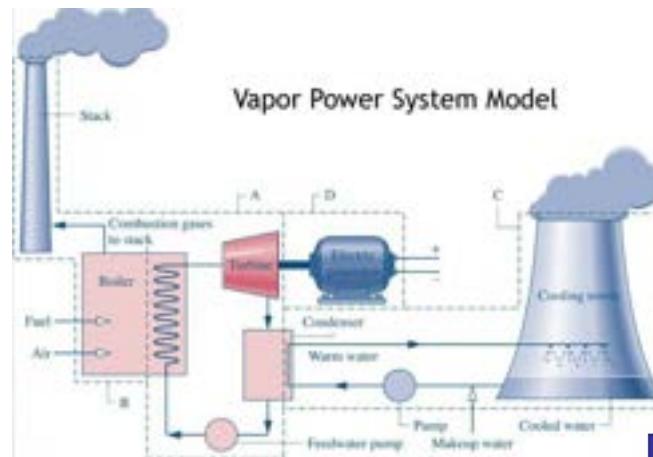


Roadmap Engineering Thermodynamics

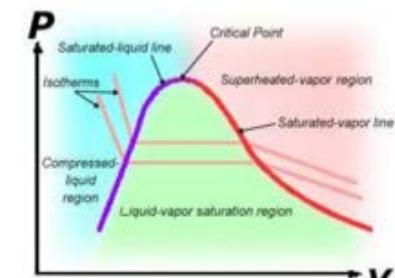
Thermodynamic cycles (Class 6)



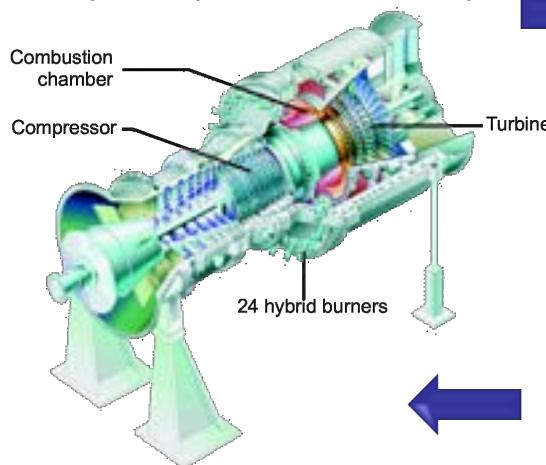
Vapor power cycles – Rankine cycle (Class 7, 8)



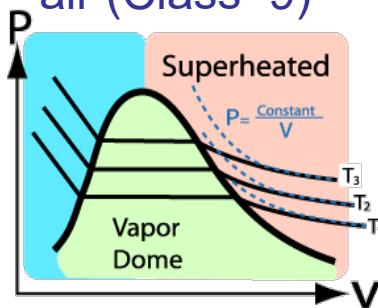
Properties of water (Class 3)



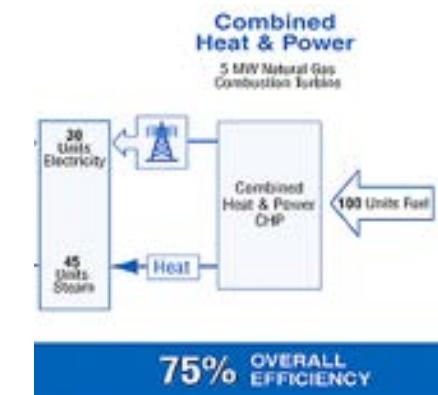
Gas power cycles – Brayton cycle (Class 10, 11)



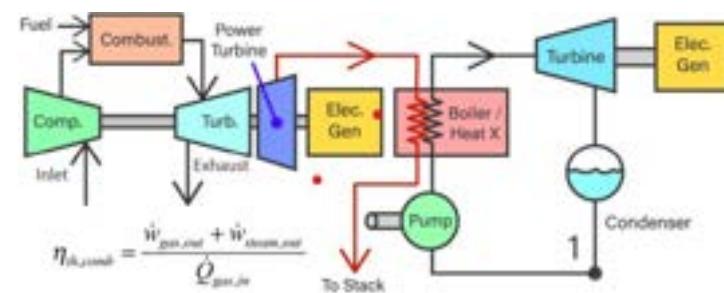
Properties of air (Class 9)



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

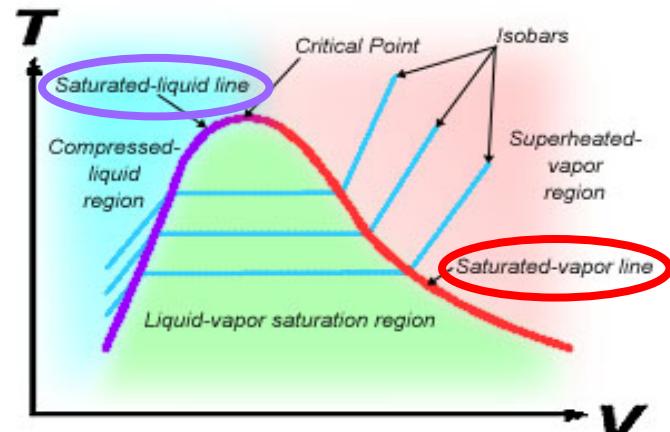


75% OVERALL EFFICIENCY



Recapitulate class 3

- Pure substances change phases
 - Solid, liquid, gas phase
 - Saturated mixtures of them
- Different regions P – v – T diagram
 - Vapor dome, critical point
 - Saturated liquid and saturated vapor line
 - Liquid-vapor saturated region
 - Saturated mixture, constant dependent P_{sat} and T_{sat} in the mixture region
 - Quality of the mixture: $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
 - Compressed liquid region
 - Superheated vapor region
- Tables to find values of v , u , s and h
- Specific heat of a liquid

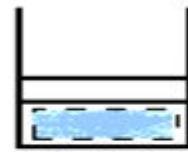


T-v diagram of water showing the vapor dome and the different regions

$$\text{Quality of the mixture: } x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$$

Content Class 4

- **The first law of thermodynamics**
- Conservation of energy, **first law of thermodynamics**
 - Closed system / open system
- Conservation of mass
- Application to steady-state steady-flow processes
 - Turbines
 - Compressors
 - Pumps, blowers
 - Nozzles and diffusers
 - Throttling valves
 - Heat exchangers
 - Mixing device
- **Learning goal:** explain the laws of thermodynamics, apply these to thermodynamic systems and interpret the effects



Air being heated inside the cylinder shows energy transfer in a closed system



A rocket demonstrates some of the energy flows that can occur in an open system

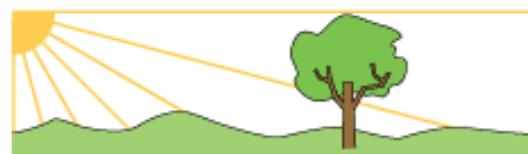
The First Law of Thermodynamics

- One of the most fundamental principles of nature, **the conservation of energy principle**, is formulated in the **first law of thermodynamics**
- It states that energy can change from one form to another during an interaction but the total amount of energy remains constant

Changing forms of energy



An automobile engine changes chemical energy to mechanical and heat energy.



A tree changes radiant energy to chemical energy.



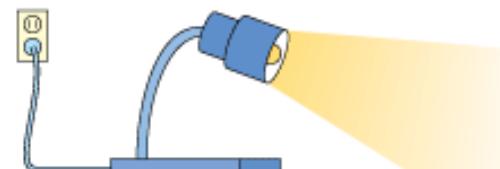
Hammering a nail changes mechanical energy to deformation and heat energy.



A thermonuclear reaction changes nuclear energy to radiant and heat energy.



An electric mixer changes electrical energy to mechanical and heat energy.



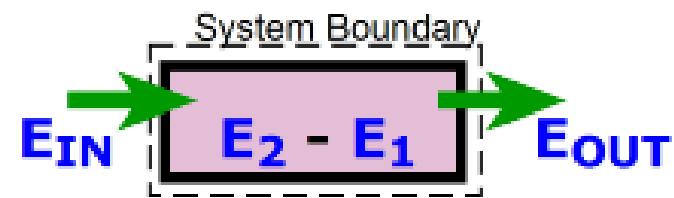
A lamp changes electrical energy to radiant and heat energy.

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The First Law of Thermodynamics

First law of thermodynamics = conservation of energy = energy cannot be destroyed or created but only be transformed into another form

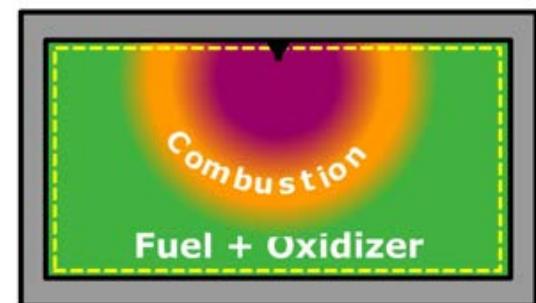
- We already met the zeroth law of thermodynamics, and in class 5 we will also meet the second and third law of thermodynamics
- In this class we will elaborate the formula for the conservation of energy for a closed and an open system and apply it to all kinds of thermodynamical devices
- $\Delta E = E_{\text{in}} - E_{\text{out}} = E_2 - E_1$
- The change in energy within the system is the energy that flows into the system minus energy that flows out of the system



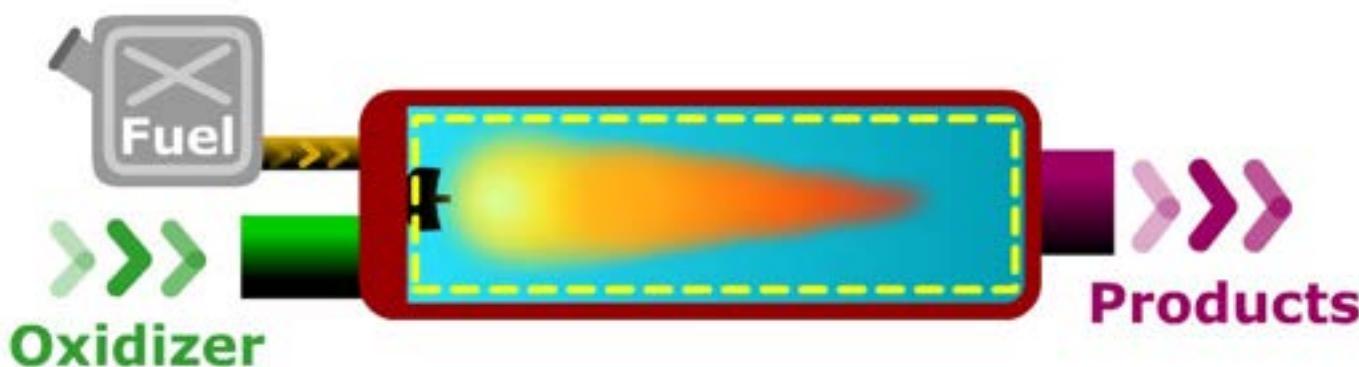
Combustion in open and closed system

- Mathematically the first law is different for open and closed systems
- What is the difference between open and closed systems?
- Mass crossing the system boundary, so also the mass plays a role in analyzing the systems

Combustion in a closed system, only heat can cross the system boundary



Combustion in an open system, also mass (fuel, oxidizer and combustion products) can cross the system boundary



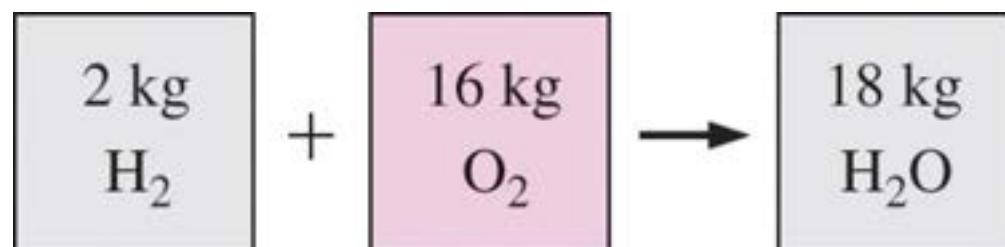
Conservation of mass

- Like energy also mass is conserved
- Like energy mass cannot be destroyed or created



- Even though the matter may change from one form to another, the same number of atoms exists before and after the change takes place
- Mass balance:

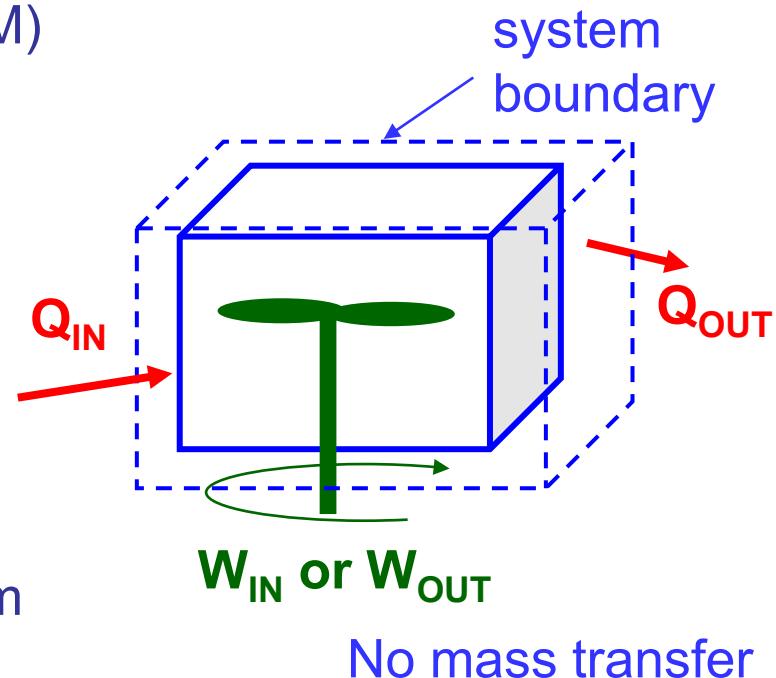
$$m_{in} = m_{out}$$



Mass is conserved even during chemical reactions

Closed systems / Control mass

- **Closed system:** mass cannot cross the system boundary, but energy (heat and work) can cross the system boundary
- Closed system is called **control mass (CM)**
- No change of mass for a closed system
- The mass balance
 - $m_{cm} = \text{constant} \rightarrow \frac{dm_{cm}}{dt} = \dot{m} = 0$
- During time, the mass of the closed system does not change
- Energy can change due to work and heat transfer



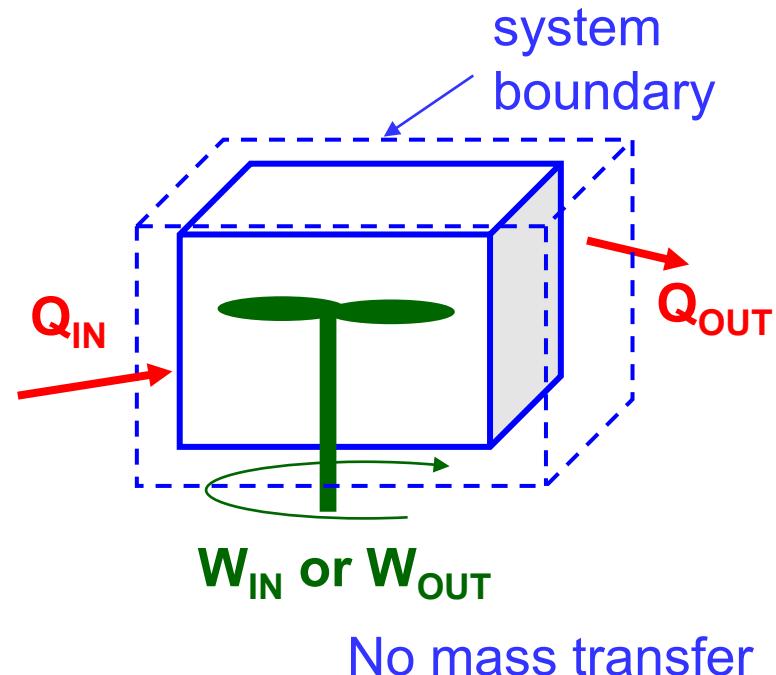
Closed systems / Control mass

- Energy balance: $\dot{E}_{in} - \dot{E}_{out} = \frac{dE_{cm}}{dt}$ [$\frac{J}{s} = W$]

- Energy in the control mass: $E_{cm} = U + KE + PE \approx U$ (*)
- Energy transfer: $\dot{E}_{in,out} = \dot{Q}_{in,out} + \dot{W}_{in,out}$
- Alternative notations

- Total energy
 $E_{in} - E_{out} = \Delta E_{cm}$ [J]
- Specific energy
 $e_{in} - e_{out} = \Delta e_{cm}$ [J/kg]

(*) In engineering applications often KE and PE are constant $\rightarrow E \approx U$ & $\Delta E \approx \Delta U$



Closed systems / Control mass

- The total energy change for a closed system is:

$$\Delta E_{cm} = E_{in} - E_{out} = (Q_{in} + W_{in}) - (Q_{out} + W_{out})$$

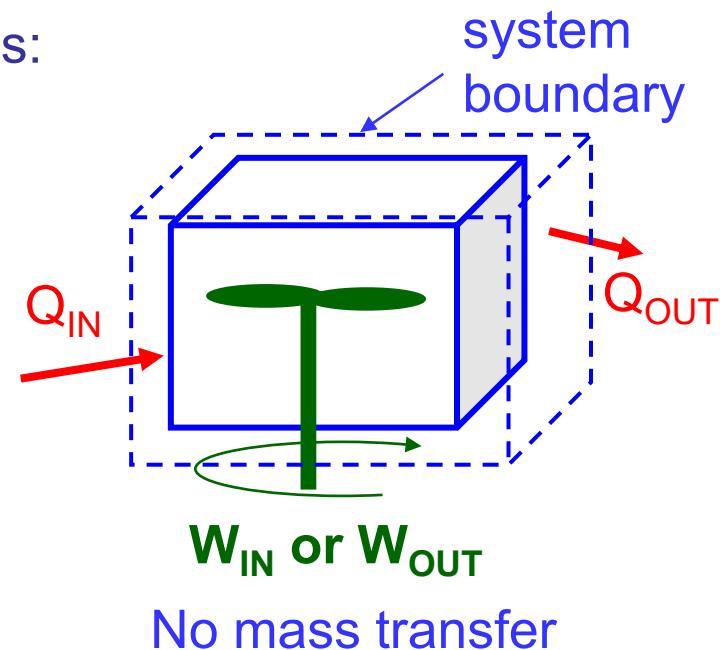
$$\Delta E_{cm} = (Q_{in} - Q_{out}) - (W_{out} - W_{in}) = Q_{net} - W_{net} \approx \Delta U_{cm}$$

- This results in the first law for closed systems:

- Total energy (J): $\Delta U_{cm} = Q_{net} - W_{net}$

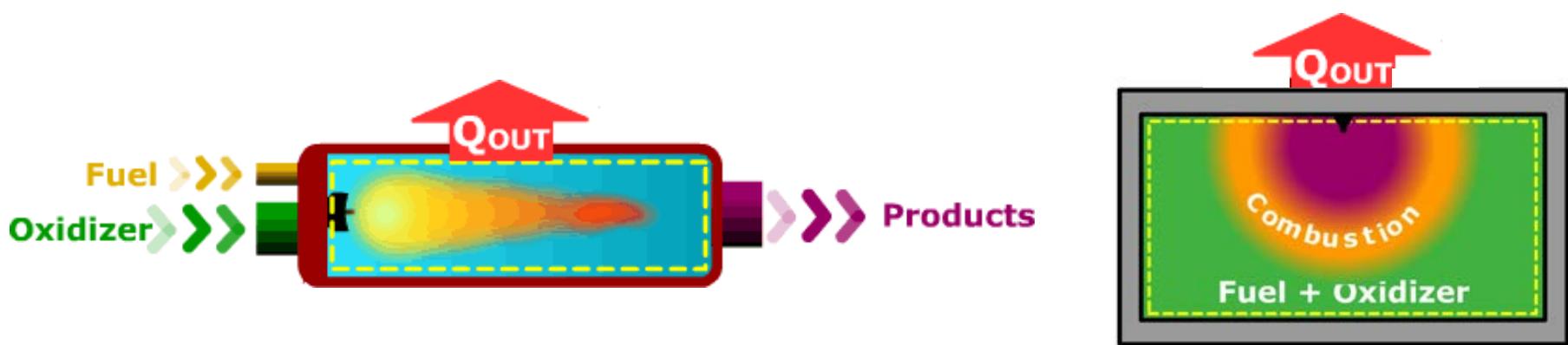
- Per unit mass (J/kg): $\Delta u_{cm} = q_{net} - w_{net}$

- Differential form: $du_{cm} = \delta q_{net} - \delta w_{net}$



Open systems / Control volume

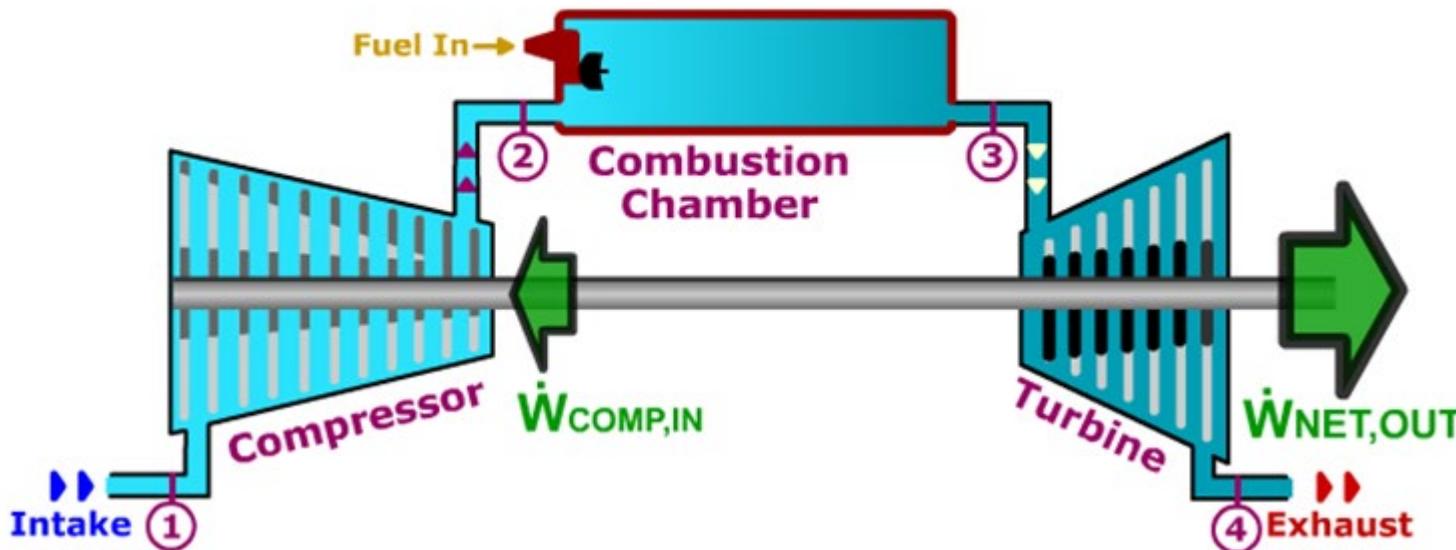
- **Open system:** both mass and energy (heat and work) can cross the system boundary
- Open system is called a **control volume (CV)**
- Compare combustion in open and closed systems



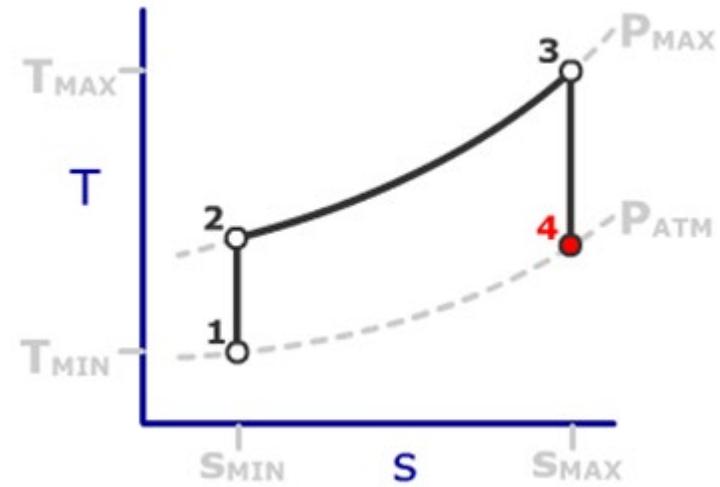
- Closed system only change of energy
- Open system change of mass and energy
 - The mass flow has to be taken into account

Open systems / Control volume

Stationary Gas Turbine



- A gas turbine or steam turbine cycle is analyzed as an open system
- The first law is applied to all individual components of the cycle



Open systems / Control volume

- For an open system, the mass balance is:

$$\dot{m}_{in} - \dot{m}_{out} = \frac{dm_{cv}}{dt} \quad [\frac{kg}{s}]$$

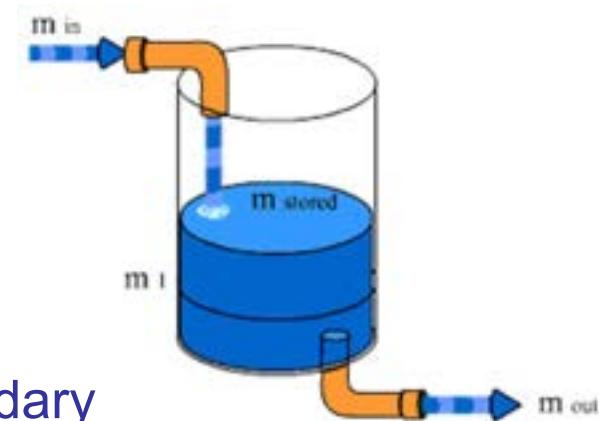
- $\dot{m}_{in,out}$ = mass transferred across system boundary per unit time [kg/s]
- m_{cv} = mass contained within the system boundary in the open system / control volume [kg]
- $\frac{dm_{cv}}{dt}$ = change of mass per unit time in the open system

- On a time interval:

$$\Delta m = \int \frac{dm_{cv}}{dt} dt = \int_{t=t_1}^{t_2} [\dot{m}_{in}(t) - \dot{m}_{out}(t)] dt = m_{cv}(t_2) - m_{cv}(t_1)$$

- So the mass balance for an open system is:

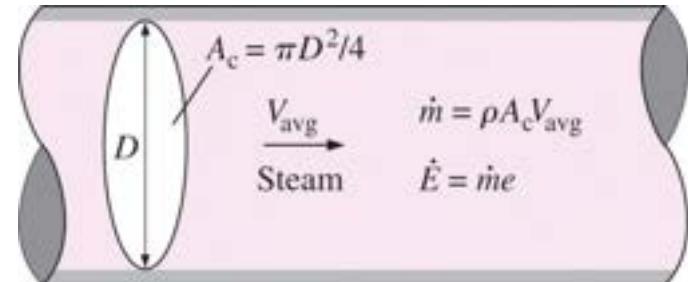
$$m_{in} - m_{out} = \Delta m_{cv} \quad [kg]$$



Mass flow and volume flow

- Relation between **mass flow** and **volume flow**

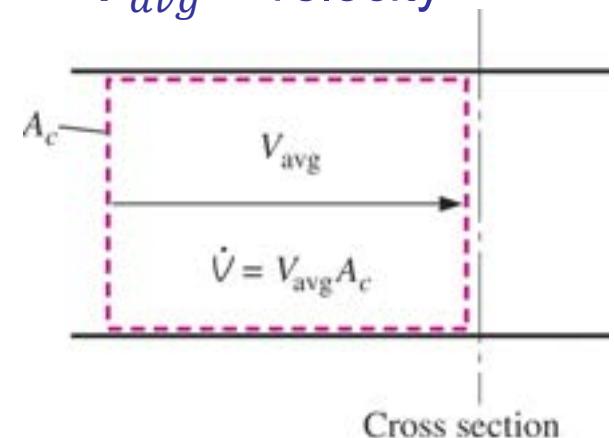
- Assume a fluid flowing through a pipe



- Mass flow:** amount of mass per unit time $\rightarrow \dot{m}$ (kg/s)
- Volume flow:** amount of volume per unit time $\rightarrow \dot{V}$ (m³/s)

$$\dot{m} = \rho \dot{V} = \rho A_c V_{avg} = \frac{A_c V_{avg}}{\nu} = \frac{\dot{V}}{\nu}$$

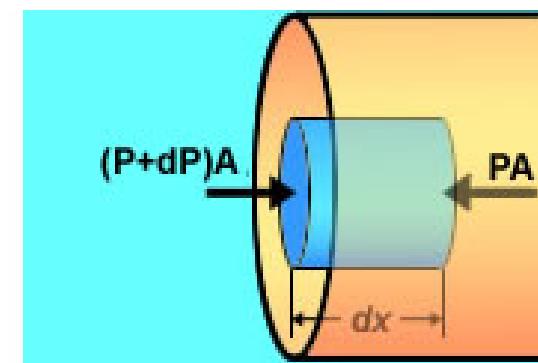
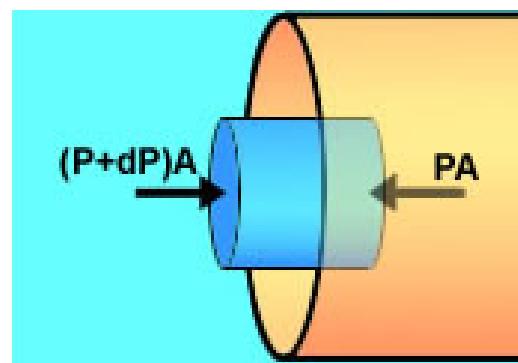
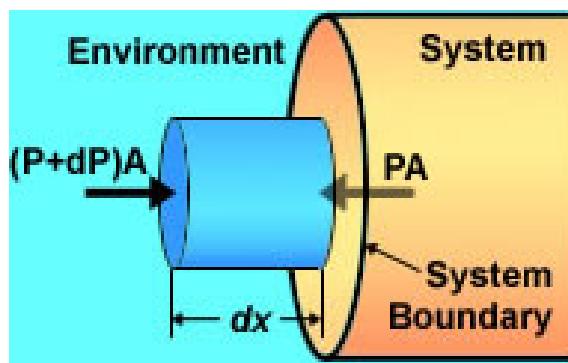
V_{avg} = velocity



- $\rho = 1/\nu$ = density [kg/m³]
- ν = specific volume [m³/kg]
- $\dot{V} = A_c V_{avg}$ = volume flow rate [m³/s]
- A_c = cross-sectional flow area [m²]
- V_{avg} = velocity perpendicular to area A_c [m/s]

Recall: Flow work & enthalpy in open systems

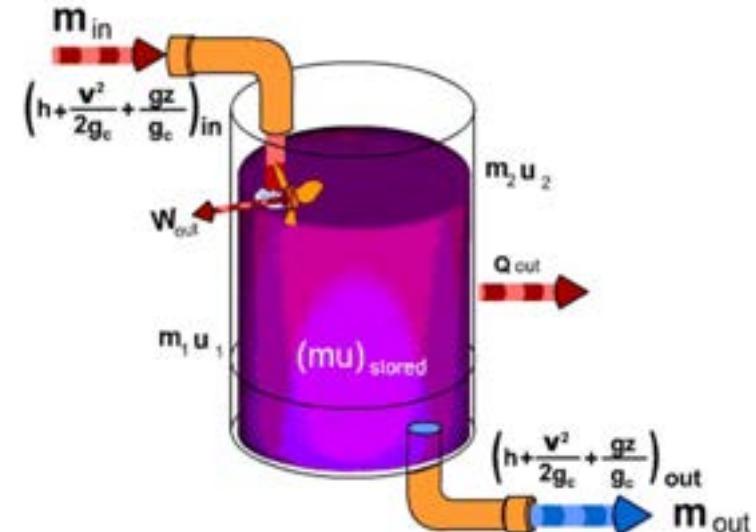
- **Flow work** is the work required to push mass across the system boundary and into the open system
 - Carries energy $u + ke + pe$ per unit mass flow
 - Does flow work Pv per unit mass flow
 - Recall enthalpy, $h = u + Pv$
 - Total energy entering / leaving system due to mass transfer is $u + ke + pe + Pv = h + ke + pe$ per unit mass flow.



Open systems / Control volume

- In an open system a change in energy can occur by:
 - Mass flowing in and out, including flow work ($h + \frac{v^2}{2g_c} + \frac{gz}{g_c}$)
 - Work (w)
 - Mechanical work: present if e.g. a rotating shaft crosses the boundary
 - Boundary (PdV) work: present if $dV_{CV}/dt \neq 0$
 - Heat Transfer (q)
- The energy inside the system can change due to an increase or decrease of mass
- The energy balance for an open system:

$$\dot{E}_{in} - \dot{E}_{out} = \frac{dE_{cv}}{dt} \quad [\frac{J}{s} = W]$$



Open systems / Control volume

- Energy balance:

$$\dot{E}_{in} - \dot{E}_{out} = \frac{dE_{cv}}{dt} \quad [\frac{J}{s} = W]$$

- Energy in the control volume:

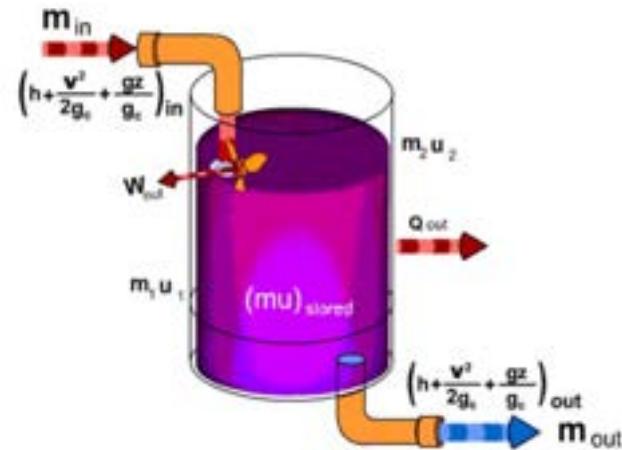
$$E_{cv} = m_{cv}(\textcolor{red}{u} + ke + pe)$$

- Energy transfer:

$$\dot{E}_{in,out} = \dot{Q}_{in,out} + \dot{W}_{in,out} + \dot{m}_{in,out}(\textcolor{red}{h} + ke + pe)$$

- Filling in results in the first law of thermodynamics for an open system / control volume

$$\frac{dE_{cv}}{dt} = [\dot{Q}_{in} + \dot{W}_{in} + \dot{m}_{in,i}(h_i + ke_i + pe_i)] - [\dot{Q}_{out} + \dot{W}_{out} + \dot{m}_{out,j}(h_j + ke_j + pe_j)]$$



Open systems / Control volume

- First law (energy conservation) for an open system

$$\frac{dE_{cv}}{dt} = [\dot{Q}_{in} + \dot{W}_{in} + \dot{m}_{in,i}(h_i + ke_i + pe_i)] - [\dot{Q}_{out} + \dot{W}_{out} + \dot{m}_{out,j}(h_j + ke_j + pe_j)]$$

- Apply to closed system, no mass flow in and out reduces the equation for an open system to the equation for the closed system $\rightarrow \dot{m}_{in,out} = 0$

$$\begin{aligned} (Q_{in} + W_{in}) - (Q_{out} + W_{out}) &= E_{in} - E_{out} \\ (Q_{in} - Q_{out}) - (W_{out} - W_{in}) &= E_{in} - E_{out} \\ Q_{net} - W_{net} &= E_{in} - E_{out} \end{aligned}$$

- First law closed systems

$$\Delta E_{cm} = \Delta U_{cm} = Q_{net} - W_{net}$$

$$du = \delta q - \delta w$$

Steady - State Steady - Flow Processes

- Many open systems of engineering interest operate continuously for long periods of time with relatively small changes in the operating conditions
- Under these conditions, the systems are often modeled as operating at **steady - state steady - flow (SSSF)**
- Along with neglecting the effects of kinetic and potential energy (NKEPE), the SSSF assumption is one of the most widely used assumptions in thermodynamics



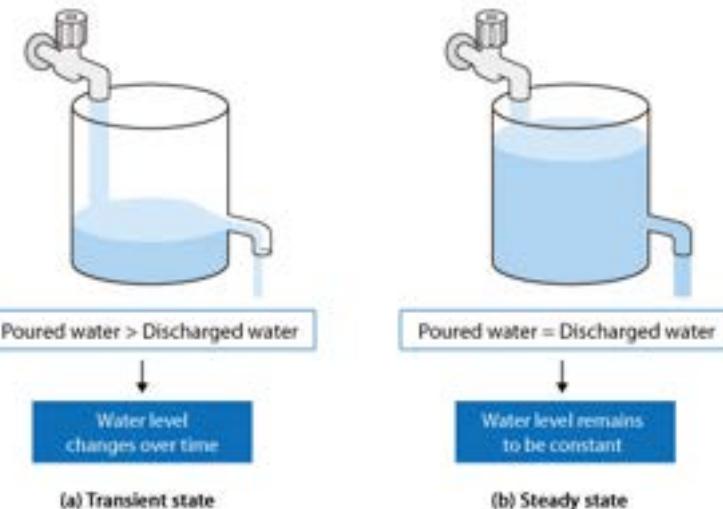
Many thermodynamic systems such as power plants operate under steady - state steady – flow (SSSF) conditions. SSSF operation is probably a good assumption when analyzing the turbofan engines powering an airplane cruising at a constant altitude and speed, but not during take-off when both the engine load and operating conditions are changing rapidly.

Steady - State Steady - Flow Processes

- Steady - state (SS) process

$$\frac{d(\)_{CV}}{dt} = 0$$

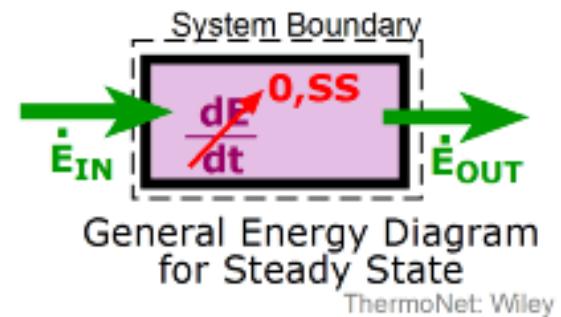
where $(\)_{CV}$ is any property of the system (e.g. m or E)



- Steady - flow (SF) process

$$\frac{d(\dot{\ })_{IN,OUT}}{dt} = 0$$

where $(\dot{\ })_{CV}$ is any transfer across the system boundary (e.g. \dot{E} , \dot{Q} , \dot{W} or \dot{m})



- All properties of the system are independent of time

Steady - State Steady - Flow Processes

- **Steady-state steady-flow (SSSF) processes:** all properties of the system are independent of time, so the right-hand side becomes zero
- The mass balance reduces to:

$$\sum_{i=1}^N \dot{m}_{in,i} - \sum_{j=1}^M \dot{m}_{out,j} = \cancel{\frac{dm_{CV}}{dt}}^0, SS \Rightarrow \sum_{i=1}^N \dot{m}_{in,i} = \sum_{j=1}^M \dot{m}_{out,j}$$

- If there is only one stream (i.e. 1-inlet and 1-outlet) it reduces to a rather simple expression:

$$\dot{m}_{in} = \dot{m}_{out} = \dot{m} \quad [kg/s]$$

Steady - State Steady - Flow Processes

- **Steady-state steady-flow (SSSF) processes:** all properties of the system are independent of time, so the right-hand side becomes zero
- The energy balance reduces to:

$$\dot{E}_{in} - \dot{E}_{out} = \cancel{\frac{dE_{CV}}{dt}}^{0, \text{ SS}} \Rightarrow \dot{E}_{in} = \dot{E}_{out}$$

$$\begin{aligned}\dot{Q}_{in} + \dot{W}_{in} + \sum_{i=1}^N \dot{m}_{in,i} (h_i + ke_i + pe_i) &= \\ \dot{Q}_{out} + \dot{W}_{out} + \sum_{j=1}^N \dot{m}_{out,j} (h_j + ke_j + pe_j) &\end{aligned}$$

- If there is only one stream and dividing by mass flow rate it becomes:

$$\begin{aligned}q_{in} + w_{in} + (h + ke + pe)_{in} &= \\ q_{out} + w_{out} + (h + ke + pe)_{out} &\end{aligned}$$

Steady - State Steady - Flow Processes

- In summary, one stream steady-state steady-slow (SSSF) processes

- **Mass Balance**

$$\dot{m}_{in} = \dot{m}_{out} = \dot{m} \quad [kg/s]$$

- **Energy Balance**

$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out} \quad [kJ/kg]$$

- These are the most general form for SSSF processes



Next slides: the energy balance will be applied to several thermodynamic devices e.g. a turbine, compressor, pump, boiler, condenser, nozzle, heat exchanger



BREAK



<https://www.cafepress.com/+thermodynamics+mugs>

Turbines

- **Turbine:** is a **work output device** which converts incoming enthalpy and kinetic energy of a fluid into shaft work
- Enthalpy → Shaft work
- Used in
 - Almost all power plants
 - Some propulsion systems (e.g. turbofan and turbojet engines)
- Working fluids
 - Liquids (e.g. hydro power plants)
 - Vapors (e.g. steam power plants)
 - Gases (e.g. gas power plants)

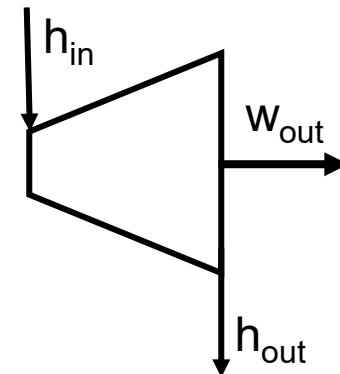


Steam Turbine Blades from a Calpine Geothermal Plant

DKB

Turbines

- Common assumptions for turbine:
 - SSSF
 - Adiabatic, no heat transfer ($q=0$)
 - No work input ($w_{in}=0$)
 - Neglect kinetic and potential energies



- **Turbine energy balance** (single stream)

$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

$$\rightarrow h_{in} = w_{out} + h_{out}$$

- Specific work output: $w_{out} = h_{in} - h_{out}$ in $\frac{kJ}{kg}$
- Power output: $\dot{W}_{out} = \dot{m}(h_{in} - h_{out})$ in $\frac{kJ}{s}$

Compressors

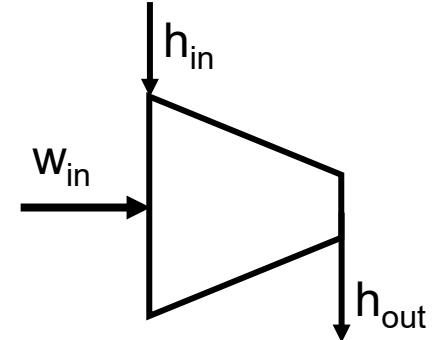
- **Compressor:** is a **work input device** used to increase the pressure and enthalpy of gases and vapors. Often like turbine run in reverse
- Shaft work → increase pressure/enthalpy of vapor/gas
- Used in
 - Gas power plants (e.g. gas turbine engine)
 - Turbo propulsion systems (e.g. turbofan and turbojet engines)
 - Industry (e.g. supply high pressure gas)
- Working fluids
 - Gas (gas turbine)
 - Vapor (cooling system)
 - Not Liquid (pump used)



Reciprocating compressor, driven by a small gasoline engine, used to provide compressed air for pneumatic tools

Compressors

- Common assumptions for **compressor**:
 - SSSF
 - Adiabatic, no heat transfer ($q=0$)
 - No work output ($w_{out}=0$)
 - Neglect kinetic and potential energies



- **Compressor energy balance (single stream)**

$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

$$\rightarrow w_{in} + h_{in} = h_{out}$$

- Specific work input: $w_{in} = h_{out} - h_{in}$ in $\frac{\text{kJ}}{\text{kg}}$

- Power work input: $\dot{W}_{in} = \dot{m}(h_{out} - h_{in})$ in $\frac{\text{kJ}}{\text{s}}$

Pumps, Fans and Blowers

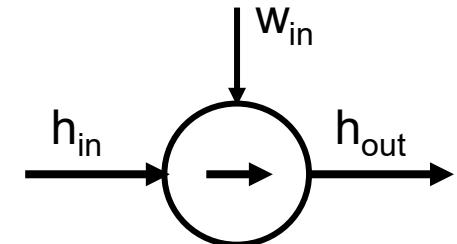
- **Pumps, fans and blowers:** Work input device, all belong to a class of devices that use mechanical work input to increase the pressure and/or velocity of a fluid
 - **Pumps:** are used for pressurizing or moving liquids
 - **Fans & Blowers:** primarily used as "air handlers" to move air through ducts and equipment
- Working fluids
 - Liquid (pump)
 - Air (fans, blowers)

Feed water pumps in a steam power plant



Pumps, Fans and Blowers

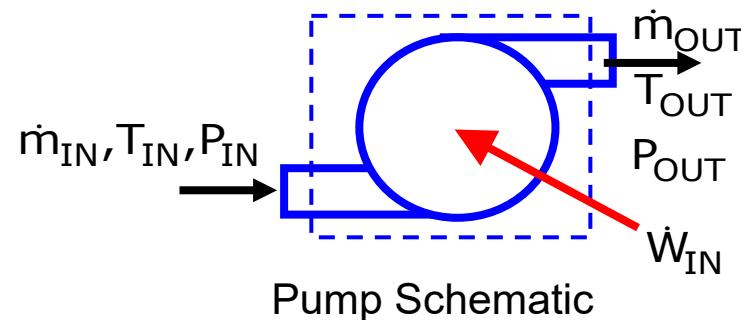
- Common assumptions for **pumps, fans, blowers**:
 - SSSF
 - No heat transfer (adiabatic, $q=0$)
 - No work output ($w_{out}=0$)
 - Neglect kinetic and potential energies



- **Pump, fan, blower energy balance**

$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

$$\rightarrow w_{in} + h_{in} = h_{out}$$



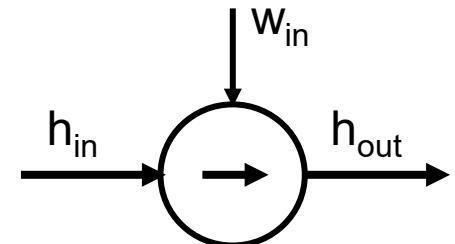
- Specific work input: $w_{in} = h_{out} - h_{in}$ in $\left[\frac{\text{kJ}}{\text{kg}}\right]$

- Power work input: $\dot{W}_{in} = \dot{m}(h_{out} - h_{in})$ in $\left[\frac{\text{kJ}}{\text{s}}\right]$

Pumps, Fans and Blowers

- For a pump in general: $w_{in} = h_{out} - h_{in}$ in [kJ/kg]
- For a pump assuming incompressible liquid (ICL)
→ $dv = 0$ and $T_{in} = T_{out} \rightarrow u_{in} = u_{out}$
- Recall: $dh = du + d(Pv) = du + Pdv + vdp = du + vdp$
→ $\Delta h = h_{out} - h_{in} = u_{out} - u_{in} + v_l(P_{out} - P_{in})$
- as $u = u(T) \rightarrow \Delta h = h_{out} - h_{in} = v_l(P_{out} - P_{in})$

$$\rightarrow w_{in} = v_l(P_{out} - P_{in}) \text{ in [kJ/kg]}$$



Steam Boilers, Combustion Chambers

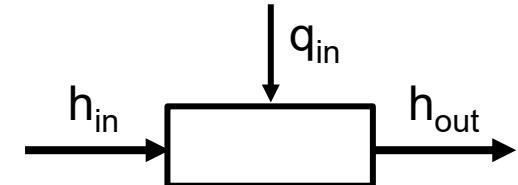
- **Steam boilers and combustion chambers:** heat input device belong to a class of devices in which heat is add to a working fluid resulting in a temperature rise and/or vaporization
 - **Boiler:** used to heat water, vaporize and superheat steam
 - **Combustion chamber:** Heats gas by combustion of fuel
- Heat is converted into enthalpy
- Used in
 - Almost all power plants
 - Some propulsion systems (e.g. turbofan turbojet engines)
- Working fluid
 - Liquid (e.g. steam power plants)
 - Gases (e.g. gas turbines)



Steam boiler *Stoomgemaal De Tuut* in Apeltern

Boilers, Combustion Chambers

- Common assumptions for **boilers, combustion chambers**:
 - SSSF
 - No heat output ($q_{out}=0$)
 - No work ($w=0$)
 - Neglect kinetic and potential energies



- **Boilers, combustion chamber energy balance**

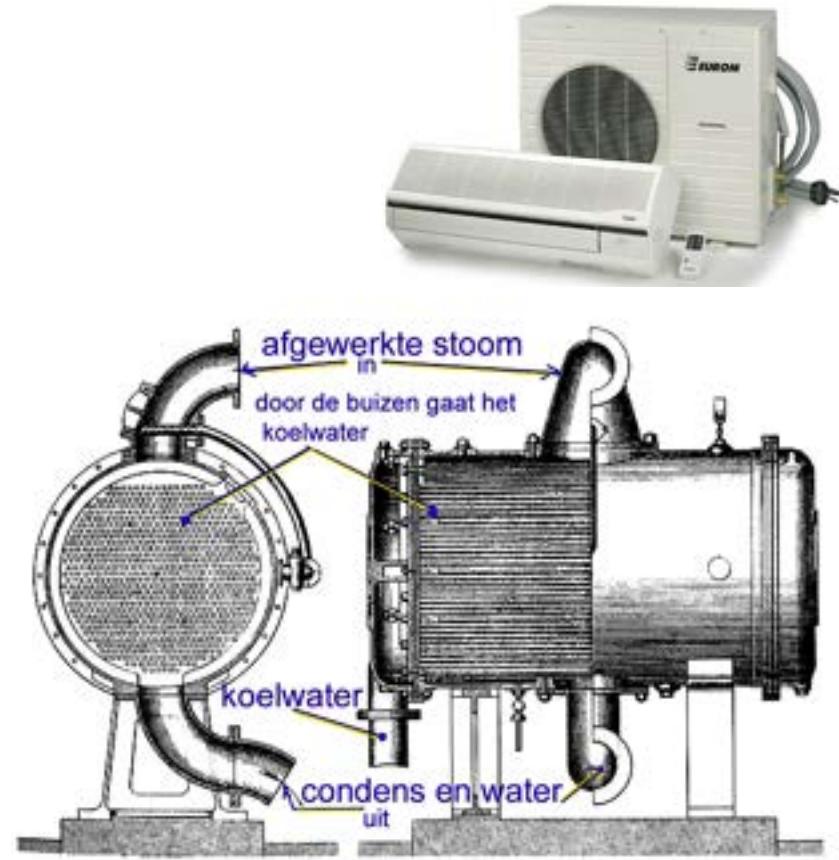
$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

$$\rightarrow q_{in} + h_{in} = h_{out}$$

- Specific heat input: $q_{in} = h_{out} - h_{in}$ in [kJ/kg]
- Power input: $\dot{Q}_{in} = \dot{m} (h_{out} - h_{in})$ in [kJ/s = kW]

Condensers

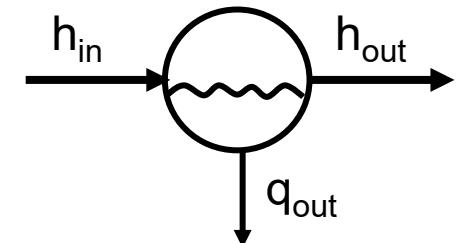
- **Condensers:** Heat output device used to condense vapor (steam) to liquid (water) after passing through a steam turbine or to condense a cooling fluid in a refrigeration system to reject heat
- Enthalpy is converted into heat
- Used in
 - Almost all power plants
 - Almost all refrigeration systems
- Working fluid
 - Liquid (e.g. steam power plants, refrigeration systems, airco's)



Hoe werkt een stoomturbine (www.stoomturbine.nl)

Condensers

- Common assumptions for **condensers**:
 - SSSF
 - No heat input ($q_{in}=0$)
 - No work ($w=0$)
 - Neglect kinetic and potential energies



- **Condenser energy balance**

$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

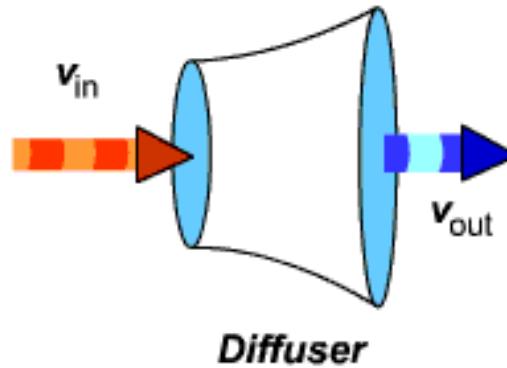
$$\rightarrow h_{in} = q_{out} + h_{out}$$

- Specific heat output: $q_{out} = h_{in} - h_{out}$ in [kJ/kg]
- Power output: $\dot{Q}_{out} = \dot{m} (h_{in} - h_{out})$ in [kJ/s = kW]

Nozzles and Diffusers

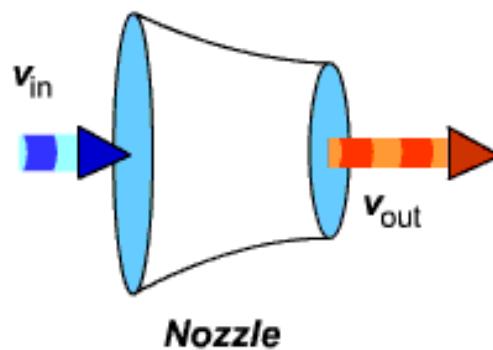
- **Nozzles and diffusers** are ducts of varying area which are intended to increase or decrease the velocity of the flow

A **diffuser** converts high speed, low pressure flow to low speed, high pressure flow



Engine intake is configured as diffuser to slow incoming air and provide uniform flow into compressor

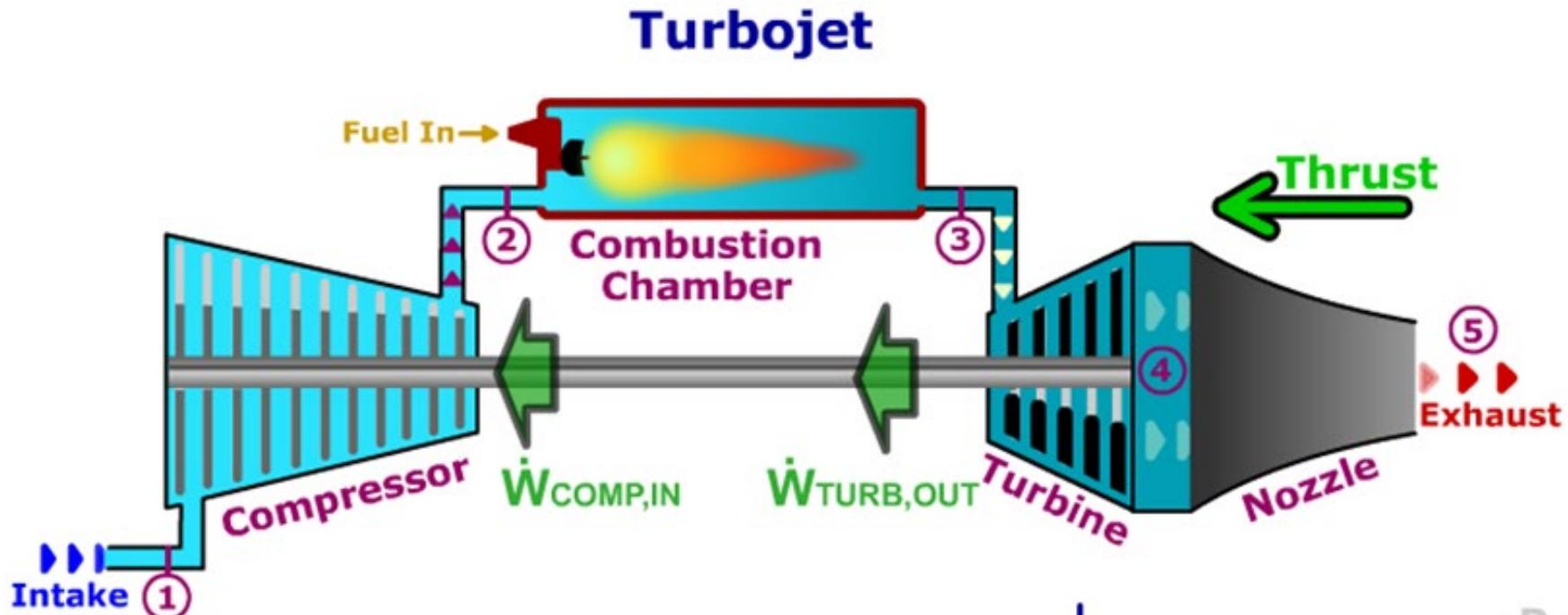
A **nozzle** converts high pressure, low speed flow to low pressure, high speed flow



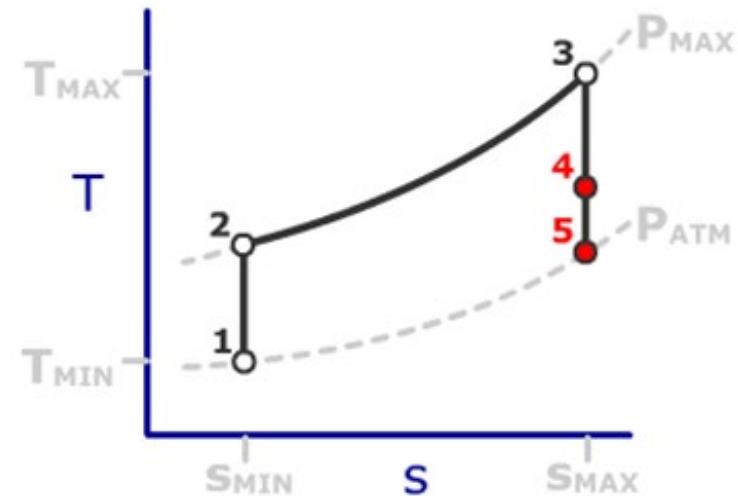
Nozzles accelerate hot gases exiting the engine to provide propulsive thrust

- On next page, see a nozzle in a turbojet engine

Nozzles and Diffusers



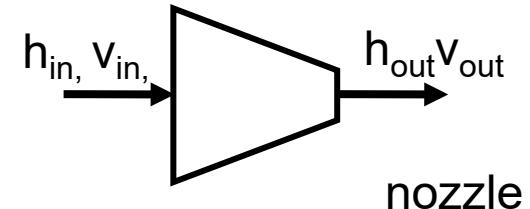
- Nozzle in a turbojet engine to accelerate the velocity of the exhaust gasses
- A diffuser is sometimes placed at the inlet to decrease the velocity of the inlet flow



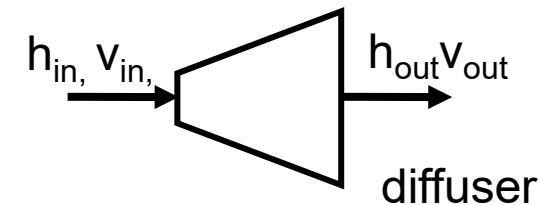
Nozzles and Diffusers

- Common assumptions for **nozzles and diffusers**:

- SSSF
- No work or heat transfer ($w=0$ and $q=0$)
- Neglect changes in pe



- **Energy balance nozzle, diffuser**



$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

$$\rightarrow h_{in} + ke_{in} = h_{out} + ke_{out} \quad \text{with} \quad ke = \frac{1}{2} v^2$$

$$\rightarrow \left(h + \frac{v^2}{2} \right)_{in} = \left(h + \frac{v^2}{2} \right)_{out}$$

Throttling

- Throttling is the process of reducing the pressure in a fluid stream by insertion of a restriction into the flow path
- Throttling may be used as a means of controlling the flow rate (valves and flow regulators), maintaining a constant downstream pressure (pressure regulator), or measuring the flow rate (flow metering orifices)
- Reduces pressure and for a lot of substances temperature is reduced, this principle is used in refrigeration



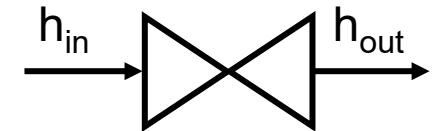
Throttling valve



This piping installation, used to control the coolant flow to a large diesel engine in an oilfield, illustrates several types of throttling devices, including valves, flow metering orifices and flow regulators.

Throttling

- Common assumptions **throttling**:
 - SSSF
 - No work or heat transfer ($w=0$ and $q=0$)
 - Neglect changes in p_e and k_e



- **Energy balance throttling**

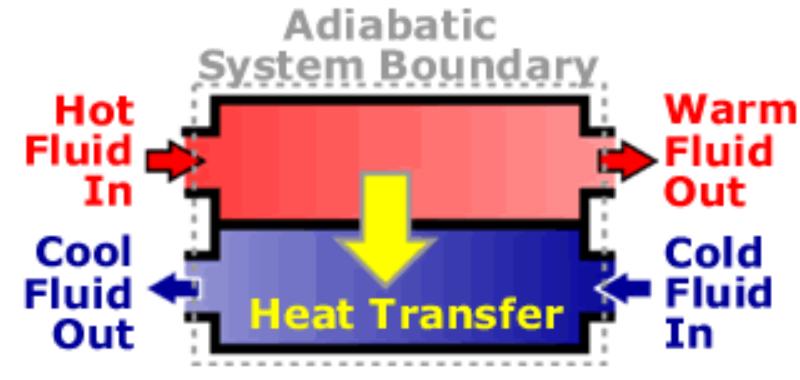
$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

$$\rightarrow h_{in} = h_{out}$$

- Isenthalpic process ($h = \text{constant} \rightarrow dh = 0$)

Heat Exchangers

- A heat exchanger allows transfer of heat from one fluid to another without mixing
- Fluids can be gas or liquid
- Example gas: Car radiator
Air conditioner

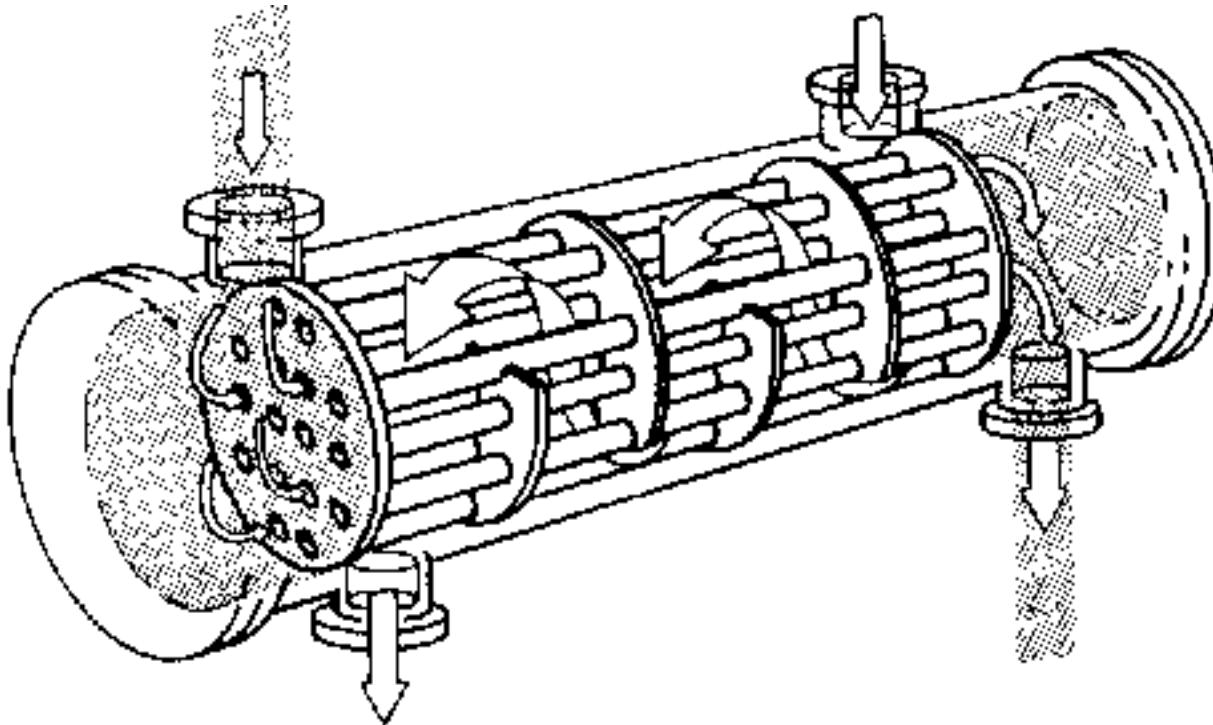


ThermoNet: Wiley

This is a section from an air-cooled cross-flow heat exchanger, such as that used in automobile radiators and home air-conditioners. Water or refrigerant flowing through the tubes is cooled by air flowing across them. The corrugated metal plates act as fins to conduct heat away from the tubes and transfer it into the air, enhancing the cooling effectiveness of the exchanger.

Heat Exchangers

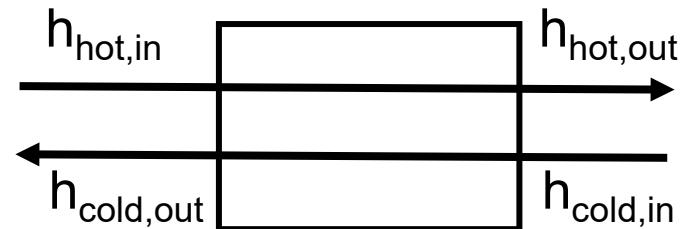
- A heat exchanger allows transfer of heat from one fluid to another without mixing
- Fluids can be gas or liquid
- Example water: Condenser in a power plant



The "shell-and-tube" exchanger shown here consists of a bundle of tubes, typically made of a good thermal conductor such as copper, enclosed in a steel vessel. The tube-side fluid enters through a manifold in the end of the exchanger, flows through the tubes, and exits from a manifold at the other end. The shell-side fluid flows back and forth over the tubes; if it is hotter than the tube-side fluid, heat will be transferred through the tube walls and into the tube-side fluid.

Heat Exchangers

- Common assumptions **heat exchanger**
 - SSSF
 - **Externally adiabatic ($q=0$)**
 - No work ($w=0$)
 - Neglect kinetic and potential energies
- **Heat exchanger energy balance (more streams take mass flow into account !!)**

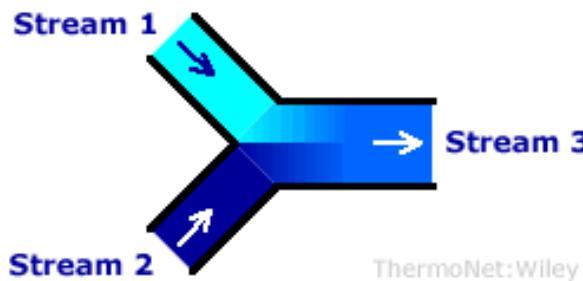


$$\left[\cancel{\dot{Q}_{in}} + \cancel{\dot{W}_{in}} + \sum [\dot{m}(h + \cancel{k_e} + \cancel{p_e})]_{in} \right] - \left[\cancel{\dot{Q}_{out}} + \cancel{\dot{W}_{out}} + \sum [\dot{m}(h + \cancel{k_e} + \cancel{p_e})]_{out} \right] = 0$$

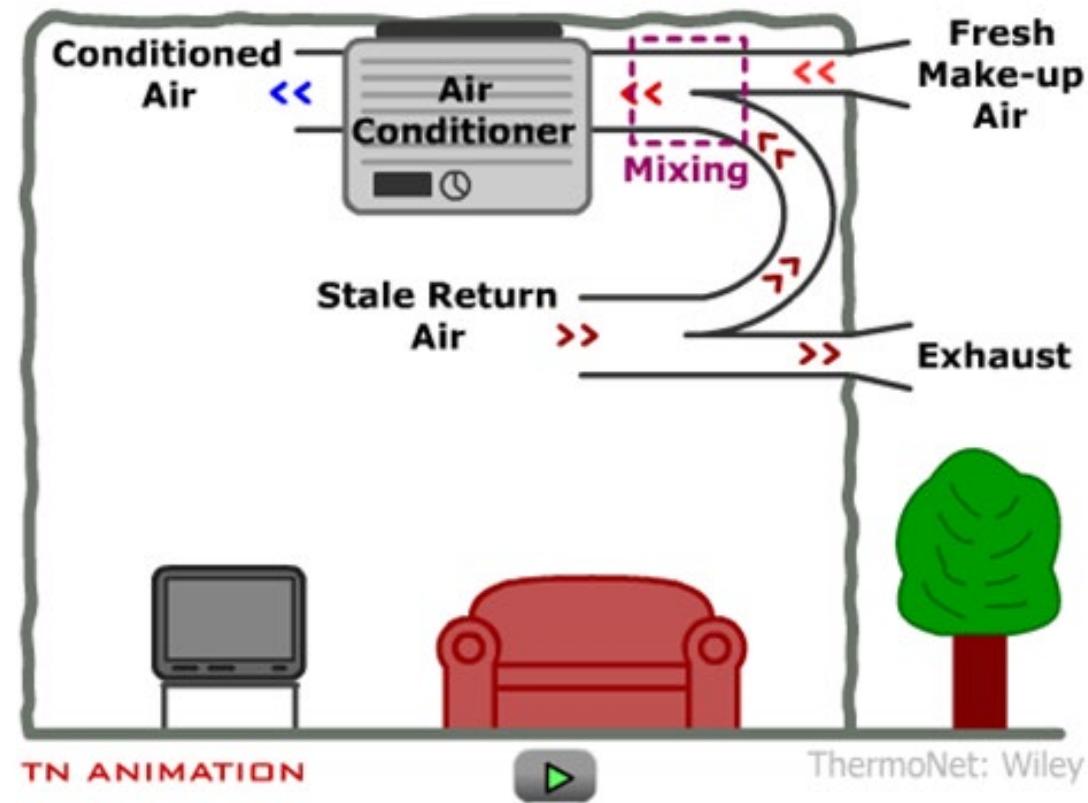
- Energy balance: $\rightarrow \dot{m}_{\text{cold}}(h_{\text{out,cold}} - h_{\text{in,cold}}) = \dot{m}_{\text{hot}}(h_{\text{in,hot}} - h_{\text{out,hot}})$

Mixing Devices

- Two or more inlet streams are combined into a single outlet stream using a **mixing device**
- A mixing device may be as simple as a sink faucet, where hot and cold inlet water streams are combined into a single warm outlet stream

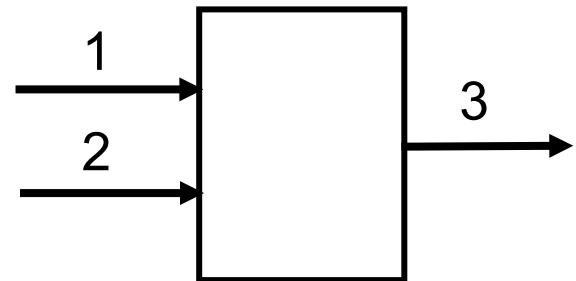


ThermoNet:Wiley



Mixing Devices

- Common assumptions mixing device
 - SSSF
 - Adiabatic ($q=0$) and no work ($w=0$)
 - Neglect kinetic and potential energies
- **Energy balance** (Streams 1 & 2 mix to form 3)



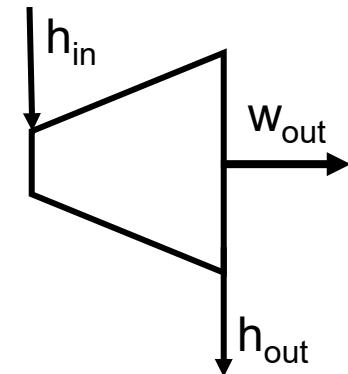
$$\left[\cancel{\dot{Q}_{in}} + \cancel{\dot{W}_{in}} + \sum [\dot{m}(h + \cancel{ke} + \cancel{pe})]_{in} \right] - \left[\cancel{\dot{Q}_{out}} + \cancel{\dot{W}_{out}} + \sum [\dot{m}(h + \cancel{ke} + \cancel{pe})]_{out} \right] = 0$$

- Energy balance: $\rightarrow \dot{m}_1 h_1 + \dot{m}_2 h_2 = \dot{m}_3 h_3$
- In a mixing device also **conservation of mass** $\rightarrow \dot{m}_1 + \dot{m}_2 = \dot{m}_3$

Example open system: Steam turbine

- Steam expands from 50 bar, 400°C to 4 bar, 150°C in a steam turbine
- What is the specific work delivered?
- What is the power at a mass flow rate of 36 ton steam/hour?
- **Solution:** start with the general energy balance for an open system

$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

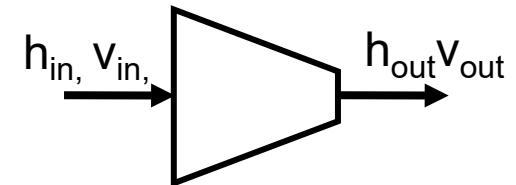


- For a turbine pe , ke are neglected, there is no heat transfer (q) and the energy balance reduces to $\rightarrow h_{in} - h_{out} = w_{out}$
- Table A6 gives the h values: $h_{in} = 3196 \text{ kJ/kg}$, $h_{out} = 2753 \text{ kJ/kg}$
- Specific work delivered: $w_{out} = h_{in} - h_{out} = 3196 - 2753 = 443 \text{ kJ/kg}$
- Convert mass flow to kg/s: $\dot{m} = 36 \text{ ton/h} \rightarrow 10 \text{ kg/s}$
- The power delivered: $\dot{W} = \dot{m} \cdot w_{out} = 10 \cdot 443 = 4.43 \text{ MW}$

Example open system: Nozzle

- Steam expands from 50 bar, 400°C to 4 bar, 150°C in a nozzle.
- What is the exit velocity (assume the exit velocity to be much larger than the inlet velocity)?

- **Solution:** start with the general energy balance for an open system

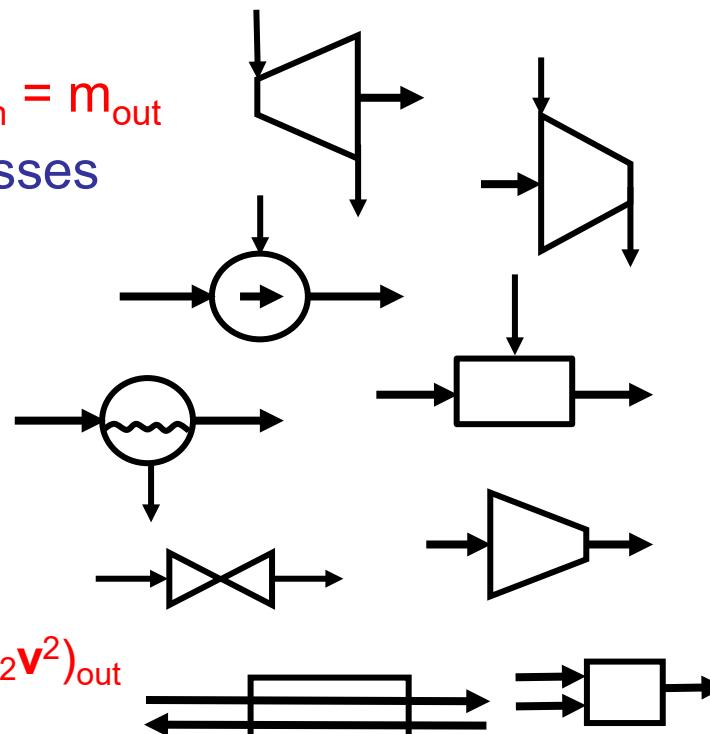


$$q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$$

- For the nozzle pe is neglected, there is no heat transfer (q) and no work (w) involved and $v_{in} \ll v_{out}$ the energy balance reduces to
 - $h_{in} + ke_{in} = h_{out} + ke_{out}$ with $ke = 1/2v^2$ ($KE = 1/2mv^2$)
 - $2h_{in} + v_{in}^2 = 2h_{out} + v_{out}^2 \rightarrow v_{out} = [2(h_{in} - h_{out})]^{0.5}$
- Table A6 gives the h values: $h_{in} = 3196 \text{ kJ/kg}$, $h_{out} = 2753 \text{ kJ/kg}$
- The exit velocity is: $v_{out} = [2(3196 - 2753) \cdot 10^3]^{0.5} = 941 \text{ m/s}$

Recapitulate class 4

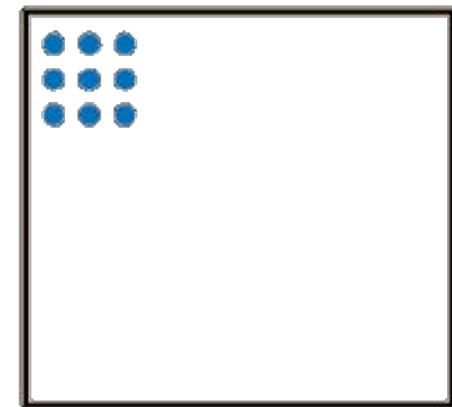
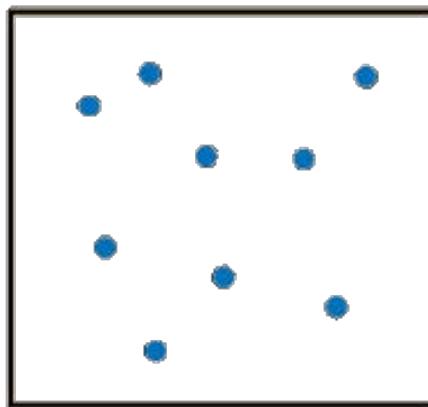
- **Conservation of energy, first law of thermodynamics**
 - Closed system $du = \delta q - \delta w \rightarrow \Delta u = q_{\text{net}} - w_{\text{net}} \rightarrow \Delta U = Q_{\text{net}} - W_{\text{net}}$
 - Open system $q_{\text{in}} + w_{\text{in}} + (h + ke + pe)_{\text{in}} = q_{\text{out}} + w_{\text{out}} + (h + ke + pe)_{\text{out}}$
 - **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

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

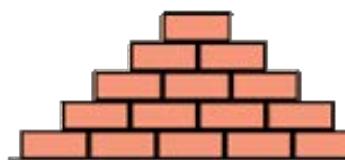
Next Class 5: Second law of thermodynamics

- Direction of processes
- Reversible and irreversible processes
- Entropy
- Second law of thermodynamics
- Second law applied to processes
- Isentropic efficiencies

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



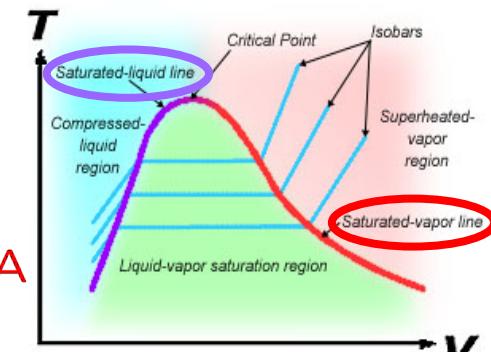
If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?



- Based on observations during your live you know what the answers are, but how can this be predicted and why does the other case not occur? The first law of thermodynamics, conservation of energy is still obeyed

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 $\eta_{thermal} = \frac{Net\ electrical\ power\ output}{Rate\ of\ fuel\ energy\ input} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Different phases in phase diagrams
- 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 $du = \delta q_{net} - \delta w_{net} \rightarrow \Delta u = q_{net} - w_{net}$
 - Open system $q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$



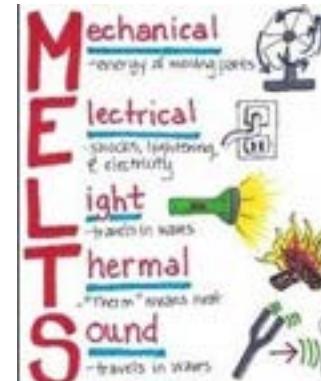
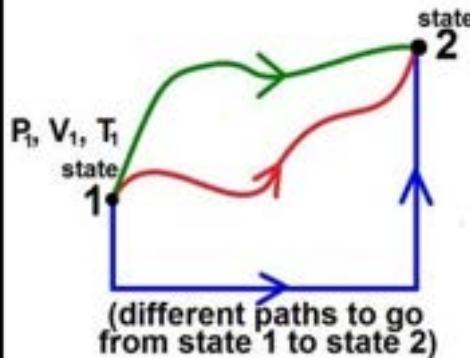
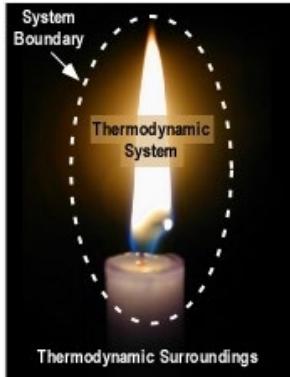
Class 5: The second law of thermodynamics and entropy

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

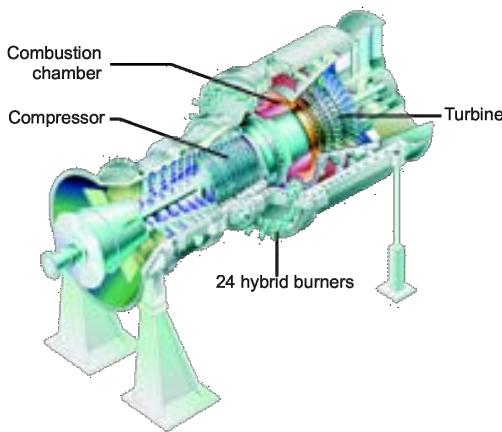


Roadmap Engineering Thermodynamics

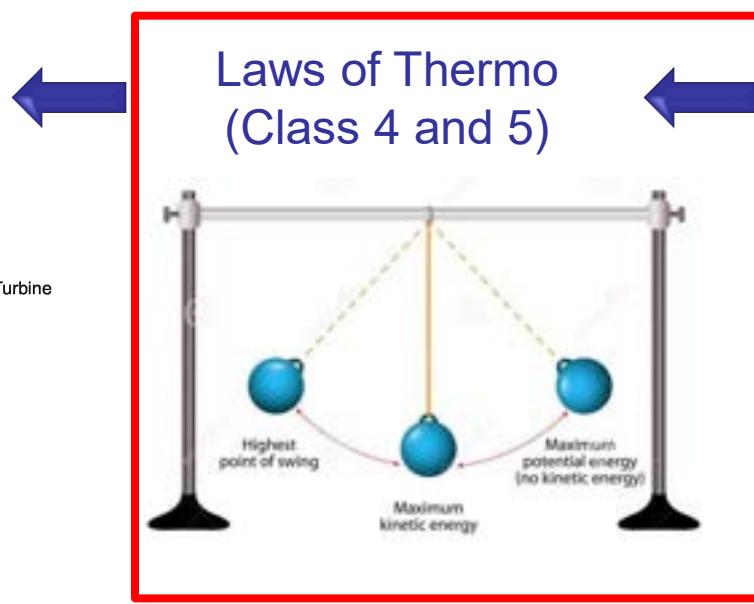
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



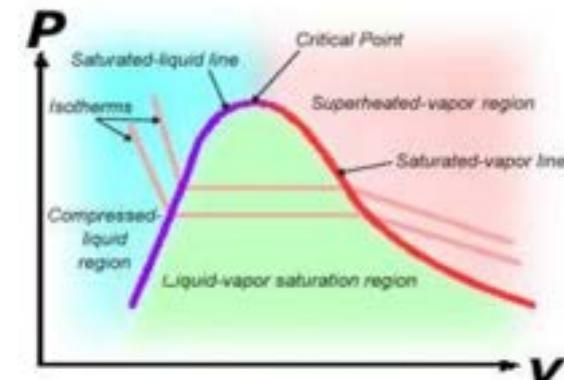
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

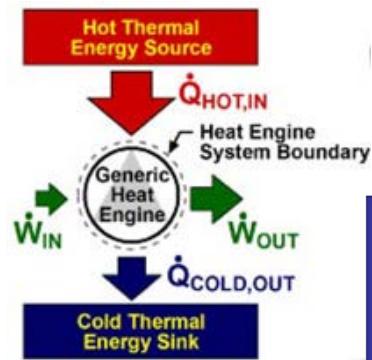


- Properties of Substances (Class 3, 9)

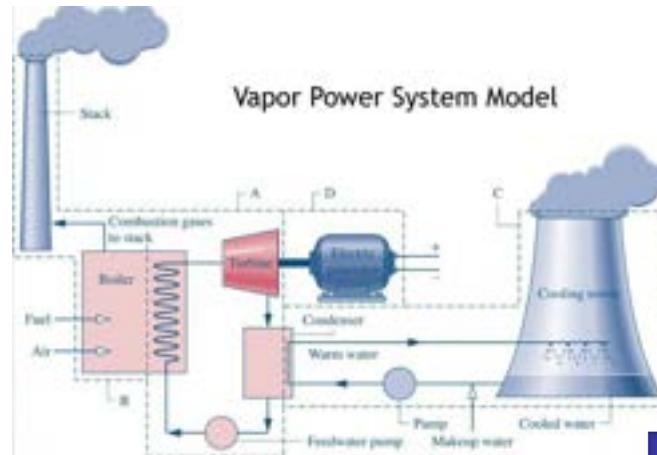


Roadmap Engineering Thermodynamics

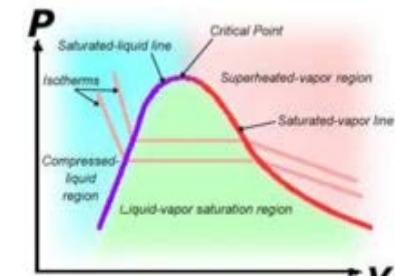
Thermodynamic cycles (Class 6)



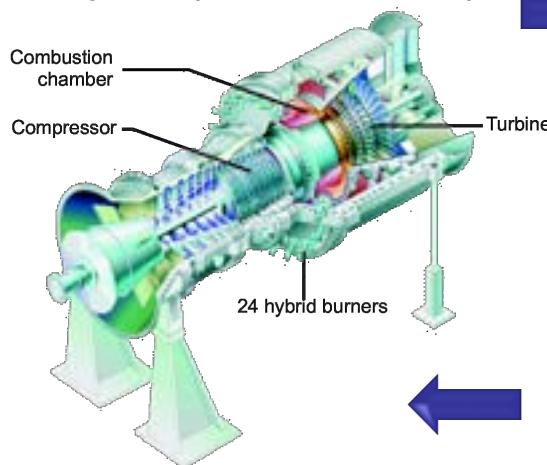
Vapor power cycles – Rankine cycle (Class 7, 8)



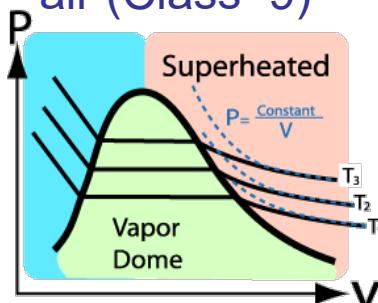
Properties of water (Class 3)



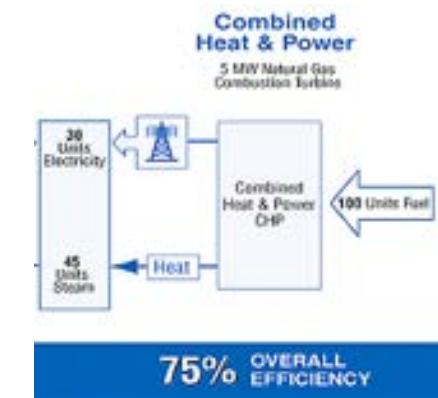
Gas power cycles – Brayton cycle (Class 10, 11)



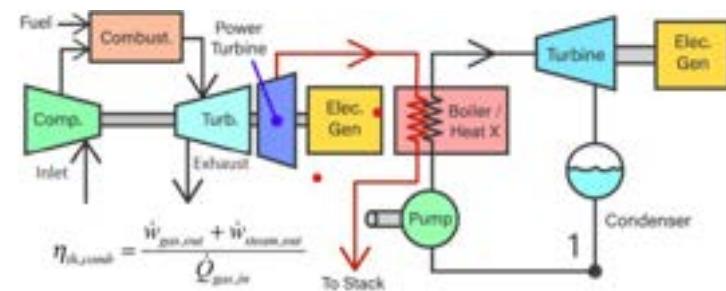
Properties of air (Class 9)



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

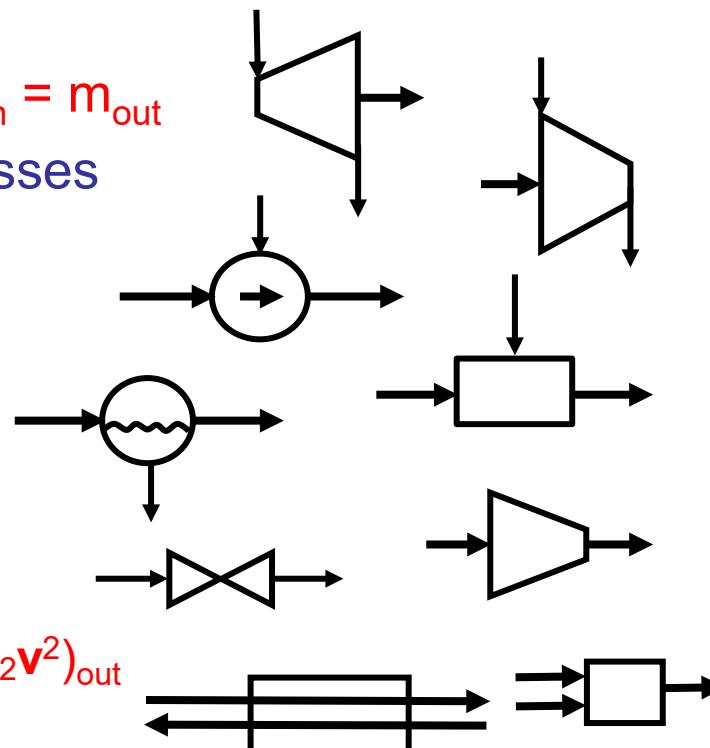


75% OVERALL EFFICIENCY



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

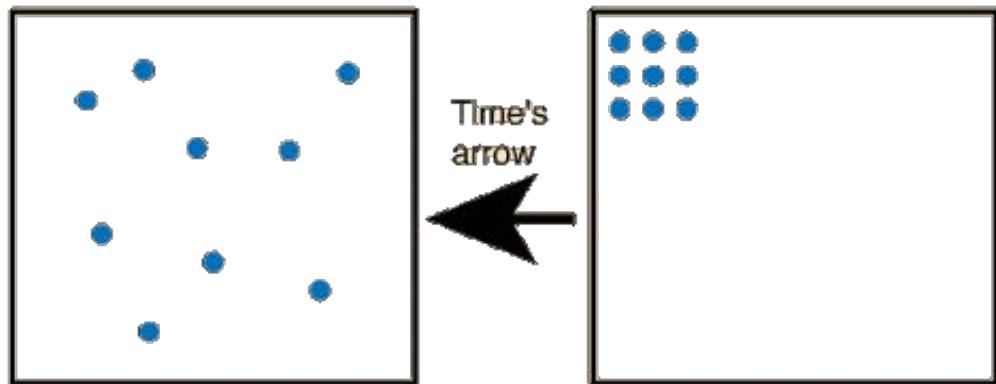
$w_{\text{out}} = h_{\text{in}} - h_{\text{out}}$
 $w_{\text{in}} = h_{\text{out}} - h_{\text{in}}$
 $w_{\text{in}} = v(P_{\text{out}} - P_{\text{in}})$
 $w_{\text{in}} = h_{\text{out}} - h_{\text{in}}$
 $q_{\text{in}} = h_{\text{out}} - h_{\text{in}}$
 $q_{\text{out}} = h_{\text{in}} - h_{\text{out}}$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

Content Class 5

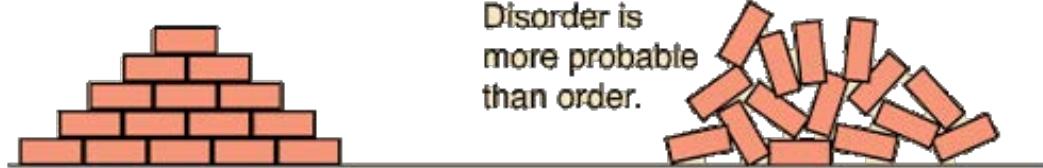
- **The second law of thermodynamics and entropy**

- 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

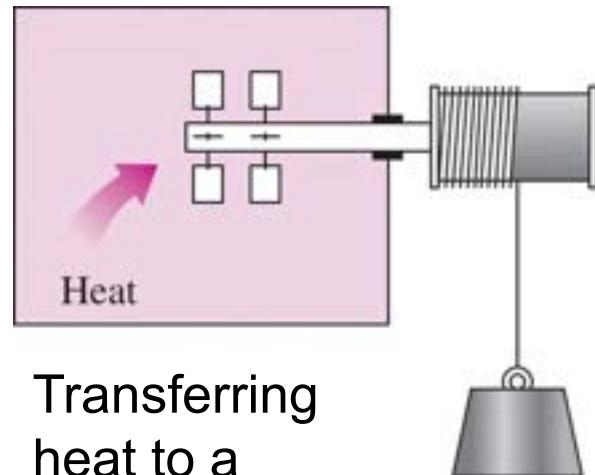
- A lot of processes cannot occur even though they are not in violation with the first law
- Why? Energy is conserved



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

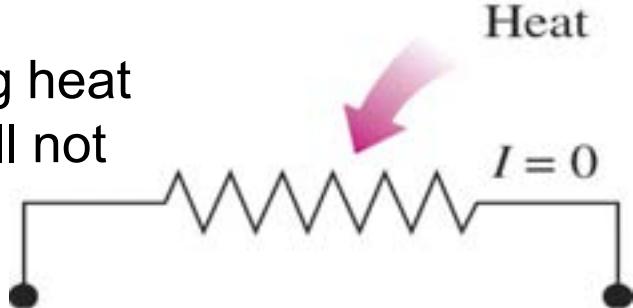


Ice cubes will not be created at room temperature



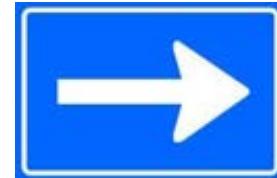
Transferring heat to a paddle wheel will not cause it to rotate

Transferring heat to a wire will not generate electricity

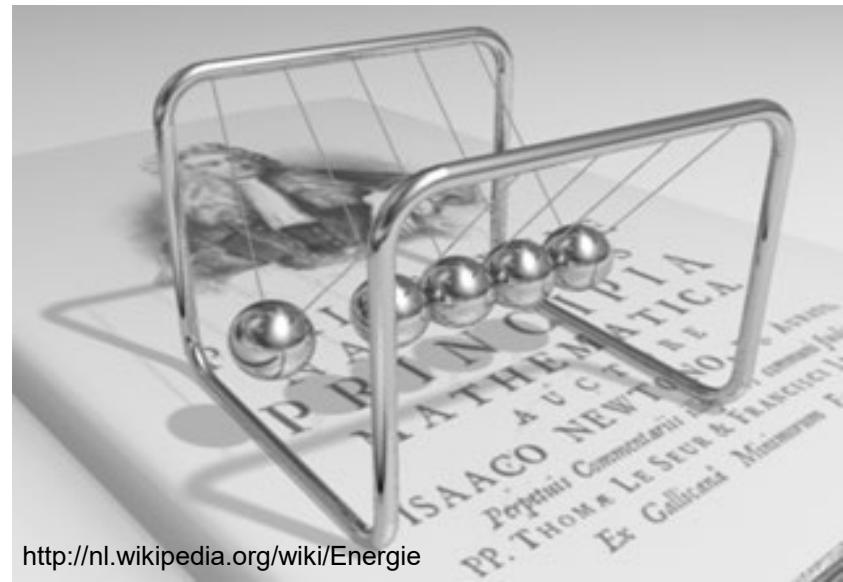


Direction of processes

- 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**



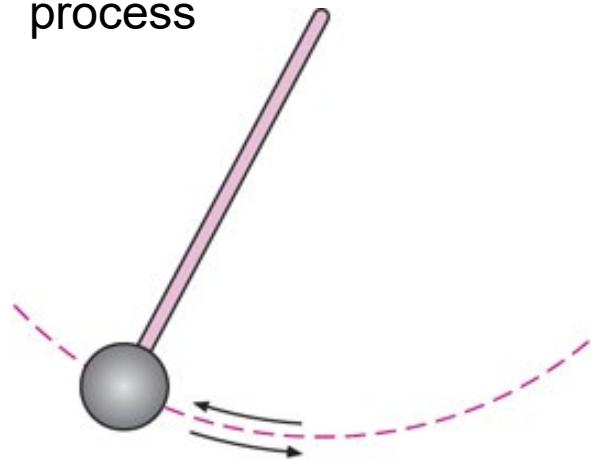
<http://nl.wikipedia.org/wiki/Energie>

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

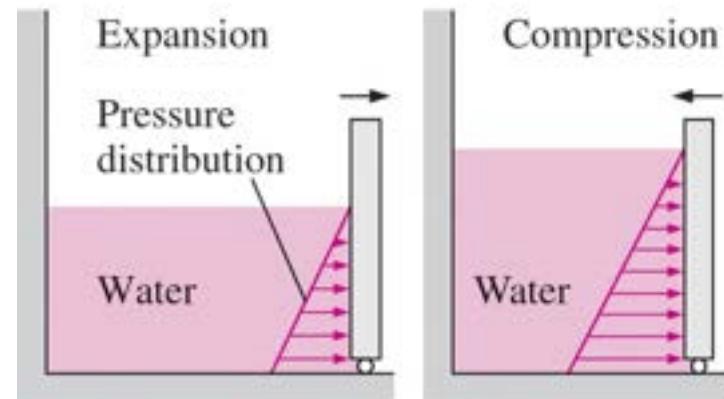


**Why should we be
interested in reversible
processes?**

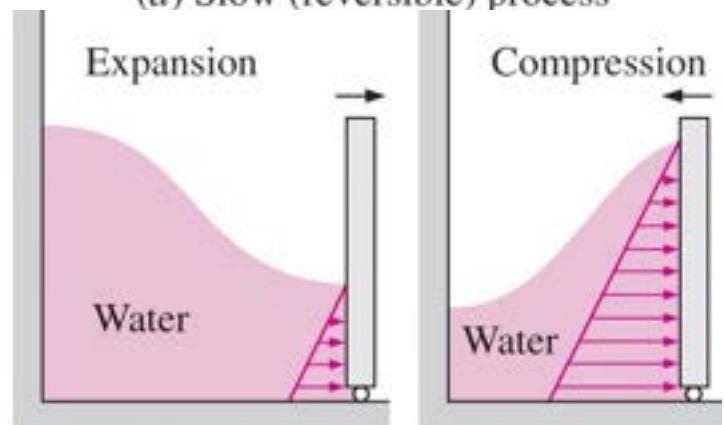
Quasi-equilibrium expansion and compression of a gas, is often used in thermodynamics to approach a reversible process

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**



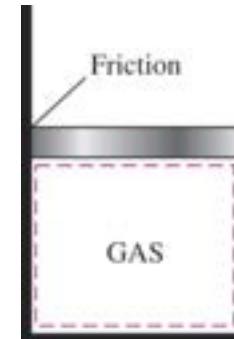
(a) Slow (reversible) process



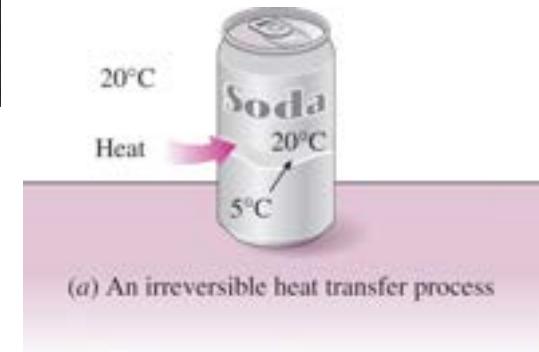
(b) Fast (irreversible) process

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

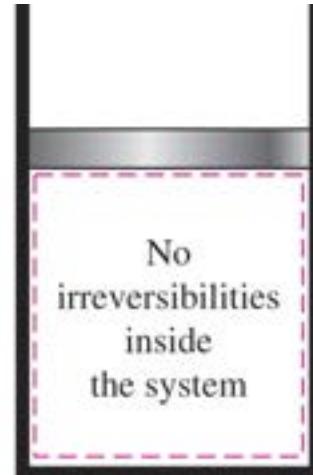
(a) Heat transfer through a temperature difference is irreversible, (b) the reverse process is impossible.

Internally and externally reversible processes

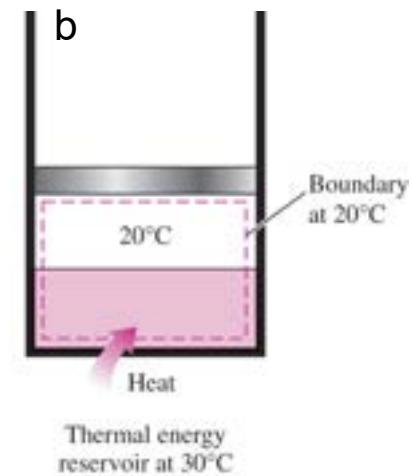
- **Internally reversible process:** If no irreversibilities occur within the boundaries of the system during the process
- **Externally reversible:** If no irreversibilities occur outside the system boundaries
- **Totally reversible process:** It involves no irreversibilities within the system or its 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



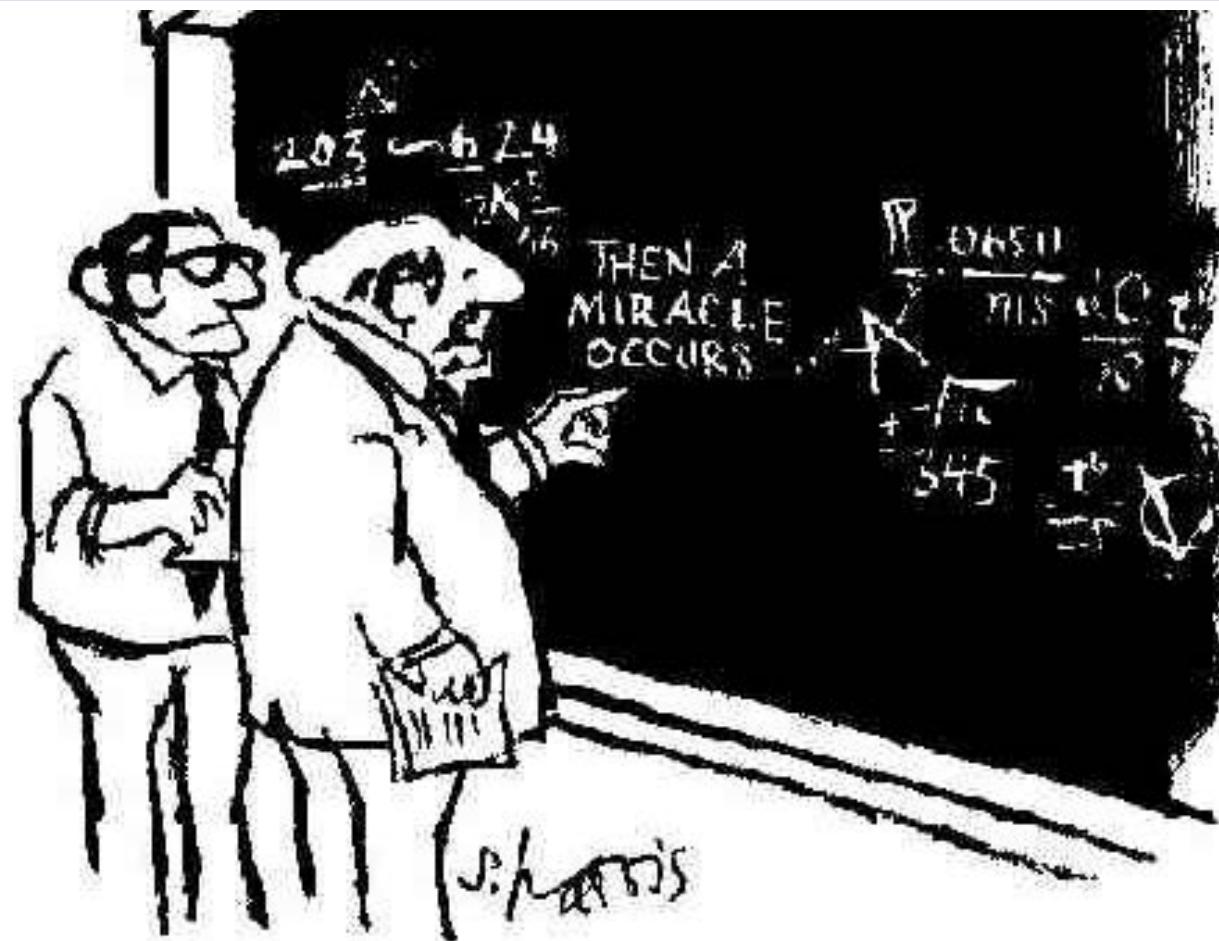
Totally (a) and internally (b) reversible
heat transfer processes



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 19th 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 J/kgK (or kJ/kgK) (or for total entropy J/K or kJ/K)
- Entropy values can be found in the tables, read from a graph or calculated

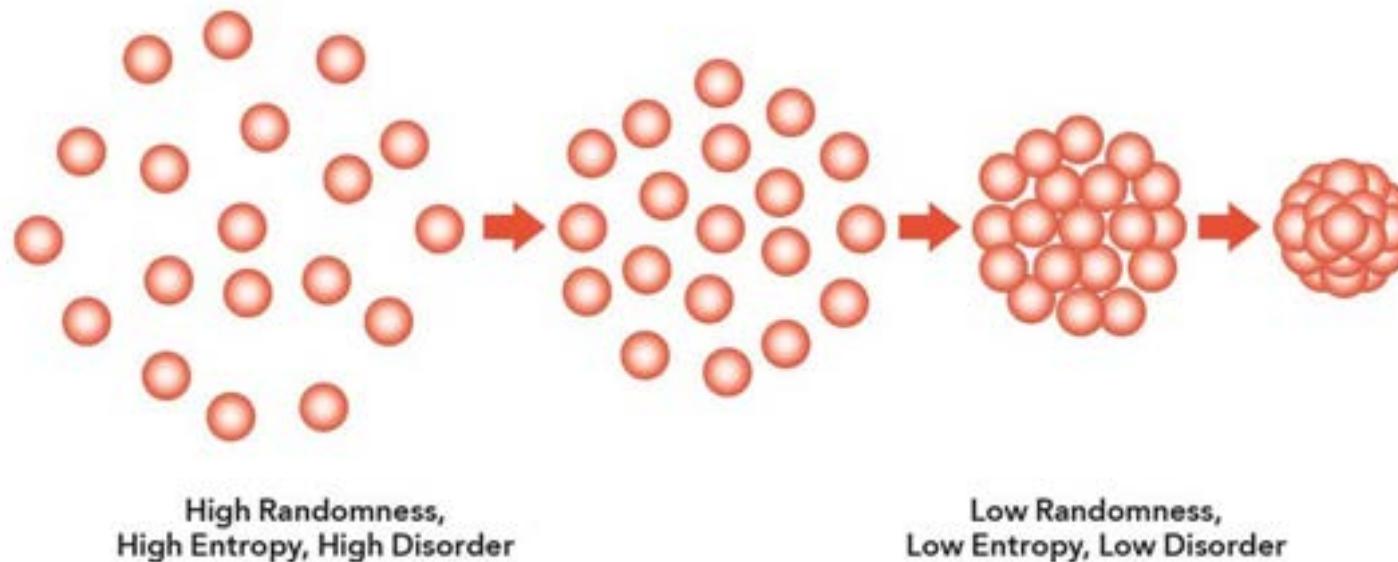


Ice melting: a classic example of the increase of entropy described in 1865 by Rudolf Clausius

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 2nd law of Thermodynamics



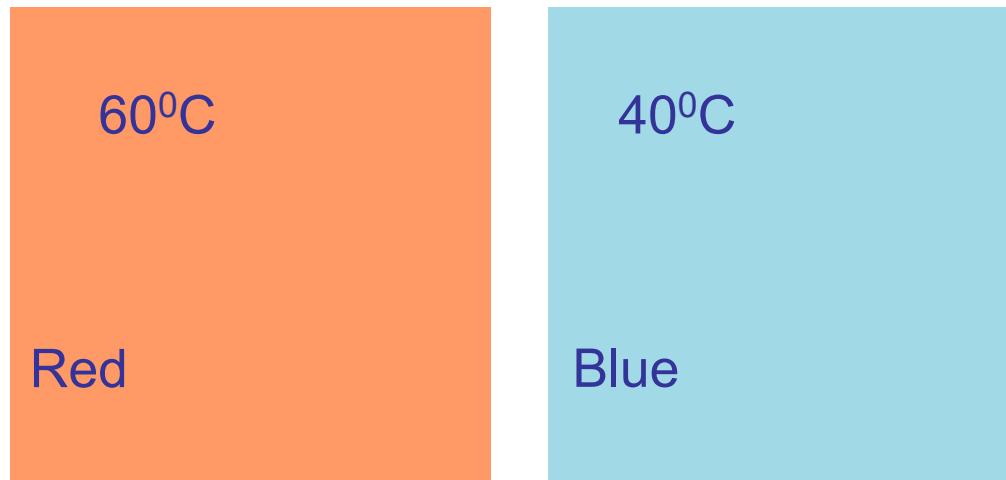
- In **equilibrium** entropy is at a **maximum**, most disorder

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

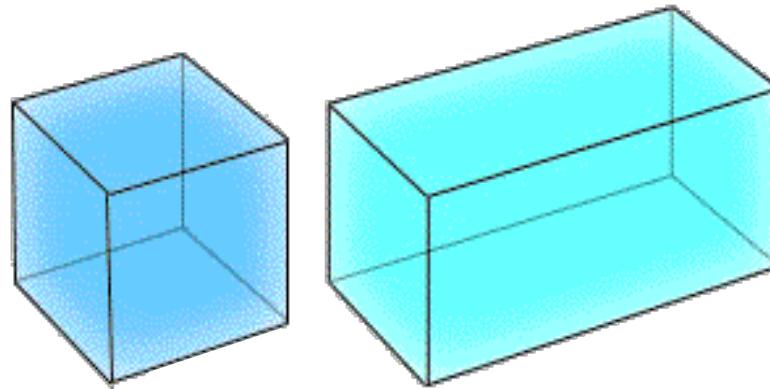
Describing our intuition about reality

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



Describing our intuition about reality

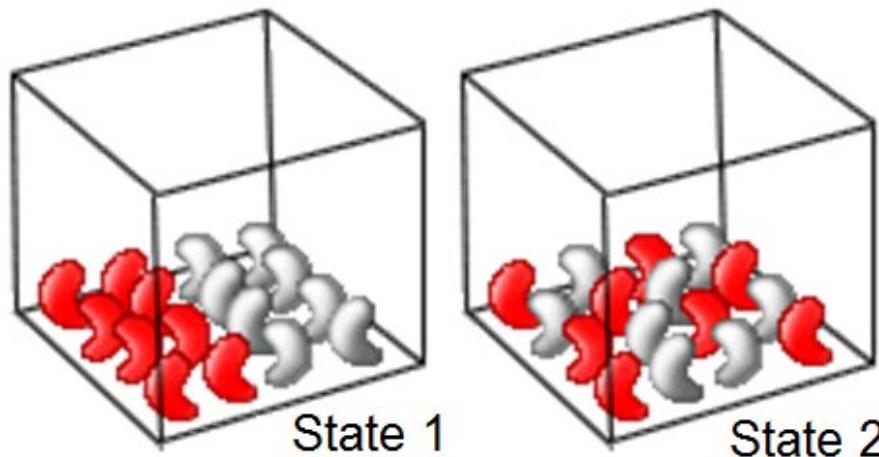
- **Entropy and pressure**
 - The small box is at a higher pressure
 - The large box has more entropy (in the large box there are less molecules per volume, they have more freedom to move and therefore they are more random)
 - Entropy increases with decreasing pressure



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

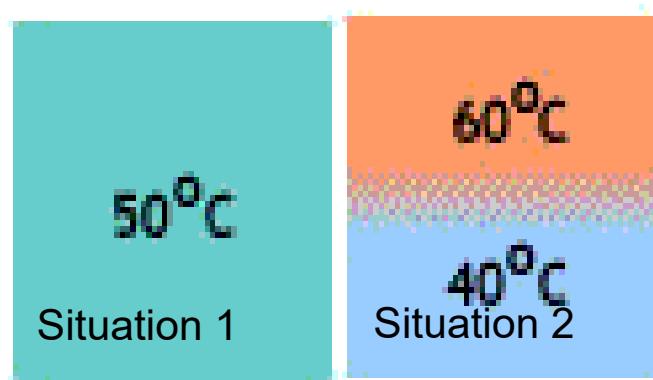
Describing our intuition about reality

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



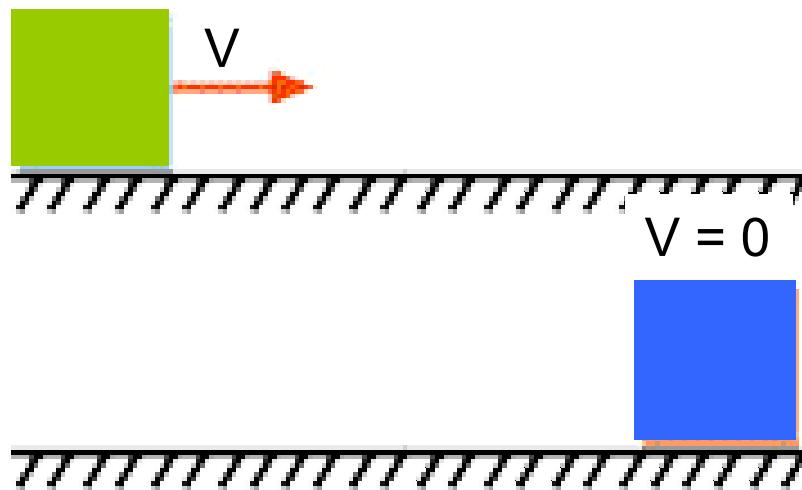
Describing our intuition about reality

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



Describing our intuition about reality

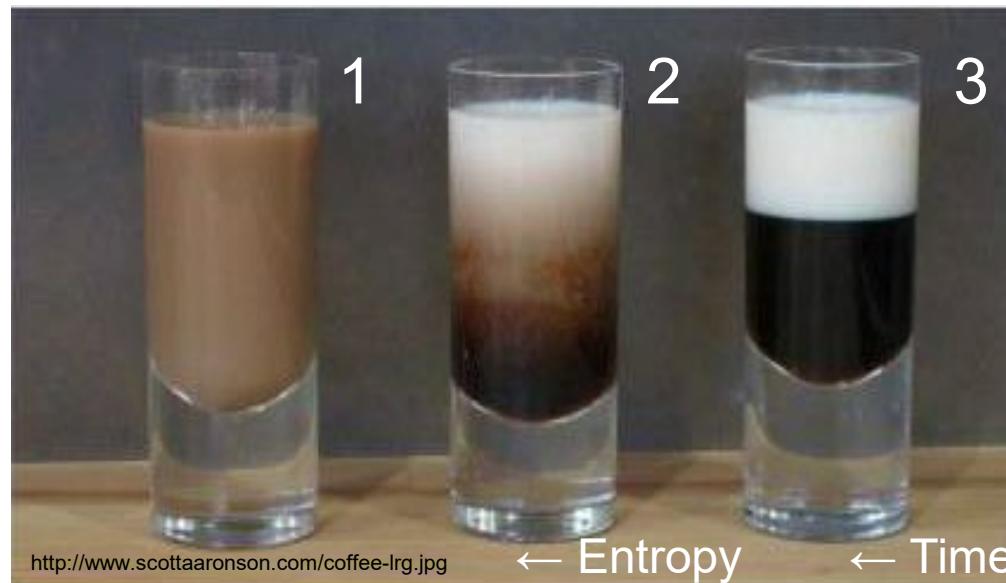
- Entropy, internal energy and kinetic energy
 - Spontaneously Green \rightarrow Blue
 - Blue one has more entropy (equilibrium)
 - U has more entropy than KE



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

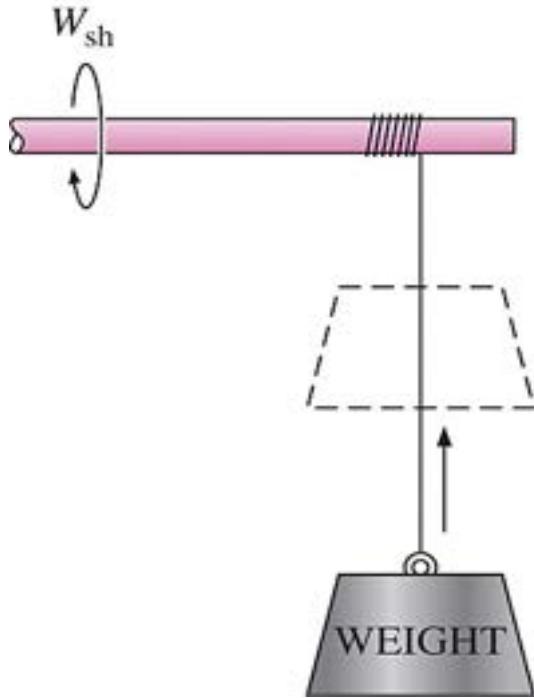
- Entropy and mixing of coffee and milk
 - Spontaneously $3 \rightarrow 2 \rightarrow 1$
 - Glass 1 has more entropy (completely mixed, most random)



Describing our intuition about reality

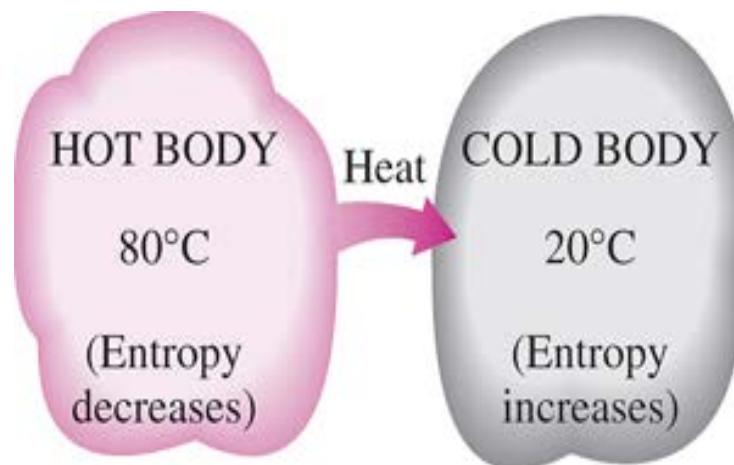
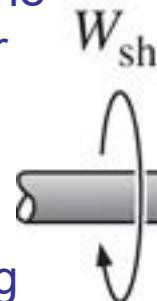
- We saw several processes and can conclude that:
 - Entropy increases with temperature
 - Entropy decreases with increasing pressure
 - Internal energy has more entropy than kinetic energy
 - Systems with uniform properties (isothermal, isobaric) have more entropy than systems with non-uniform properties (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.

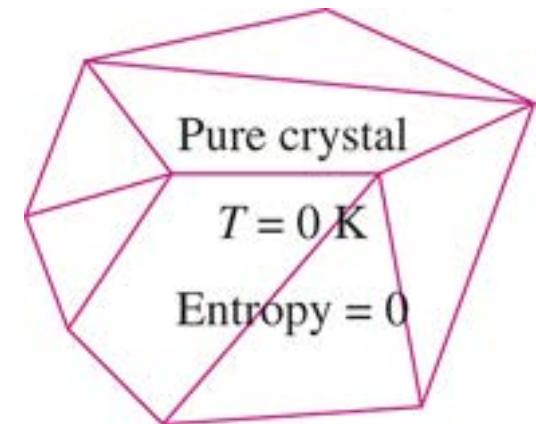
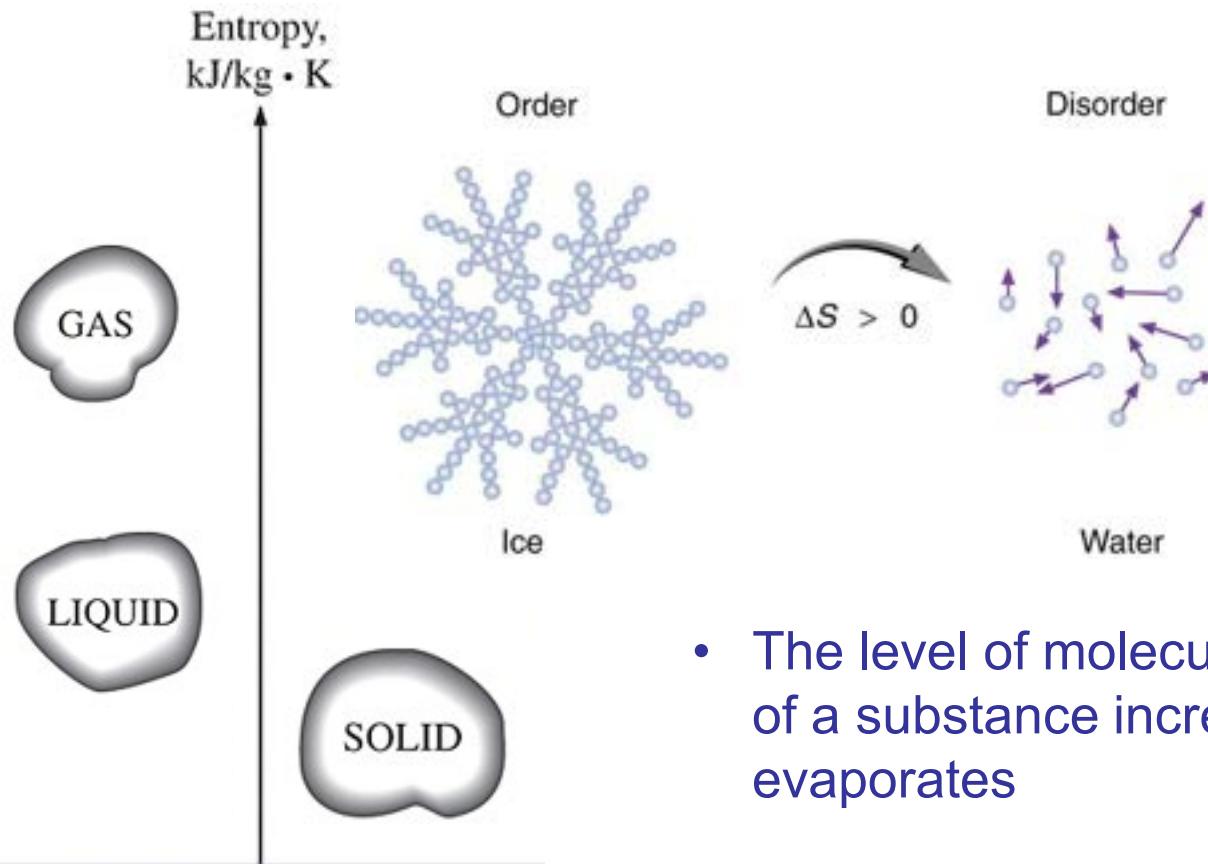
The paddle-wheel work done on a gas increases the level of disorder (entropy) of the gas, and thus energy is degraded during this process.



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

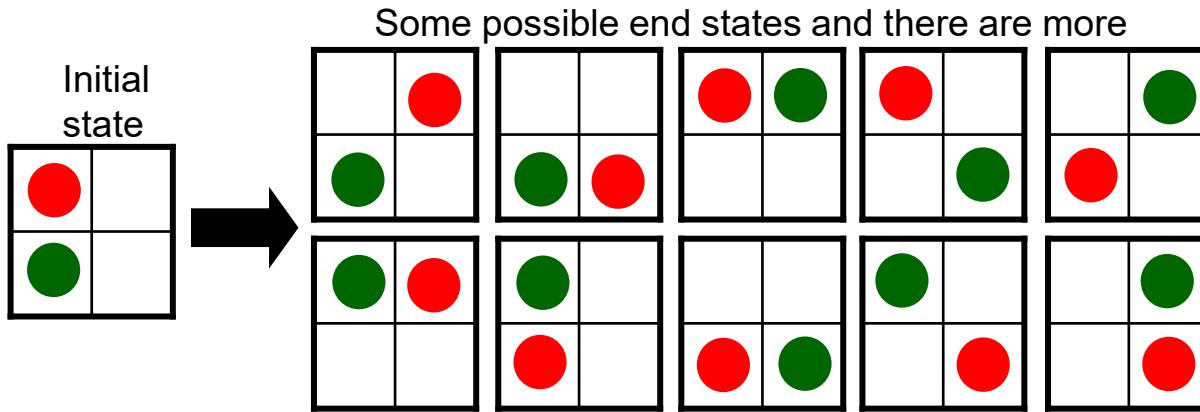
- **Third law of thermodynamics:** a pure crystalline substance at absolute zero temperature is in perfect order, and its entropy is zero



- 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

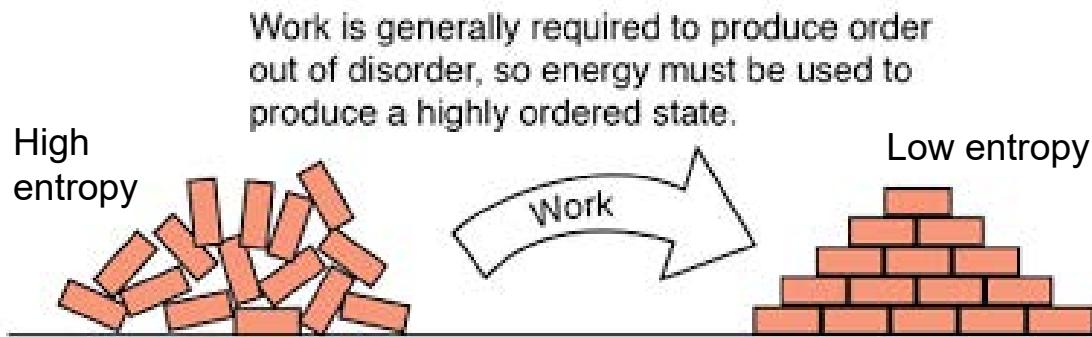
FOKKE & SUKKE
LEIDEN HUN COLLEGA ROND

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

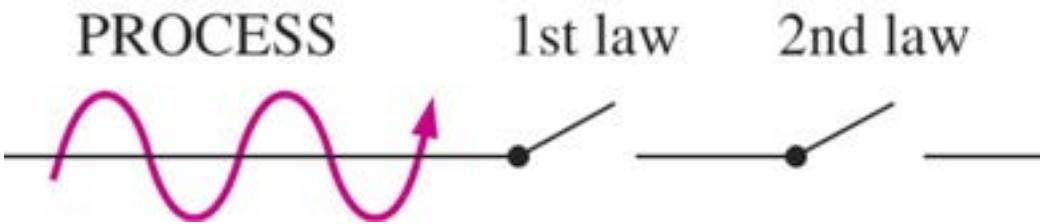
1. Spontaneous processes can occur in a certain direction only, not in any direction. A process must proceed in the direction that complies with the increase of entropy principle, that is, $S_{gen} \geq 0$. A process that violates this principle is impossible.
2. Entropy is a non conserved property, 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 ierwat nerdij stripverhalen, of in de hoofden van fysici. Wie? Het duiveltje van Maxwell dat fysici decennia lang heeft dwarsgezeten.

James Clerk Maxwell (1831-1879), beklaamd wegens zijn vergelijkingen die elektromagnetisme beschrijven, bedacht het sluwe duiveltje in 1867 als figurant in een gedachte-experiment. Maxwell wilde ermete aantonen dat de beroemde tweede hoofdwet van de thermodynamica (de warmteleer) niet stejd 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 vellen 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 duivelse 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*.

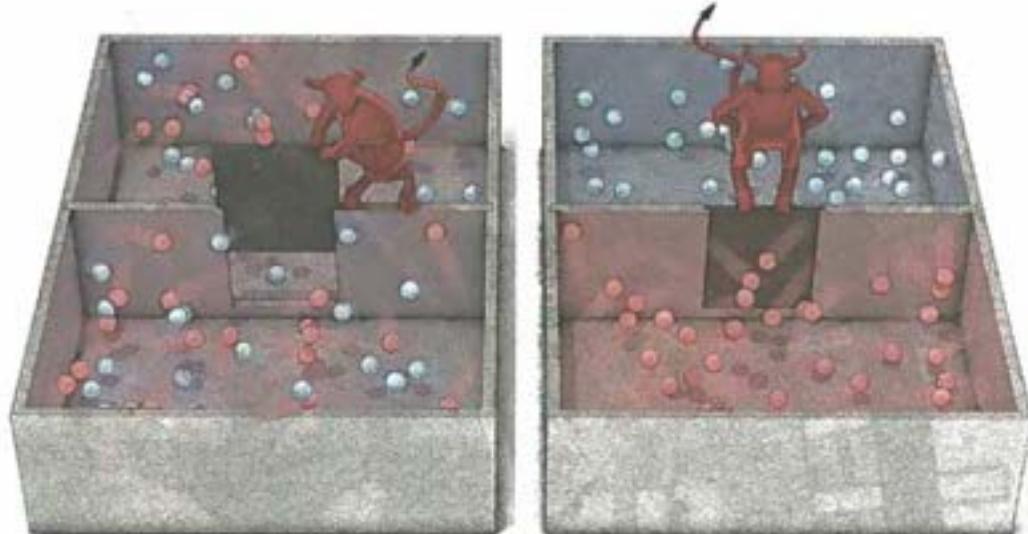
Hoe zit dat? Eerst die tweede hoofdwet. Een formulering ervan is dat er nooit spontaan warmte van een koud voorwerp naar een warmer voorwerp kan stromen. Een hete kop koffie bijvoorbeeld, koelt af doordat warmte eruit wegstromt naar de omgeving – net zolang tot de koffie en de omgeving even warm zijn. En nooit keert die warmtestroomb zaam 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 raagschikken dat ze gemiddeld genomen hun bewegingsvrijheid (trillen, draaien of rondsuzen) optimaal benutten. Ook dat bewijst de praktijk telkens weer: als gas een lege ruimte binnenstroomb 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 daarvan 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. En 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 stellen 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 (die 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 nauwē en intrigerende 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

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)

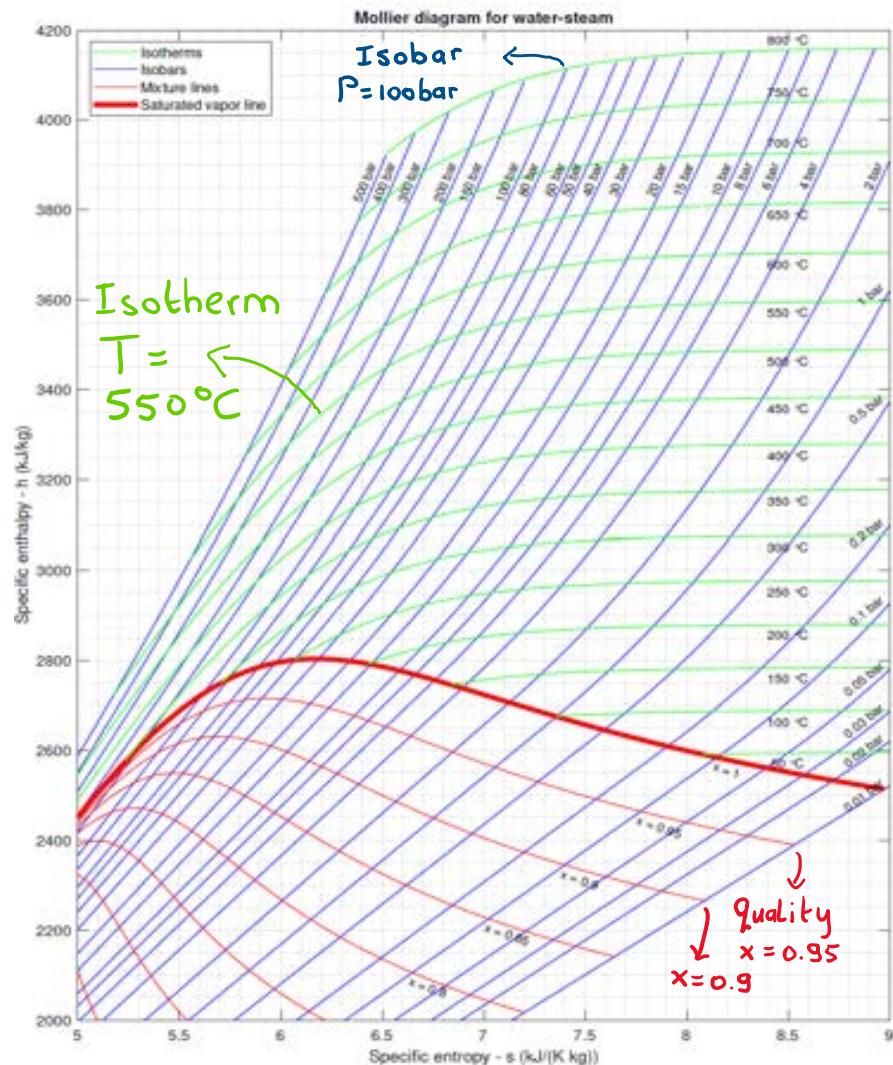
T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/(kg·K)
P = 8000 kPa				
(295.04)	(0.0235)	(2569.6)	(2757.8)	(5.7431)
300	0.02426	2590.5	2784.6	5.7901
350	0.02995	2746.7	2986.3	6.1286
400	0.03431	2863.5	3138.0	6.3630
450	0.03816	2966.9	3272.2	6.5554
500	0.04174	3064.6	3398.5	6.7243

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

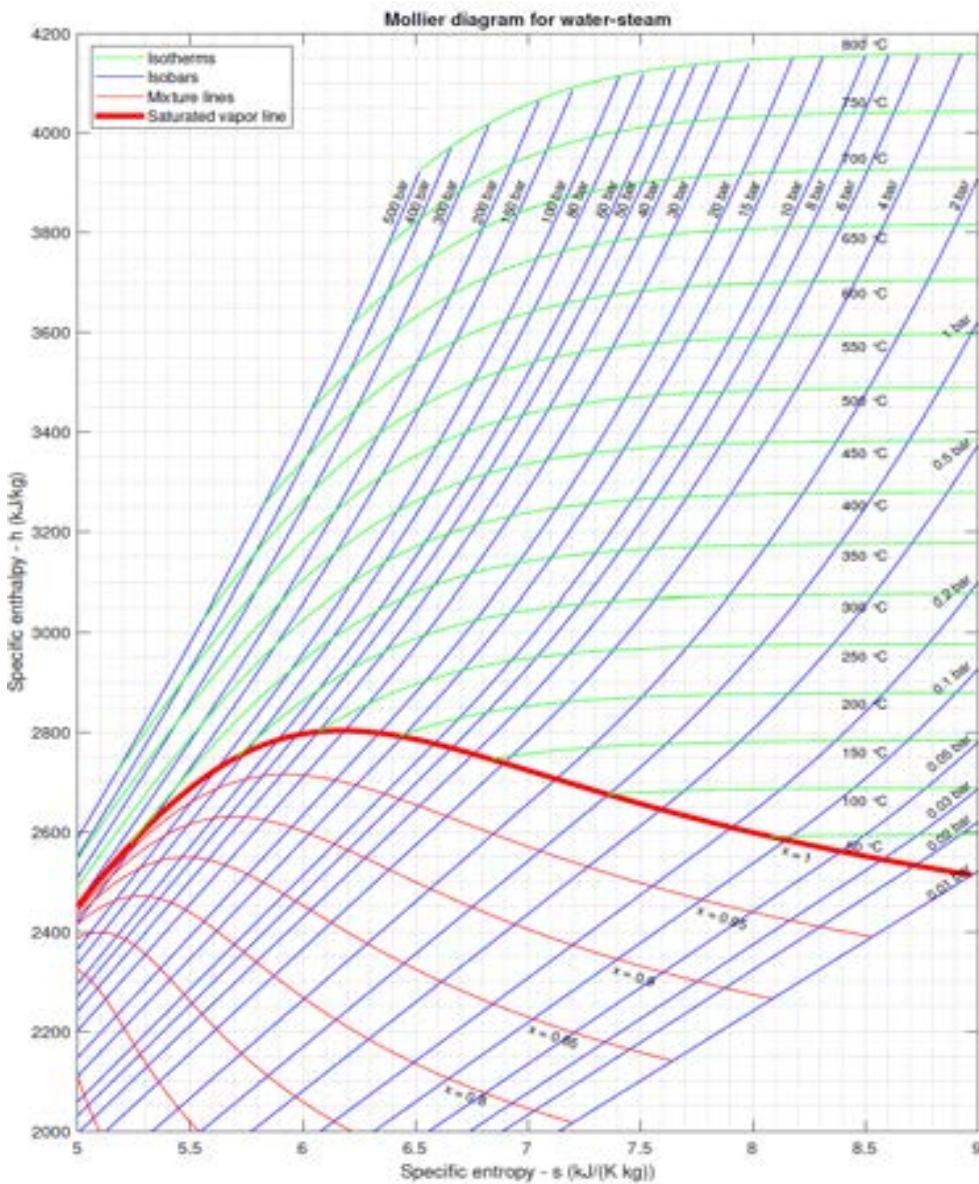
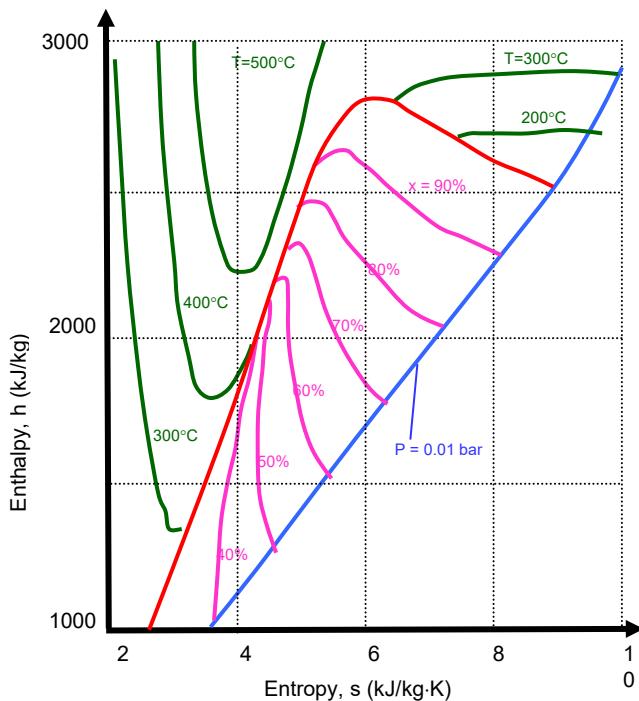
Mollier Diagram Water for Rankine Cycle

- 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)?



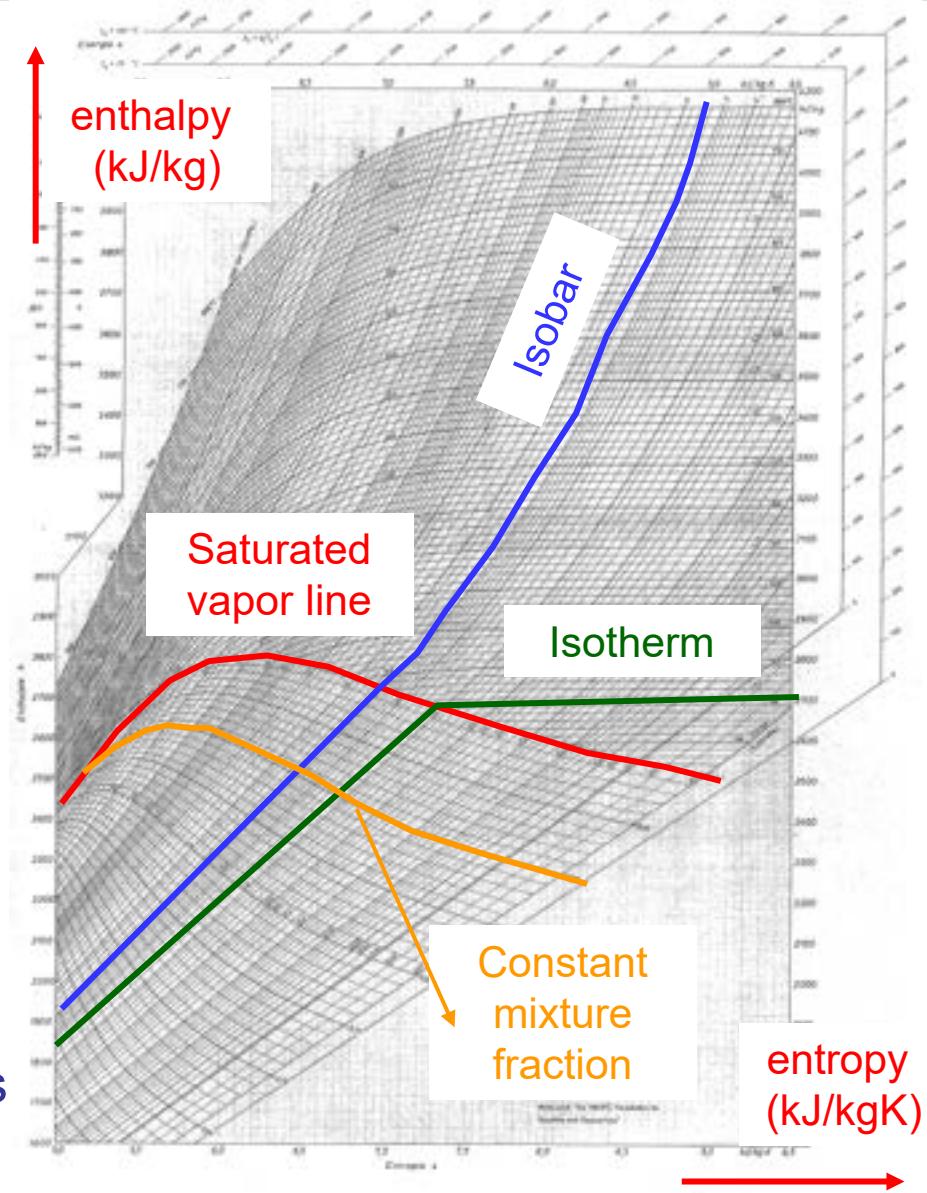
Mollier Diagram Water for Rankine Cycle

- 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

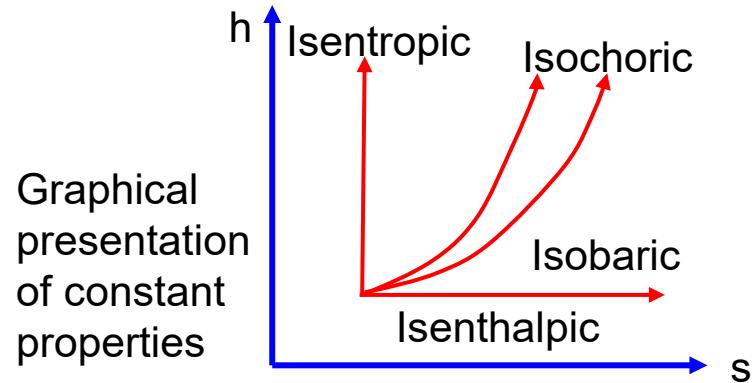
Temperatuur $\left(\frac{\partial U}{\partial S}\right)_V \equiv T$

(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



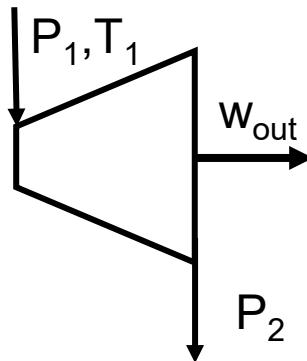
- For an isentropic processes for an incompressible substance follows from the Gibbs Equation ($Tds = dh - vdP$)

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

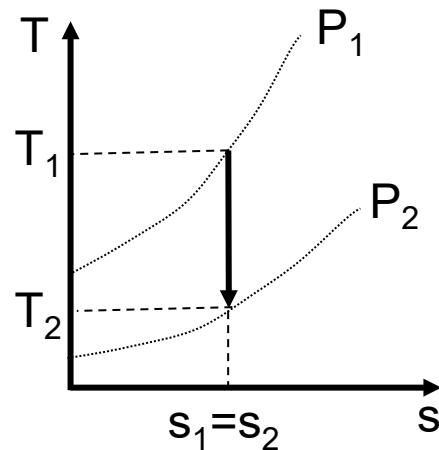
- The relation $\Delta h = v(P_2 - P_1)$ is used for analyzing ideal pumps (and often forgotten at the exam.....)

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

2nd 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**

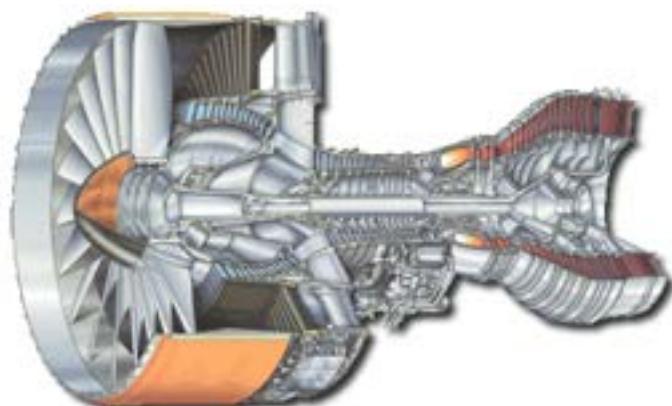
An ideal, reversible turbine delivers the maximum amount of work. A real, irreversible turbine working between the same end states produces less than the maximum amount of work



GE Steam Turbine

2nd 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

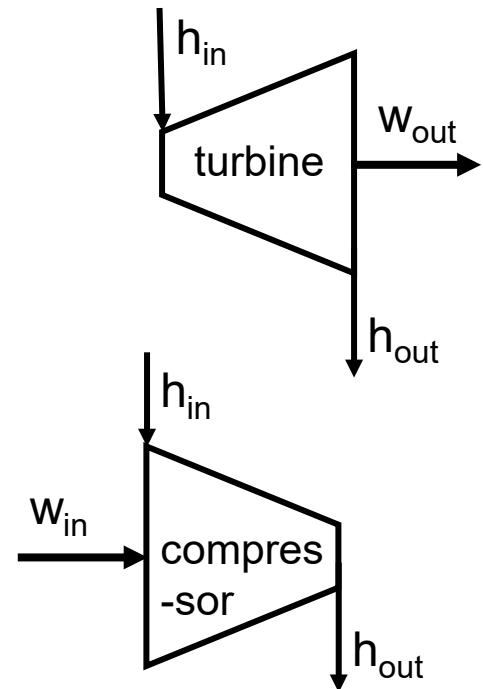


A real pump requires more power than an ideal one due to irreversibility's

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 $W_{in,ideal} < W_{in}$



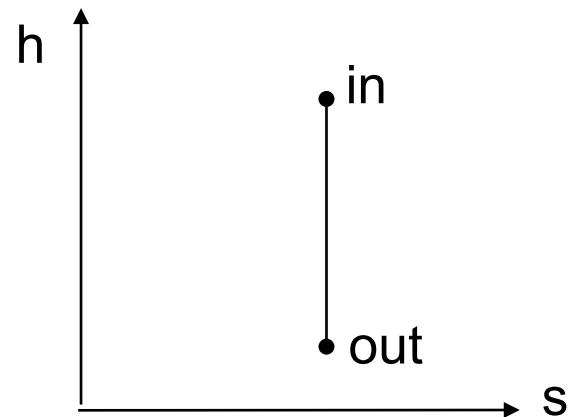
Ideal devices: open systems

- 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



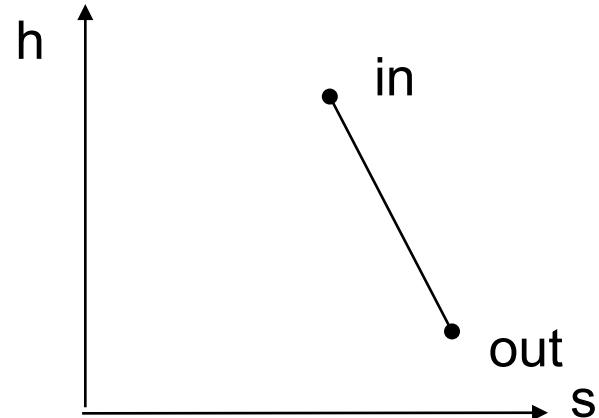
Real devices: open systems

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

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

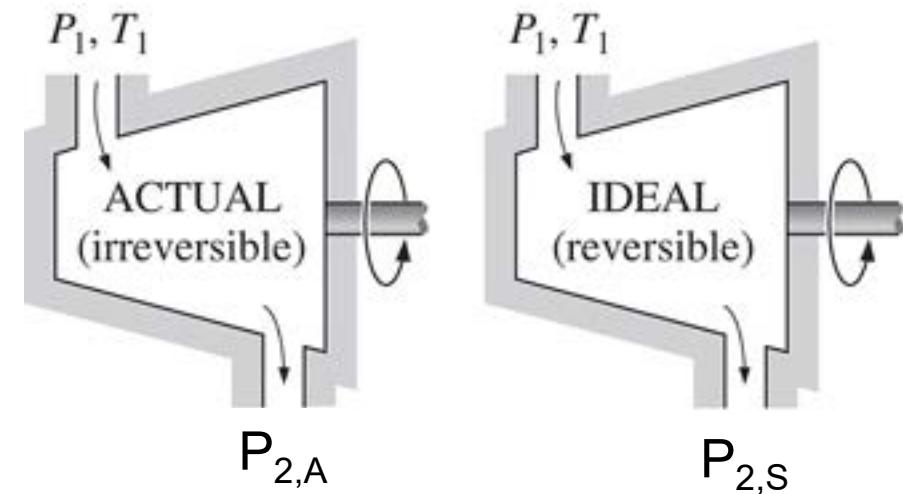
$$\dot{W}_{NET,A} = \dot{m}(h_{IN} - h_{OUT,A}) \quad \text{with} \quad h_{OUT,A} = h(P_{OUT}, s_{OUT})$$

- 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



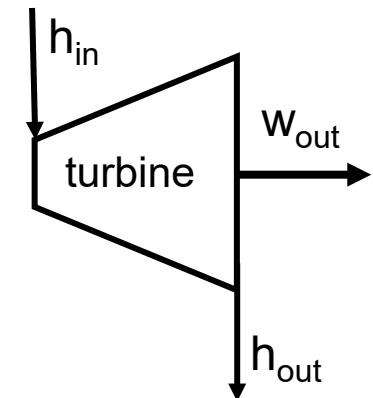
The isentropic process involves no irreversibilities and serves as the ideal process for adiabatic devices.

Real devices: Isentropic efficiencies

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

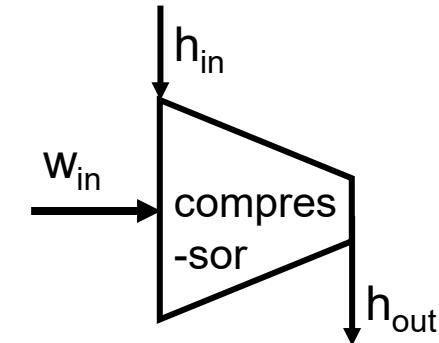
- Output, producing device (e.g. turbine)

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



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

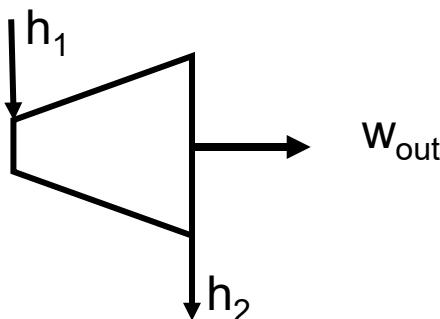
$$\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}} \quad \text{note always} \quad w_{IN,S} \leq w_{IN,A}$$



- 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**

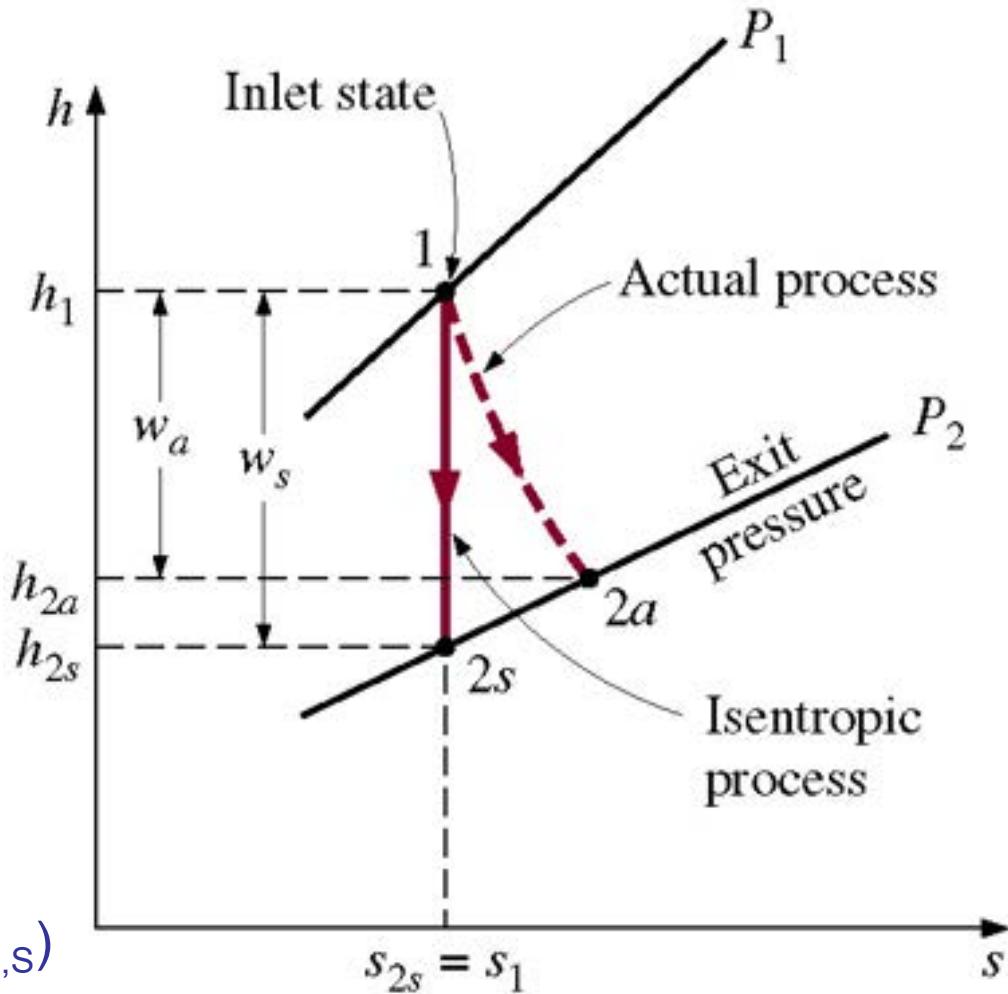


- Actual process $1 \rightarrow 2,A$
- Isentropic process $1 \rightarrow 2,S$
ideal process
where $P_{2,S} = P_{2,A}$
and $s_{2,S} = s_1$

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

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

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

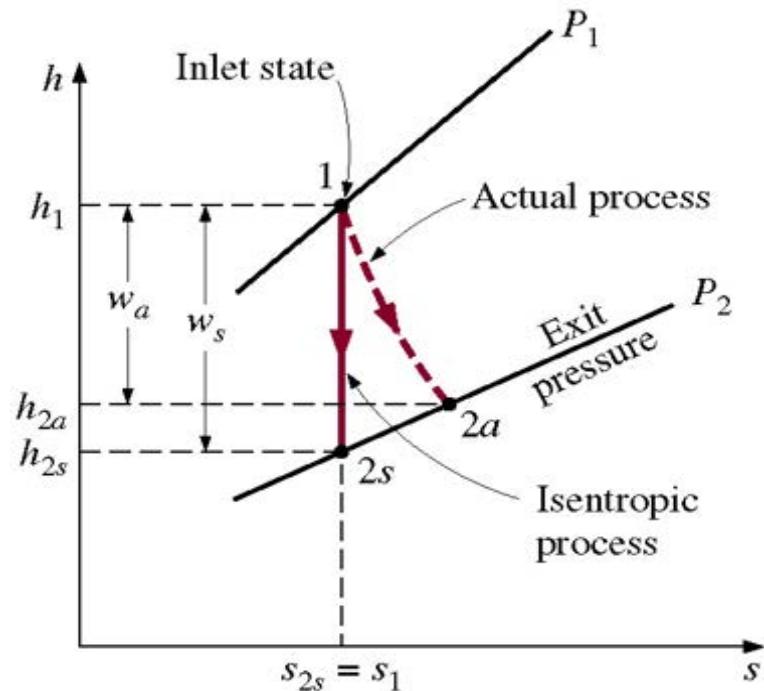


ISENTROPIC efficiencies: open output system

- 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 $s_{OUT,S} = s_{IN}$

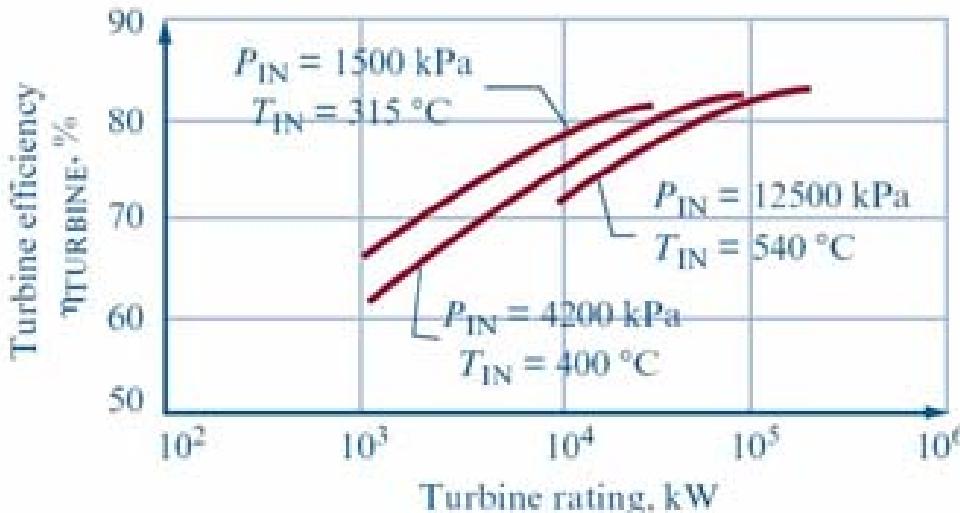
- The **isentropic efficiency**



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

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

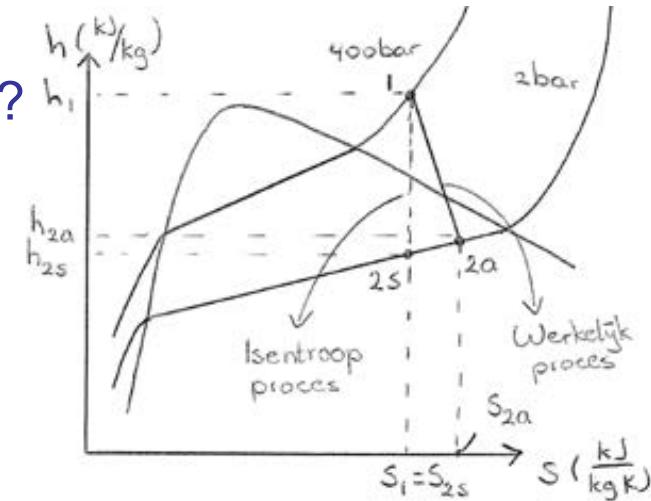


Typical condensing steam turbine isentropic efficiency curves, as supplied by the manufacturer, $P_{out} = 15 \text{ kPa}$ at 3600 rpm

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?

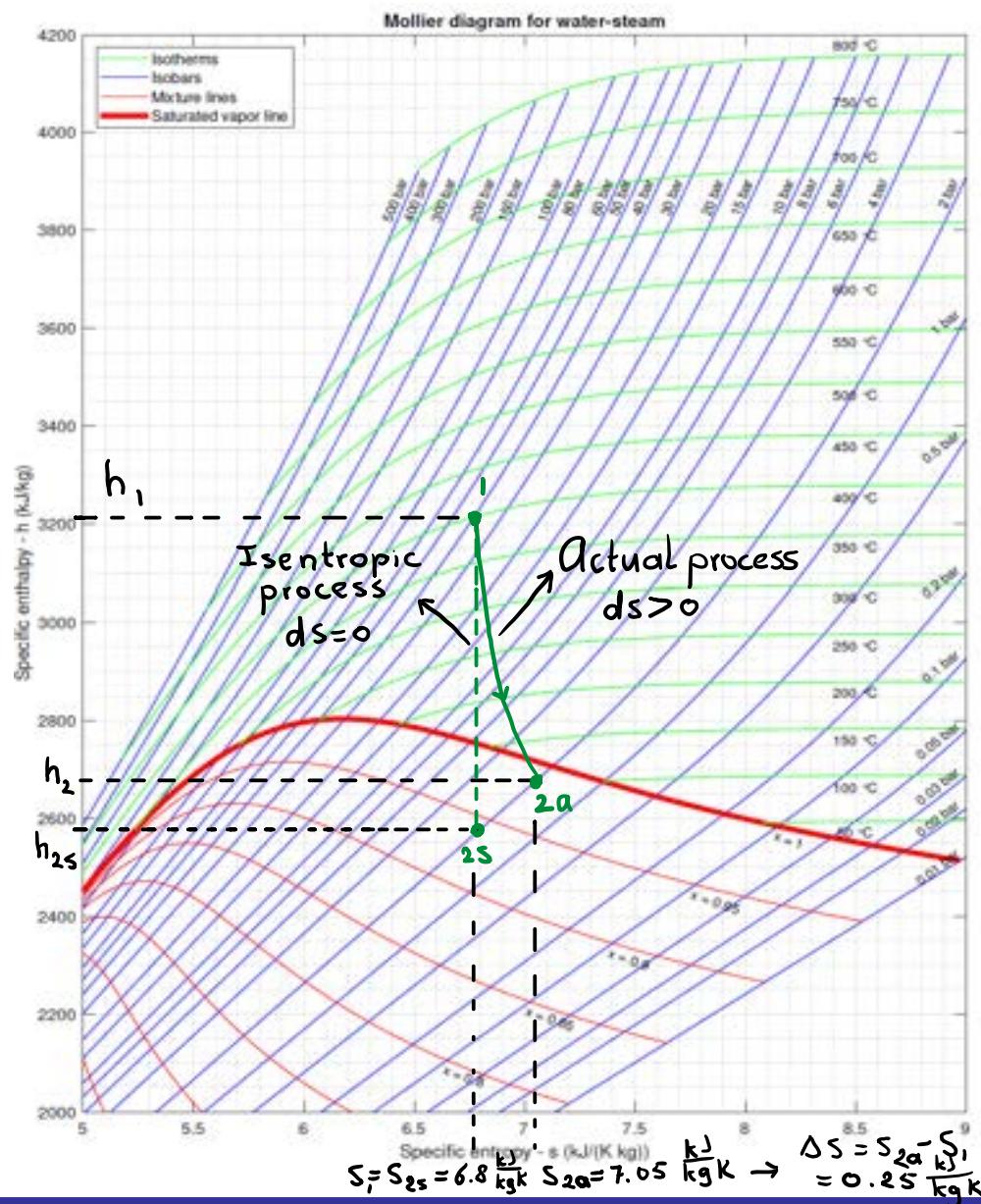
Solution: $\eta_{\text{OUTPUT},s} = \frac{w_{\text{OUT},A}}{w_{\text{OUT},s}} = \frac{h_1 - h_{2,A}}{h_1 - h_{2,s}}$
 $\rightarrow w_{\text{OUT},A} = h_1 - h_{2,A} = \eta_{\text{OUTPUT},s}(h_1 - h_{2,s})$



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

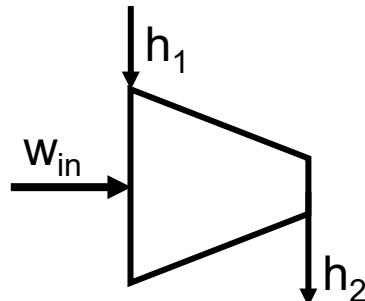
Example: Isentropic efficiency steam turbine

- 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

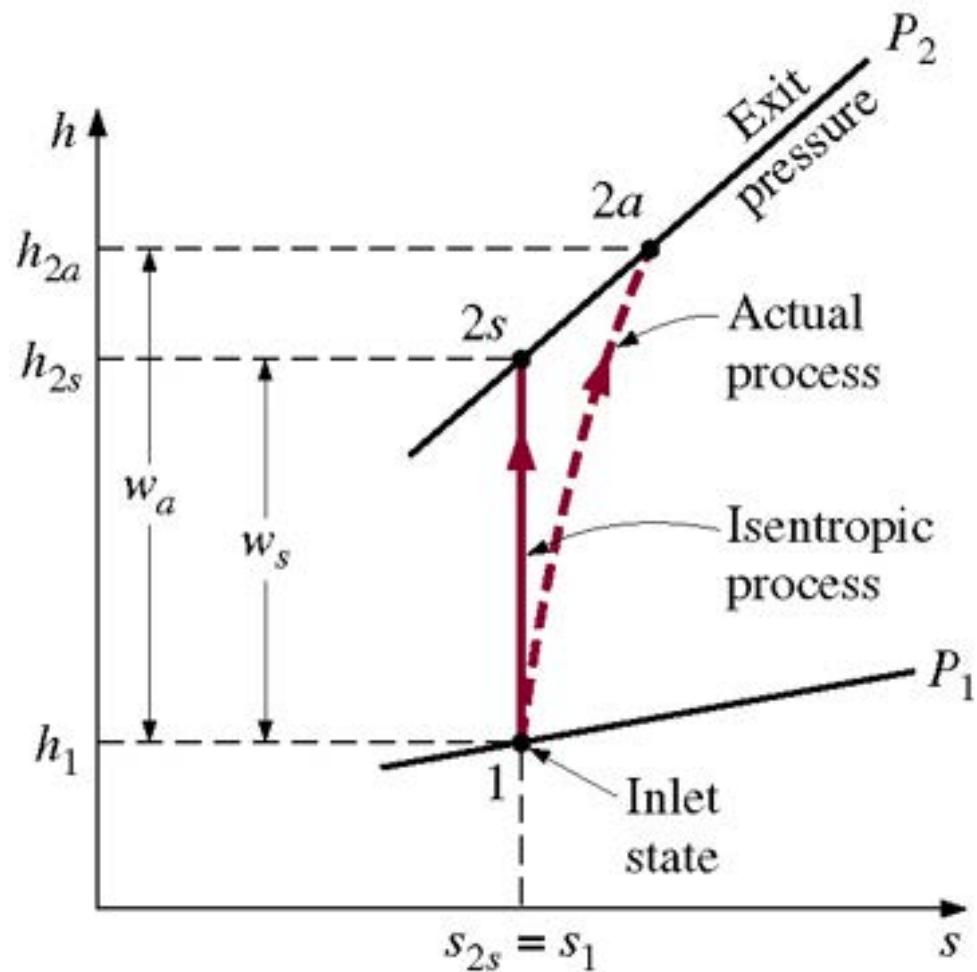
where $P_{2,S} = P_{2,A}$

and $s_{2,S} = s_1$

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

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

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



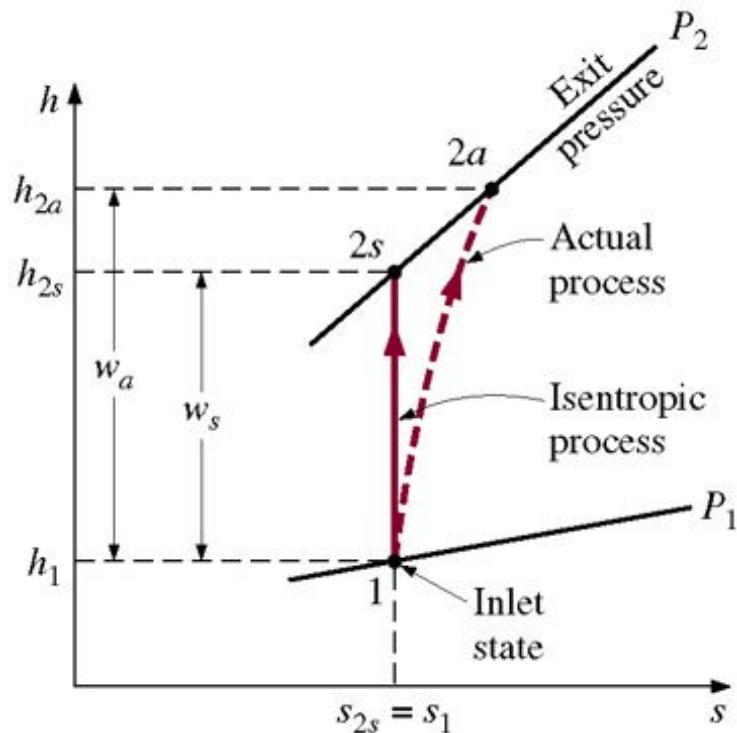
Isentropic efficiencies: Open input system

- 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**

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



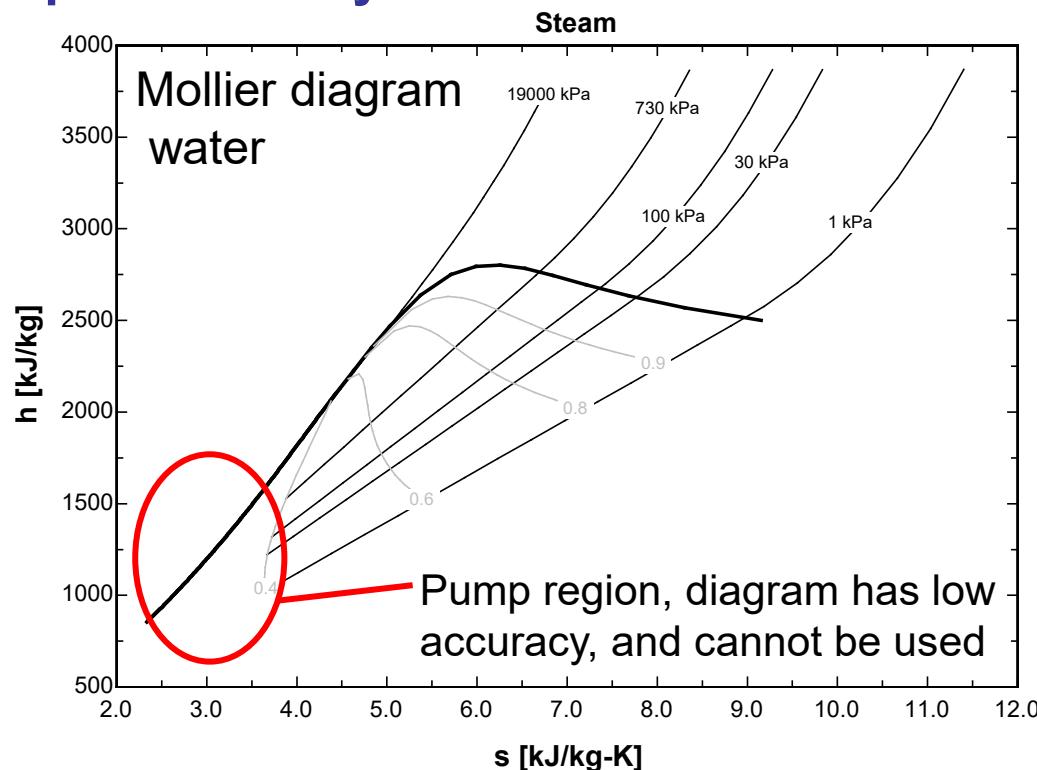
Isentropic efficiencies: Open input system

- 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

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

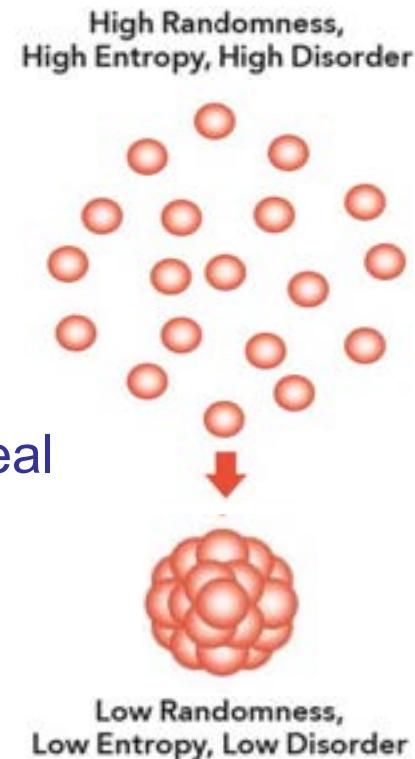
- Ideal pump ($ds=0$) used for incompressible ($dv=0$) fluid therefore (Gibbs equation)

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



Recapitulate class 5

- Entropy (s [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: $\eta_{\text{INPUT},s} = \frac{w_{\text{IN},s}}{w_{\text{IN},A}}$

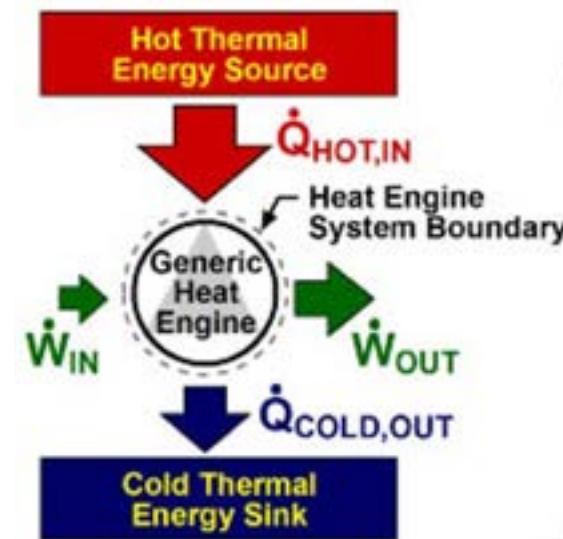


Next Class 6: Cycles for work, cold and heat, Carnot

- 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?

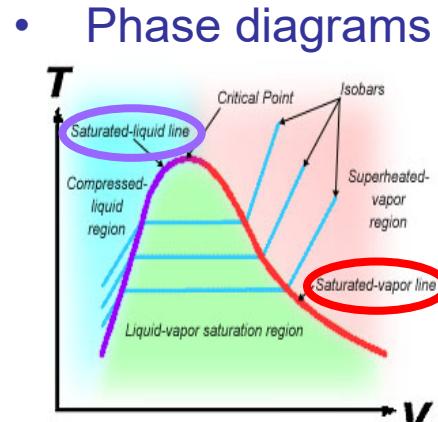


A perpetual – motion machine, an impossible cycle (M.C. Escher)



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 $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$



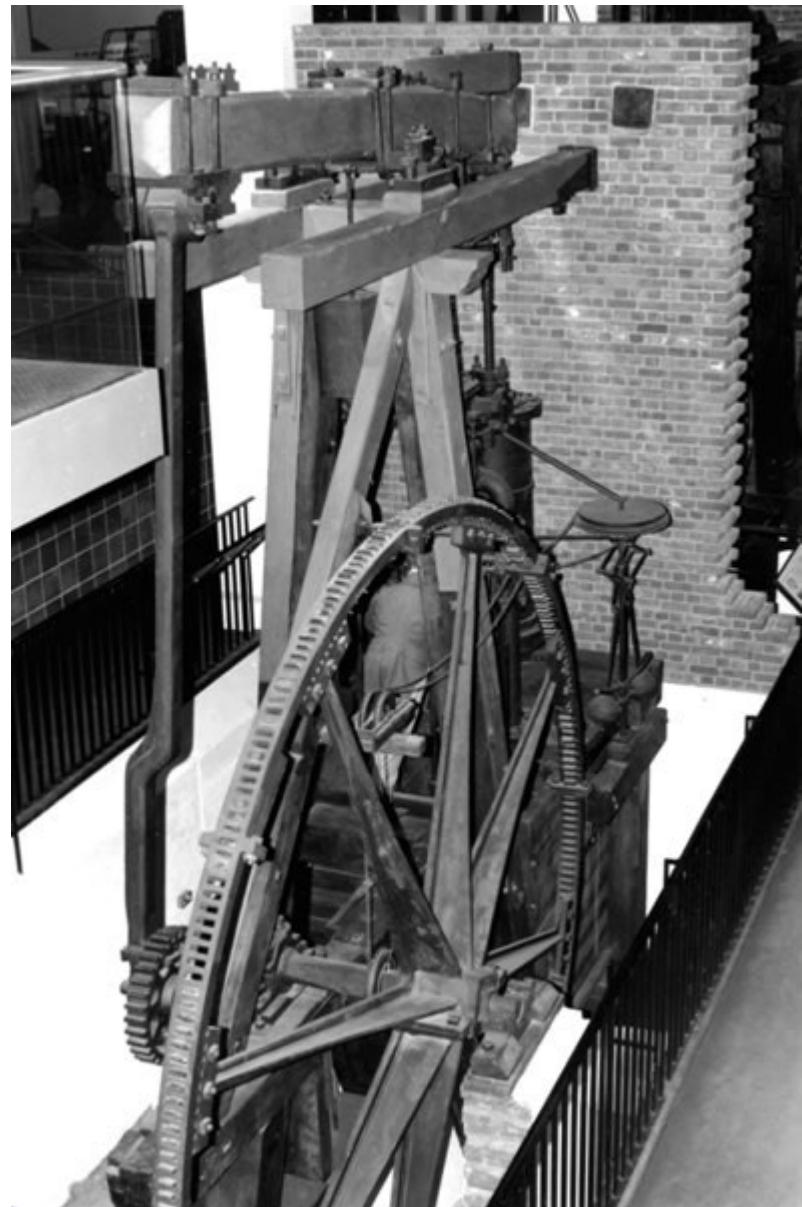
Class 6

Analysis of

Thermodynamic

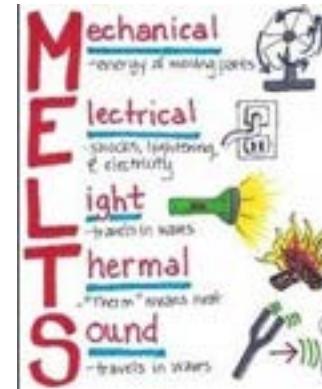
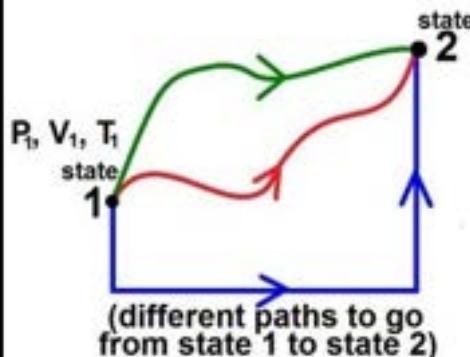
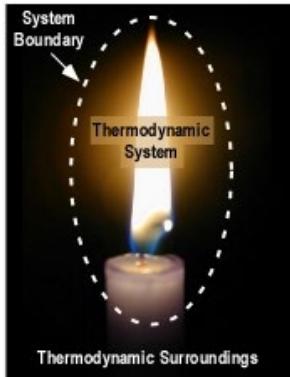
Cycles

Boulton and Watt Steam Engine.
Watt's use of the double-acting piston, an external condenser, and planetary gearing to change reciprocal into rotary motion made the steam engine into a practical power producer.
(British Science Museum, London)

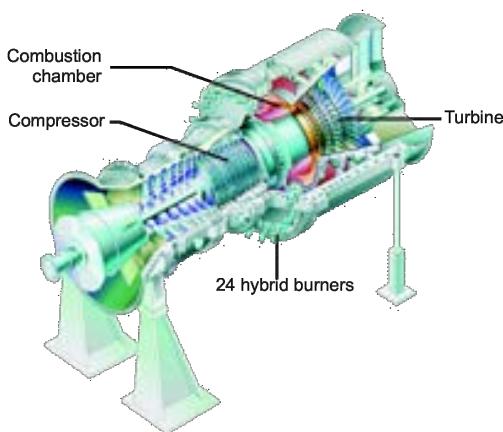


Roadmap Engineering Thermodynamics

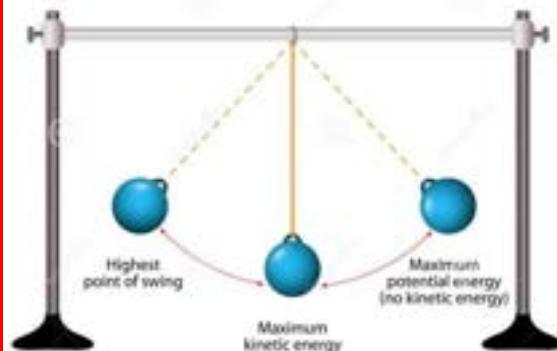
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



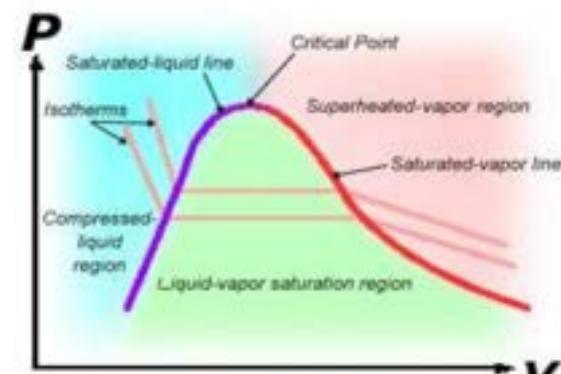
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

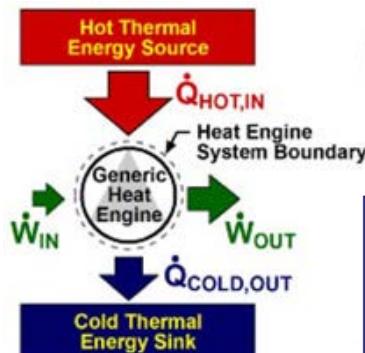


- Properties of Substances (Class 3, 9)

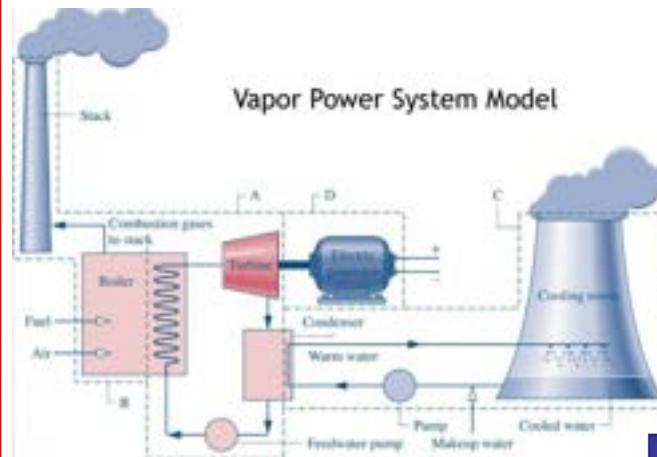


Roadmap Engineering Thermodynamics

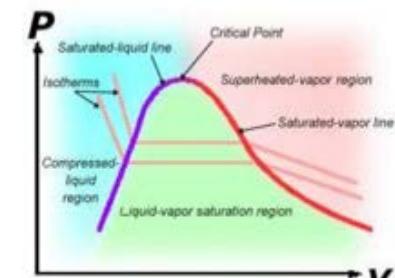
Thermodynamic cycles (Class 6)



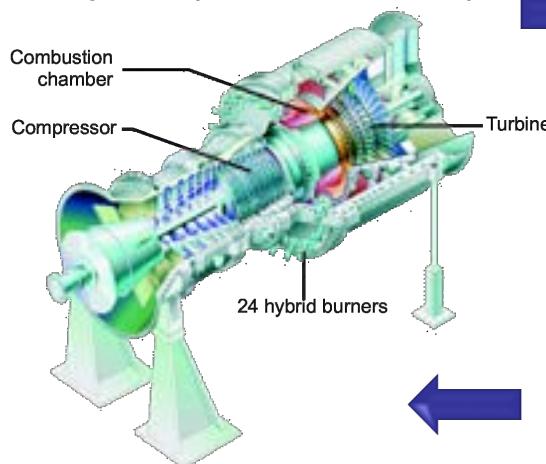
Vapor power cycles – Rankine cycle (Class 7, 8)



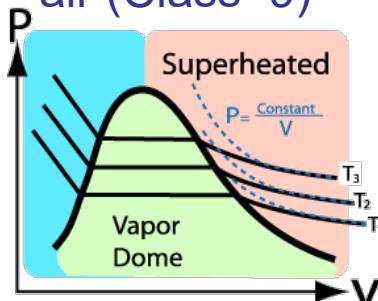
Properties of water (Class 3)



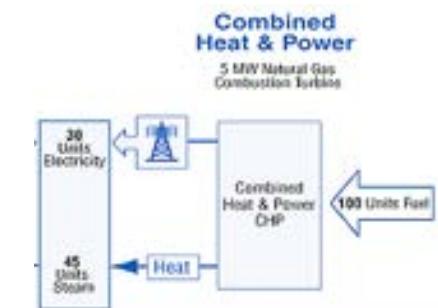
Gas power cycles – Brayton cycle (Class 10, 11)



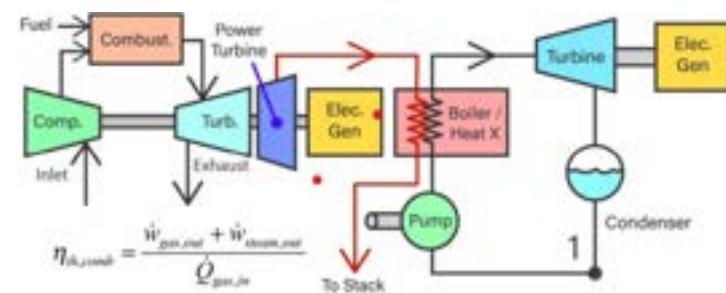
Properties of air (Class 9)



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

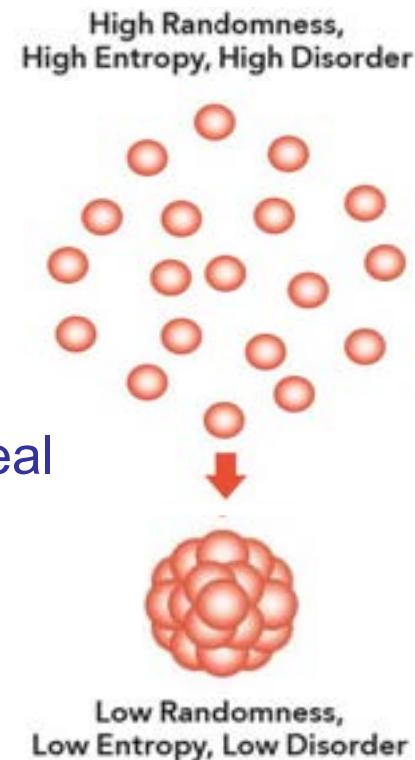


75% OVERALL EFFICIENCY



Recapitulate class 5

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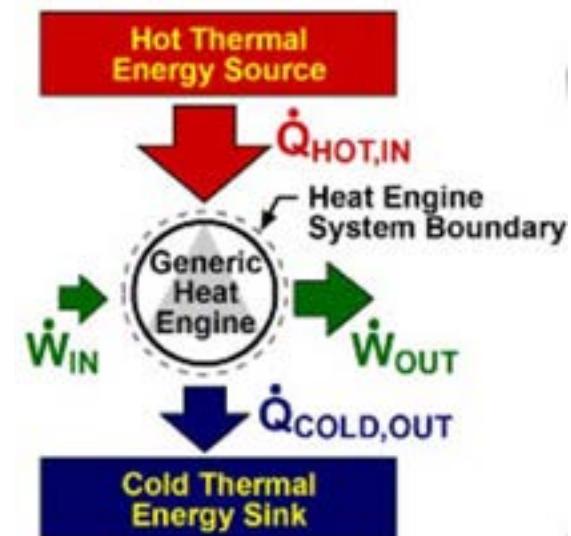
Content class 6

- **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



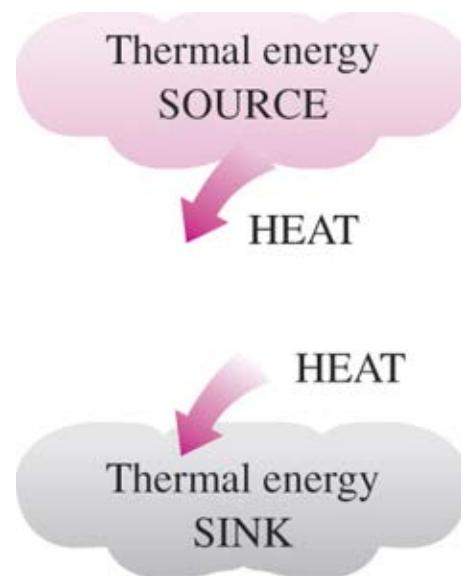
- The laws of thermodynamics for cycles
- Thermal efficiency of a heat power cycle
- Carnot cycle and Carnot efficiency
- COP of refrigeration and heat pump cycles
- Kelvin-Planck and Clausius statement
- Perpetual - Motion Machines
- **Learning goal:** explain the working of general thermodynamic power and refrigeration cycles

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



Thermal energy reservoirs

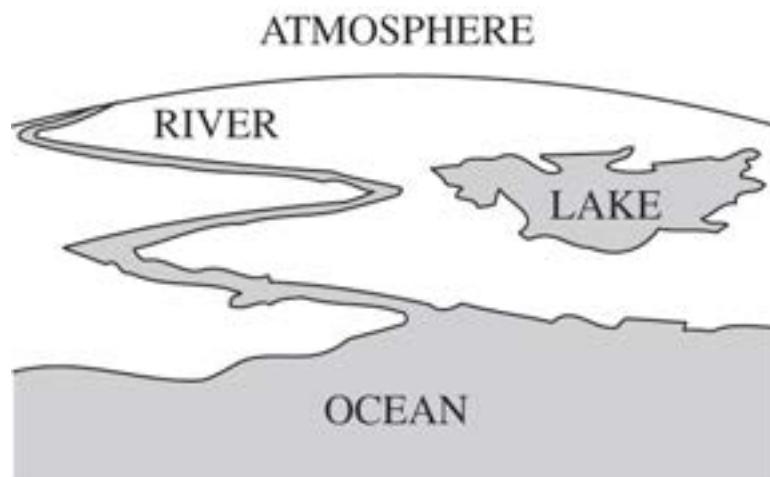
- **Thermal energy reservoir:** a hypothetical body with a relatively large thermal energy capacity (mass x specific heat) that can supply (source) or absorb (sink) finite amounts of heat without undergoing any change in temperature



A source supplies energy in the form of heat, and a sink absorbs it

Thermal energy reservoirs

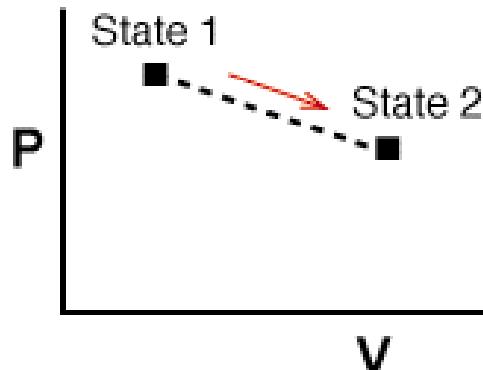
- In practice, large bodies of water such as oceans, lakes, and rivers as well as the atmospheric air can be modeled accurately as thermal energy reservoirs because of their large thermal energy storage capabilities or thermal masses



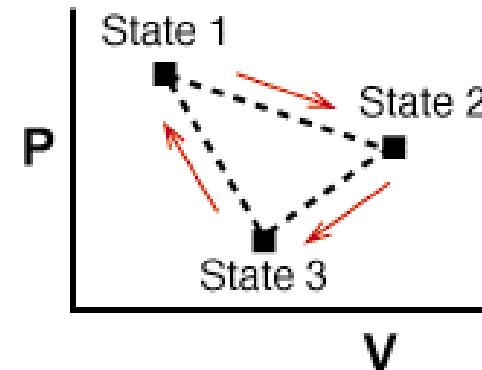
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs

Thermodynamic cycles

- **Thermodynamic cycle:** series of thermo-dynamic processes where the initial and final states are the same



Not a thermodynamic cycle, no enclosed area, this is a process.



A thermodynamic cycle,
closed area.

Thermodynamic cycles

- Two kind of thermodynamic cycles
 1. Thermodynamic **power** cycles are used in **heat engines** and produce mechanical power by converting thermal energy from a hot source into work
 2. Thermodynamic cycles are also used in refrigerators, air conditioners and heat pumps to **move thermal energy** from a **cold** source to a **hot sink** using power



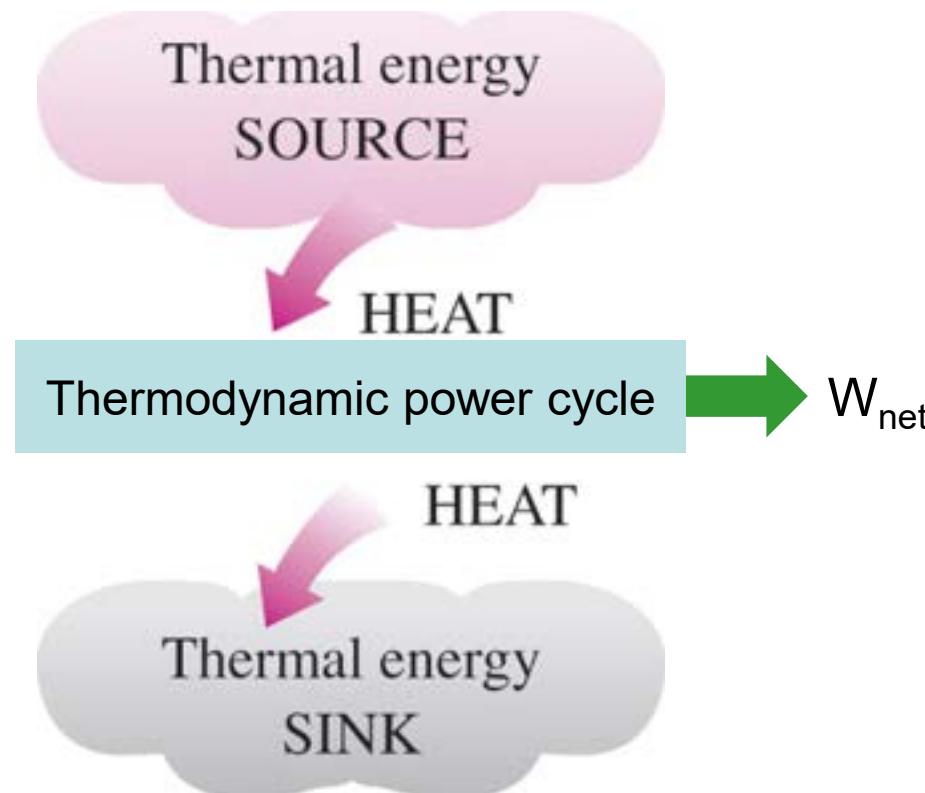
1: Thermodynamic power cycle



2: Thermodynamic refrigeration cycle

Thermodynamic cycles

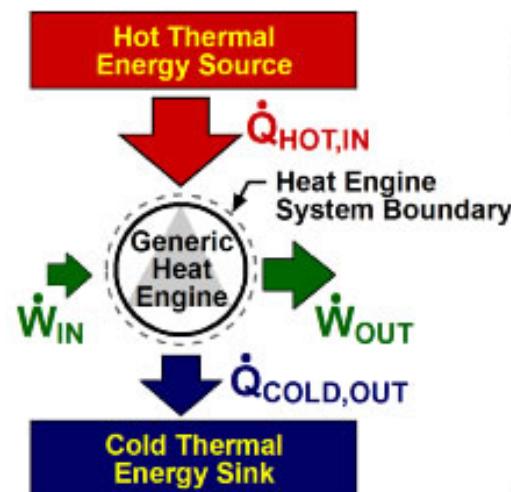
- In a thermodynamic cycle heat (energy) is always transported **between two thermal temperature reservoirs**, a source and a sink



Examples of thermodynamic cycles

1. Examples of thermodynamic power cycles

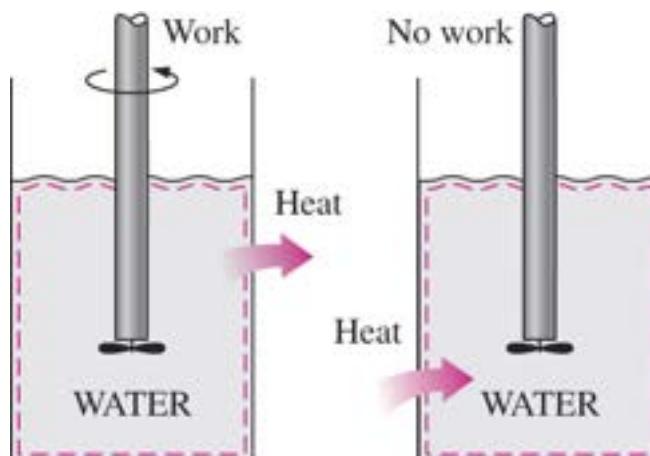
- Steam power plants
- Diesel engines
- Steam machines
- Gasoline engines
- Gas turbines
- Turbo jet engines



ThermoNet: Wiley

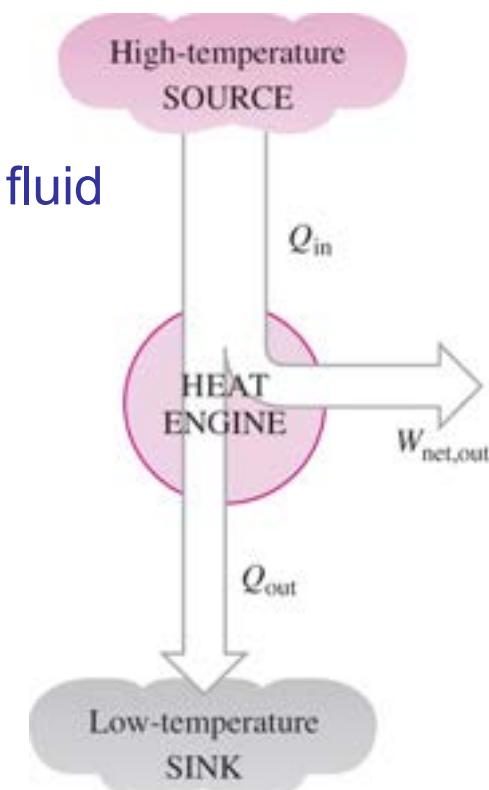
Power cycles / Heat engines

- A **heat engine** is the devices that converts heat to work
 1. It receives heat from a high-temperature thermal source (solar energy, oil furnace, nuclear reactor, geothermal etc.)
 2. Is converts part of this heat to work (often in the form of a rotating shaft)
 3. Is rejects the remaining waste heat to a low-temperature thermal sink (the atmosphere, rivers, etc.)
 4. It operates on a cycle, that usually involves a fluid to and from which heat is transferred while undergoing a cycle, this fluid is called the working fluid



Work can always be converted to heat directly and completely, but the reverse is not true

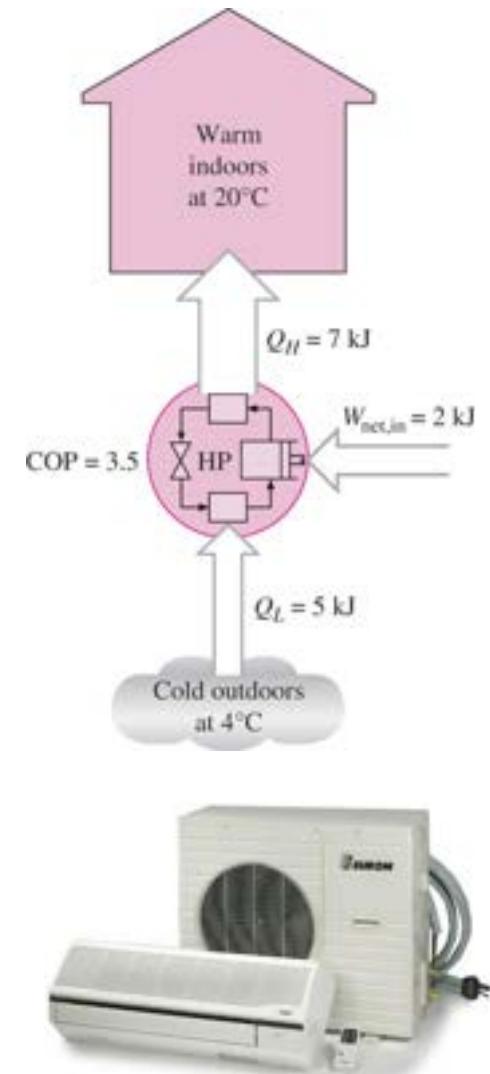
Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink



Examples of thermodynamic cycles

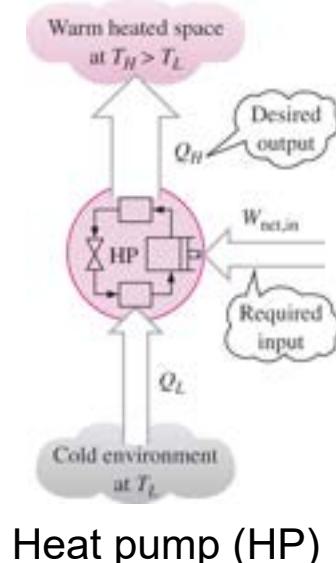
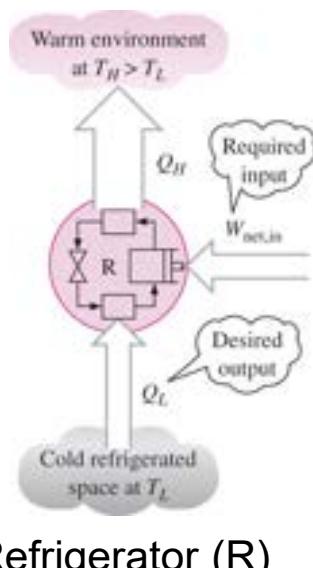
2. Thermodynamic refrigeration cycles and heat pumps

- Air conditioners
- Refrigerators
- Chillers
- Heat pumps

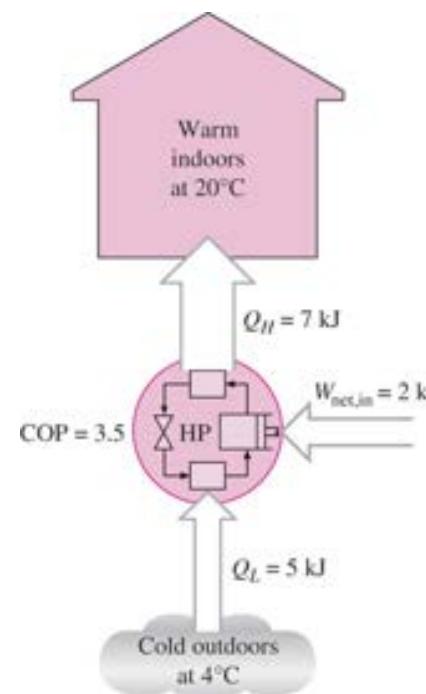


Refrigerators and heat pumps

- A **refrigerator or heat pump** is a device that transfers heat from a cold space to a warm environment
 1. Receives heat (cold) from a low-temperature thermal source
 2. Uses work to transport this heat
 3. Rejects heat to high-temperature thermal sink
 4. Heat transferred by working fluid in cyclic process
 5. Working fluid → refrigerant
 6. Vapor-compression refrigeration



The objective of a refrigerator is to remove Q_L from the cooled space. The objective of a heat pump is to supply heat Q_H into the warmer space.



The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.

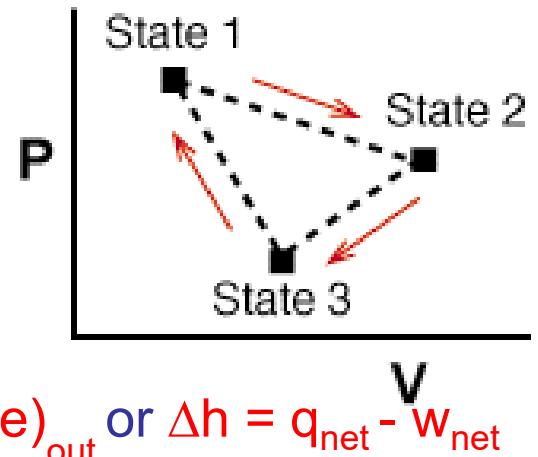
First law for cycles

- Conservation of energy for a cycle (first law)
- Change in any thermodynamic property (e.g. T, P, v, s, u, h) over a cycle = 0
- First law for closed systems
 $du = \delta q - \delta w$ or $\Delta u = q_{\text{net}} - w_{\text{net}}$
- First law for open system
 $q_{\text{in}} + w_{\text{in}} + (h + ke + pe)_{\text{in}} = q_{\text{out}} + w_{\text{out}} + (h + ke + pe)_{\text{out}}$ or $\Delta h = q_{\text{net}} - w_{\text{net}}$
- First law applied to a cycle (recall for a cycle: $\Delta u = \Delta h = \Delta ke = \Delta pe = 0$, state functions)

$$\oint (\delta q_{in} - \delta q_{out}) + \oint (\delta w_{in} - \delta w_{out}) = \\ q_{in} - q_{out} + w_{in} - w_{out} = \oint de_{cm} = 0$$

- For all complete thermodynamic cycles

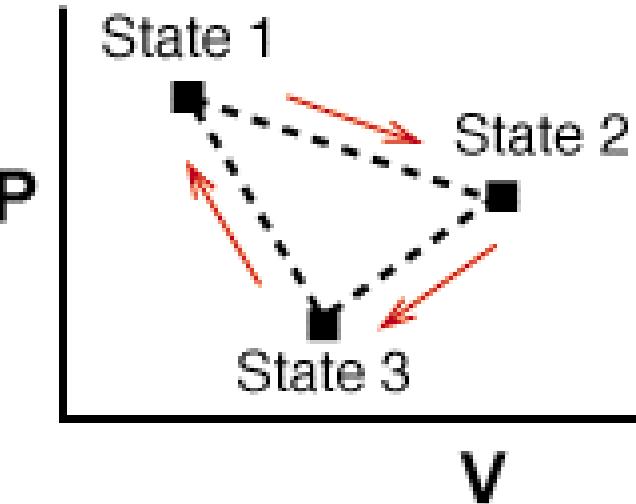
$$q_{\text{in}} - q_{\text{out}} = w_{\text{out}} - w_{\text{in}} \rightarrow q_{\text{net}} = w_{\text{net}}$$



\oint = cyclic integral
= integral over a closed circle

Second law for cycles

- Generation of entropy (second law) for a cycle
- Recall $(\Delta s)_{\text{cycle}} = 0$ (s is a state function, its value depends only on the state and not on the path followed)



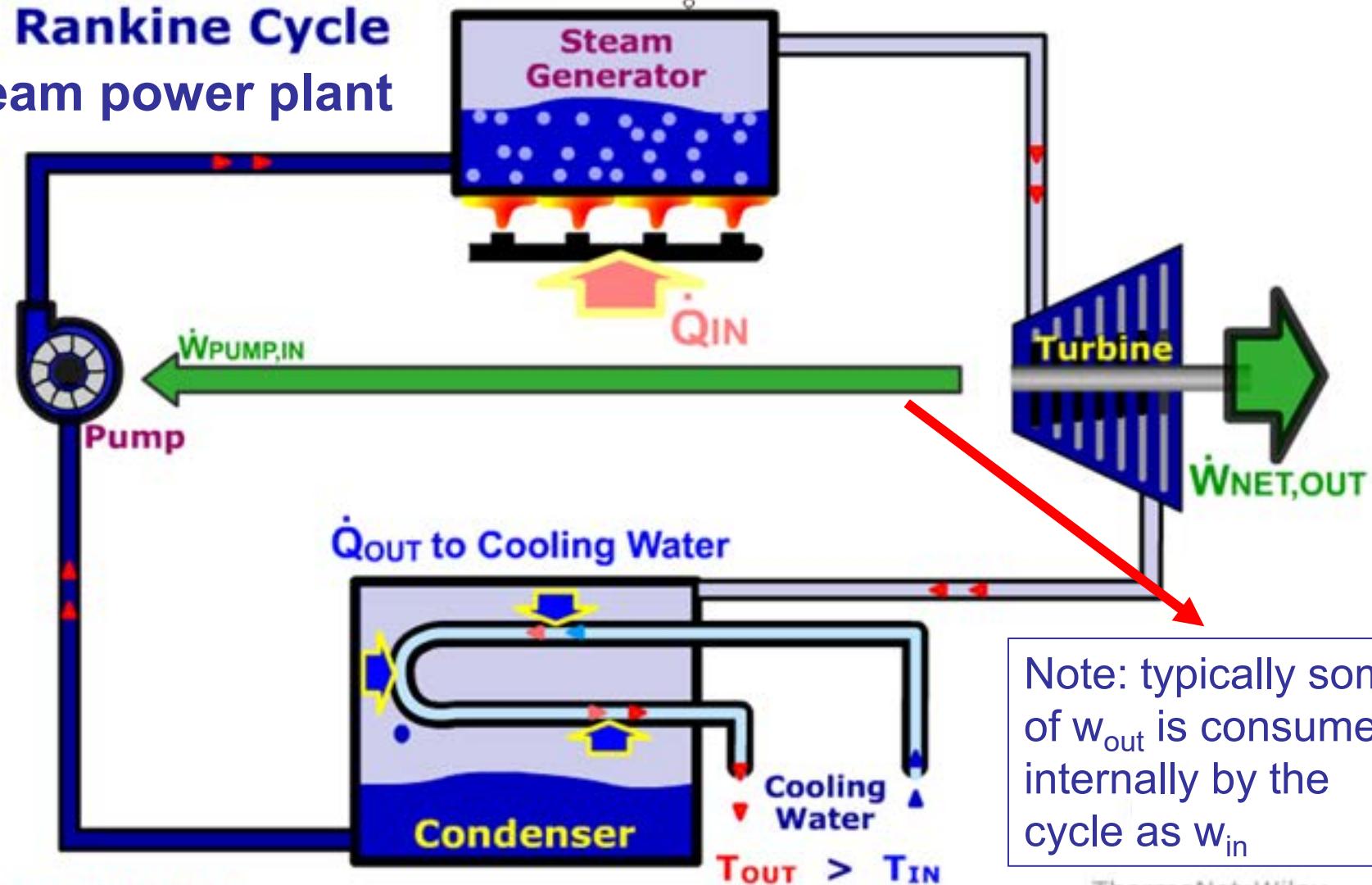
- Entropy, $\frac{\delta q_{net}}{T} \leq ds$, applied to a cycle:

$$\oint \sum_{i=1}^n \frac{\delta q_{net,i}}{T_i} = \sum_{i=1}^n \oint \frac{\delta q_{net,i}}{T_i} = \sum_{i=1}^n \frac{q_{net,i}}{T_i} \leq \oint ds_{cm} = 0$$

- Second law for a complete cycle: $\sum_{i=1}^n \frac{\delta q_{net,i}}{T_i} \leq 0$ or $\oint \frac{\delta q_{net,i}}{T_i} \leq 0$
- The net entropy of all heat transfer processes in a cycle should increase

Example: 1st & 2nd law for cycle

Rankine Cycle Steam power plant



ThermoNet:Wiley

Example: 1st & 2nd law for cycle

- Consider the steam cycle (see class 7)

- Energies in and out (see class 7)

- $w_{in} = 1 \text{ kJ/kg}$
- $q_{in} = 3182 \text{ kJ/kg}$ at $T_{in} \approx 311^\circ\text{C}$
- $w_{out} = 1000 \text{ kJ/kg}$
- $q_{out} = 2183 \text{ kJ/kg}$ at $T_{out} = 45^\circ\text{C}$

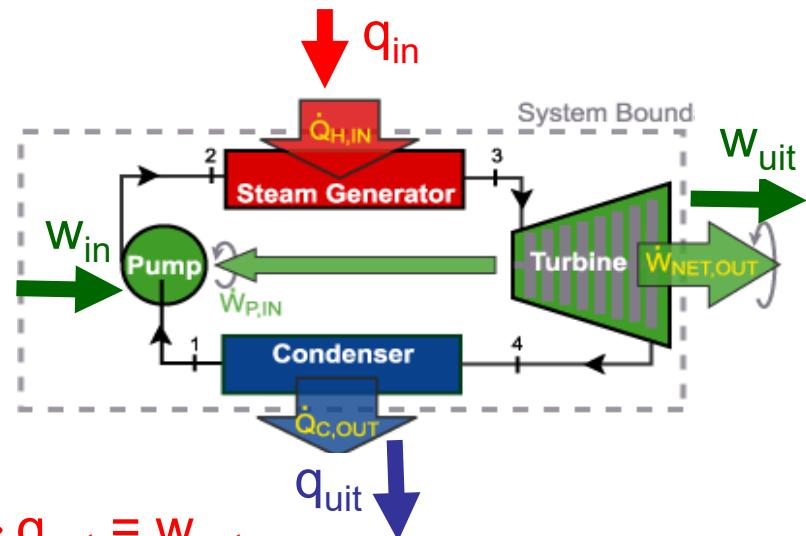
- Check the first law: $q_{in} - q_{out} = w_{out} - w_{in} \rightarrow q_{net} = w_{net}$

$$\left. \begin{aligned} q_{net} &= q_{in} - q_{out} = 3182 - 2183 = 999 \text{ kJ/kg} \\ w_{net} &= w_{out} - w_{in} = 1000 - 1 = 999 \text{ kJ/kg} \end{aligned} \right\} \rightarrow q_{net} = w_{net} \rightarrow \text{Right!}$$

- Check the second law: $\sum_{i=1}^n \frac{q_{net,i}}{T_i} \leq 0$ (Clausius inequality: $\frac{\delta q_{net}}{T} \leq ds$)

$$\sum_{i=1}^n \frac{q_{net,i}}{T_i} = \underbrace{\frac{q_{in}}{T_{in}} - \frac{q_{out}}{T_{out}}}_{ds_{in} - ds_{out}} = \frac{3185}{584} - \frac{2183}{318} = 5.45 - 6.86 = -1.41 \text{ kJ/kgK} \leq 0 \text{ kJ/kgK} \rightarrow \text{Right!}$$

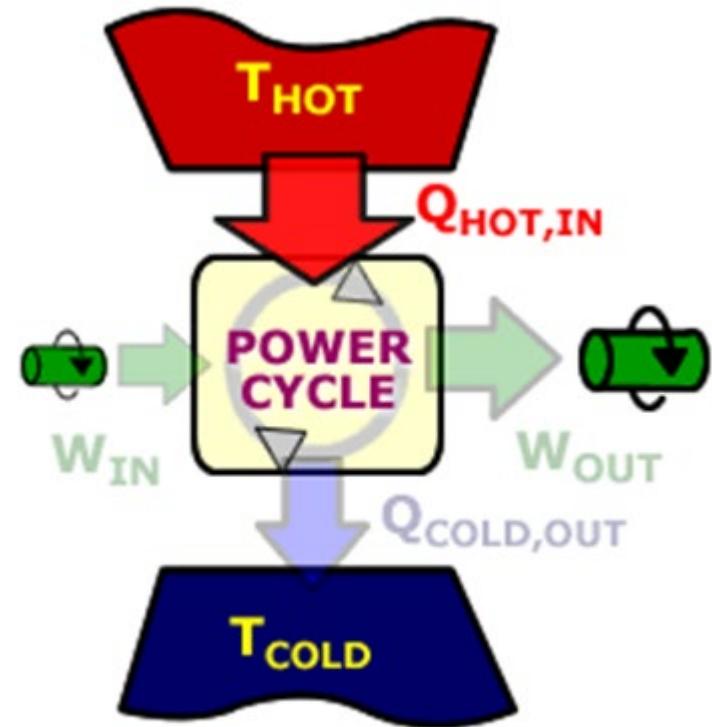
- Both laws are valid for this cycle 1: energy is conserved ($e_{in} = e_{out}$)
2: entropy is created ($ds_{out} > ds_{in}$)



Thermodynamic power cycle efficiency

- Power cycle efficiency, also called:
 - Heat engine efficiency (η_{he})
 - Thermal efficiency (η_{th})
 - Cycle efficiency
 - Thermodynamic efficiency
- Defined as

$$\eta_{he} = \eta_{th} = \frac{\text{What we want}}{\text{What we pay for}}$$



ThermoNet: Wiley

$$\eta_{he} = \eta_{th} = \frac{w_{out} - w_{in}}{q_{in}} = \frac{q_{in} - q_{out}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$$

- Note: the efficiency is only 100% if $q_{out} = 0$, which is impossible! see later

Carnot cycle

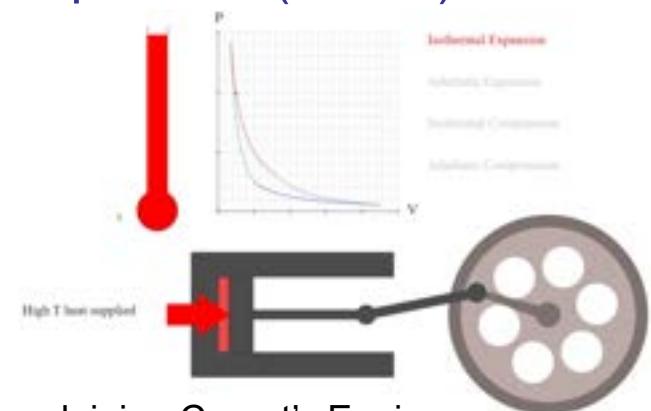
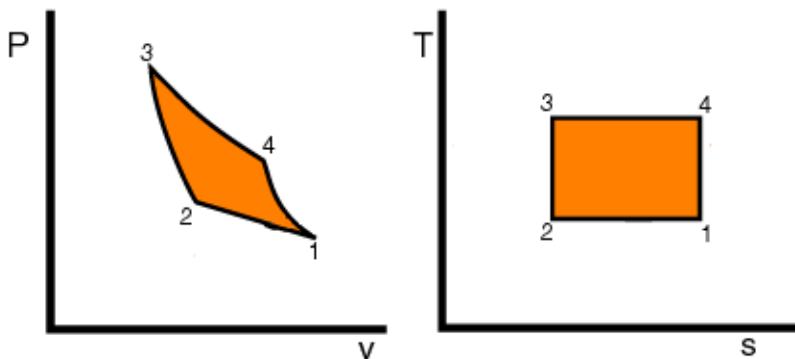
- Real processes generate entropy and therefore are irreversible
- The most efficient processes are reversible processes which are only possible in theory
- Isentropic efficiencies compare real processes to reversible (ideal) processes
- Analogue, real cycles generate entropy and are therefore irreversible
- Analogue, irreversible real cycles are compared to reversible ideal cycles to determine how closely a real cycle approaches its theoretical efficiency
- Not all reversible cycles have the same maximum efficiency, it depends on the temperatures
- The cycle with the highest possible efficiency is the **Carnot Power Cycle**
- Developed by Sadi Carnot (1796 – 1832)



Sadi Carnot

Carnot power cycle

- The **Carnot cycle** is a completely reversible cycle that is only possible in theory ($\delta s_{\text{gen}} = 0$ for all processes)
- It sets a limit for actual cycles; the efficiency of a real cycle cannot be higher than the Carnot efficiency
- The Carnot cycle consists out of 4 reversible processes:
 - $1 \rightarrow 2$ Isothermal compression ($dT = 0$)
 - $2 \rightarrow 3$ Isentropic (adiabatic & reversible) compression ($ds = 0$)
 - $3 \rightarrow 4$ Isothermal expansion ($dT = 0$)
 - $4 \rightarrow 1$ Isentropic (adiabatic & reversible) expansion ($ds = 0$)

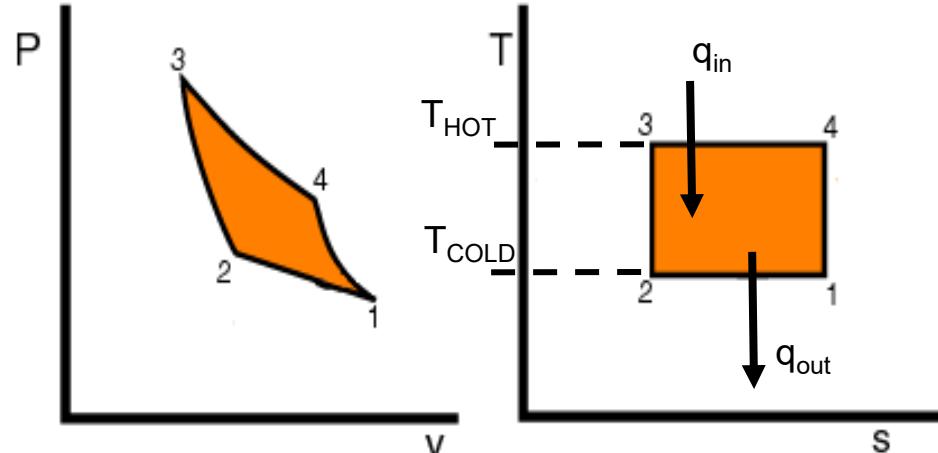


Movie explaining Carnot's Engine

http://galileoandeinstein.phys.virginia.edu/more_stuff/Applets/carnot_cycle/carnot_cycle.html

Carnot power cycle

- The Carnot Power Cycle consists of two isentropic & two isothermal processes
- A gas undergoing a Carnot cycle in a piston-cylinder device undergoes the following reversible processes



Pv and Ts diagram of a Carnot cycle

- Process 1-2: **Isothermal compression** with heat transfer to a cold thermal reservoir at T_{cold} ($W_{in} > 0$, $Q_{out} > 0$ and $T_{cold} = \text{constant}$)
- Process 2-3: **Isentropic compression** causing the temperature of the gas to increase from T_{cold} to T_{hot} ($W_{in} > 0$, $Q = 0$ and $s = \text{constant}$)
- Process 3-4: **Isothermal expansion** with heat transfer from a hot thermal reservoir at T_{hot} ($W_{out} > 0$, $Q_{in} > 0$ and $T_{hot} = \text{constant}$)
- Process 4-1: **Isentropic expansion** causing the temperature of the gas to decrease from T_{hot} to T_{cold} ($W_{out} > 0$, $Q = 0$ and $s = \text{constant}$)

Carnot power cycle

- Consider the **Carnot cycle** where

- All q_{in} occurs at T_{hot} ($q_{in,hot}$)
- All q_{out} occurs at T_{cold} ($q_{out,cold}$)

- Second law**

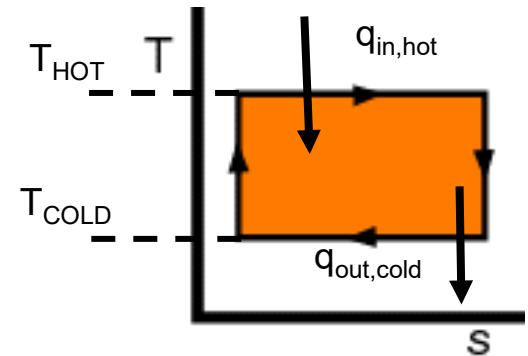
- Reversible (ideal / theoretical) cycle

$$\sum_{i=1}^2 \frac{q_{net,i}}{T_i} = \frac{q_{in,hot}}{T_{hot}} - \frac{q_{out,cold}}{T_{cold}} = 0 \rightarrow \frac{q_{out,cold}}{q_{in,hot}} = \frac{T_{cold}}{T_{hot}}$$

- Irreversible (real) cycle

$$\sum_{i=1}^2 \frac{q_{net,i}}{T_i} = \frac{q_{in,hot}}{T_{hot}} - \frac{q_{out,cold}}{T_{cold}} < 0 \rightarrow \frac{q_{out,cold}}{q_{in,hot}} > \frac{T_{cold}}{T_{hot}}$$

- For any real power cycle, 2nd Law requires $q_{out,cold} > 0$ for $T_{cold} > 0$ K → always a cold thermal reservoir is required in addition to the hot thermal reservoir



Carnot power cycle

- $\frac{q_{out,cold}}{q_{in,hot}} \geq \frac{T_{cold}}{T_{hot}}$ places an upper limit on heat engine efficiency or thermal efficiency

$$\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} \leq 1 - \frac{T_{cold}}{T_{hot}}$$

- **Carnot efficiency:** Maximum efficiency for any power cycle operating between T_{hot} and T_{cold}

$$\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$$

- The higher T_{hot} or the lower T_{cold} the higher the efficiency that can be achieved

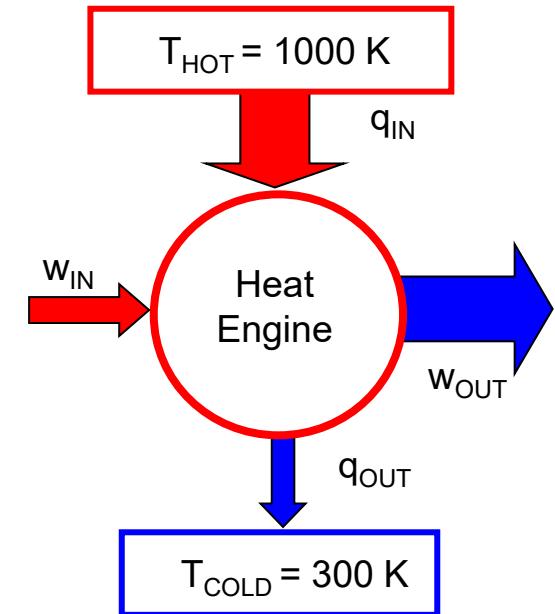
$\eta_{carnot} \rightarrow 1$ (100%) as $T_{cold} = 0$ Kelvin or as $T_{hot} \rightarrow$ Infinite

Carnot cycle: example

- A Carnot engine operates between a source at 1000 K and a sink at 300 K. If the heat engine is supplied with heat at a rate of 600 kJ/min determine
 1. The thermal efficiency
 2. The net power output

- **Solution:**

$$T_{hot} = 1000 \text{ K}, T_{cold} = 300 \text{ K}, \dot{Q}_{in} = 600 \text{ kJ/min}$$



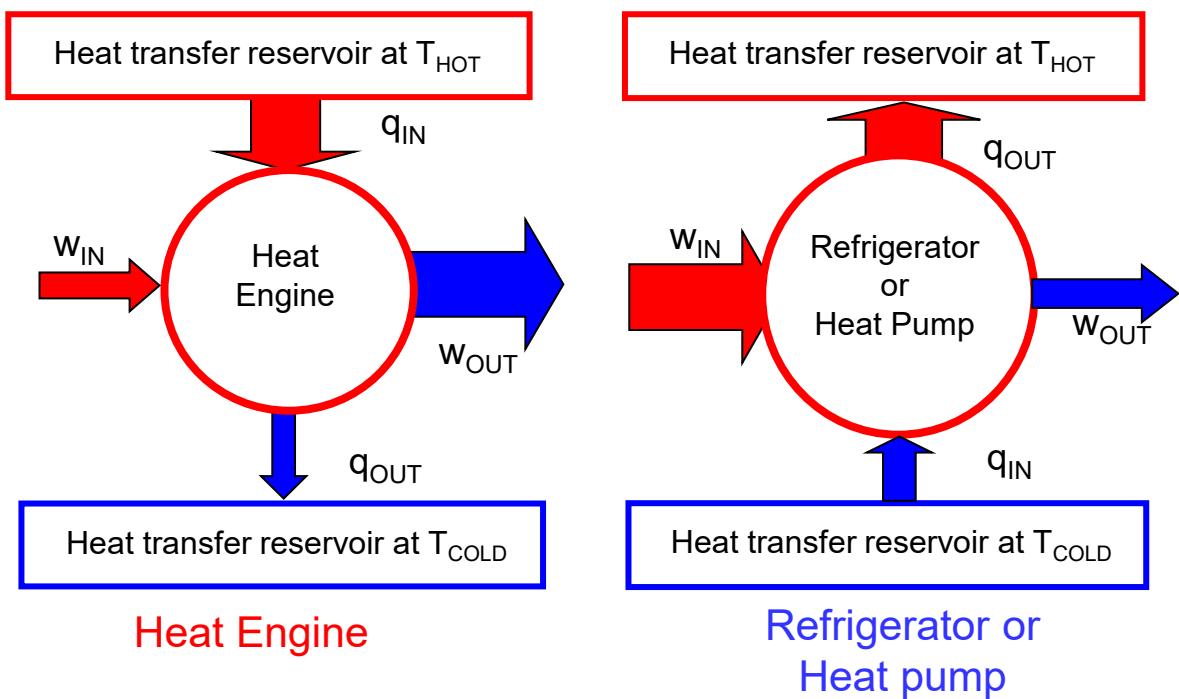
$$1. \eta_{Carnot} = \eta_{he} = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{300}{1000} = 0.7 \rightarrow 70\%$$

$$2. \eta_{he} = \frac{\dot{W}_{out} - \dot{W}_{in}}{\dot{Q}_{in}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} \rightarrow \dot{W}_{net} = \eta_{he} \dot{Q}_{in} \rightarrow \dot{W}_{net} = 0.7 \frac{600}{60} = 7 \text{ kW}$$

- 70% of the 10 kW input heat is converted to work (7 kW) in reality it will be only around half of this due to irreversibility's

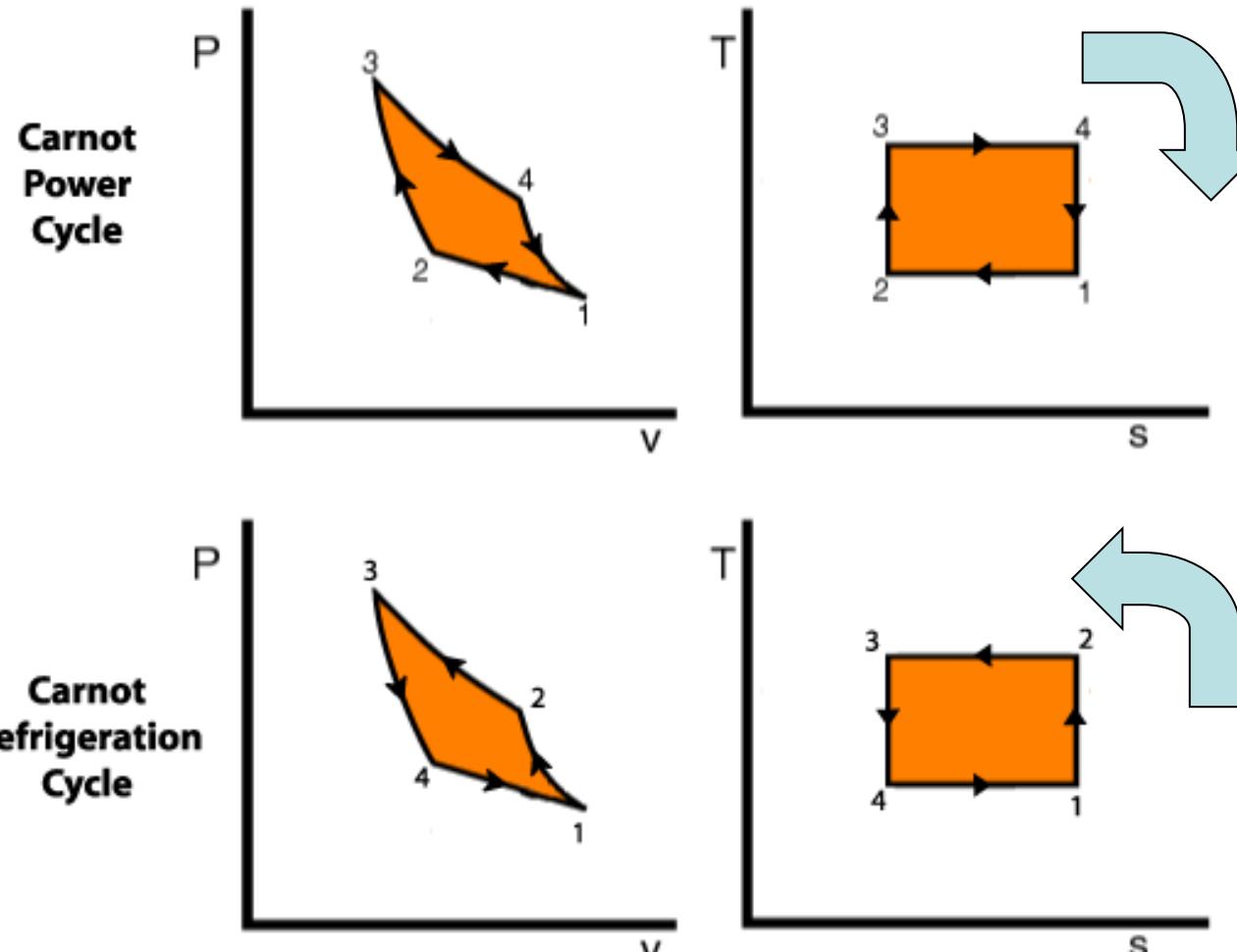
Compare heat engine and refrigeration cycle

- The purpose of a **heat engine (power cycle)** is to convert heat from a hot thermal reservoir into **power** (and it should rejects some heat to a cold reservoir)
- In **refrigeration cycles power is used to transport heat from a cold to a hot place** (opposite to the natural direction)
- Refrigeration cycles have reversed energy flows compared to the heat engine
 - Refrigerator
 - Heat pump
- Often $w_{out} = 0$
- Note **always two temperature reservoirs, flow direction reversed**



Refrigeration and Heat Pump Cycles

- Reverse Carnot Power Cycle → Carnot Refrigeration Cycle



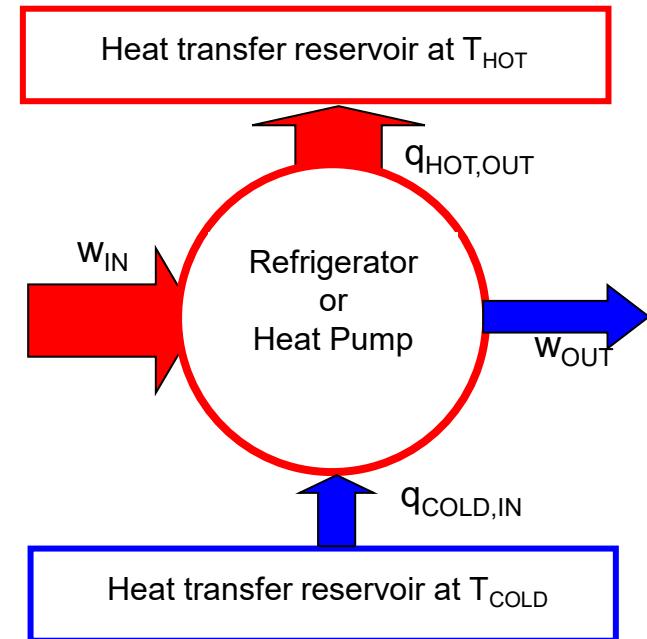
Pv and Ts diagram of a Carnot Power Cycle and a Carnot Refrigeration Cycle
Note the direction of the cycle is reversed, arrows go the other way around

Coefficient of Performance (COP)

- Coefficient of performance says how good a device is
 - A better system has a higher COP
 - COP can be larger than 1
- Air conditioning, refrigeration and chiller cycle
- Assume $w_{out} = 0$ (typical)

$$\eta_{he} = \frac{\text{What we want}}{\text{What we pay for}}$$

- We want q_{cold} and we pay for the power w_{in}



$$COP_{ref} = \frac{q_{cold,in}}{w_{in}} = \frac{q_{cold,in}}{q_{hot,out} - q_{cold,in}} = \frac{1}{\frac{q_{hot,out}}{q_{cold,in}} - 1}$$

Coefficient of Performance (COP)

- For a heat pump cycle the COP is a bit different as the goal of the heat pump cycle is to heat while it for the refrigeration cycle is to cool, here we want $q_{hot,out}$ (instead of $q_{cold,in}$) and still pay w_{in}
- Assume again $w_{out} = 0$ (typical)

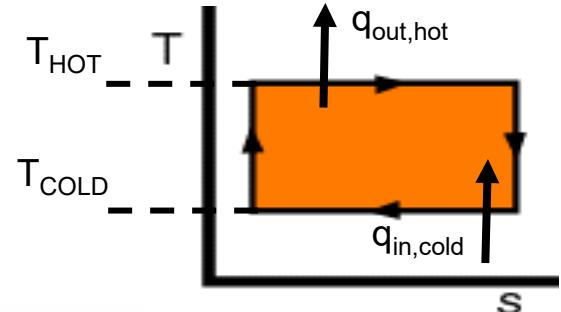
$$COP_{hp} = \frac{q_{hot,out}}{w_{in}} = \frac{q_{hot,out}}{q_{hot,out} - q_{cold,in}} = \frac{1}{1 - \frac{q_{cold,in}}{q_{hot,out}}}$$

- Same cycle used for refrigeration and heat pump
- Relation between $(COP)_{hp}$ and $(COP)_{ref}$

$$COP_{hp} - COP_{ref} = \frac{\frac{q_{hot,out}}{q_{hot,out} - q_{cold,in}} - \frac{q_{cold,in}}{q_{hot,out} - q_{cold,in}}}{1} = 1$$

Maximum (COP)_{REF} and (COP)_{HP}

- **2nd Law for any cycle where**
 - All q_{in} occurs at T_{cold} ($q_{in,cold}$)
 - All q_{out} occurs at T_{hot} ($q_{out,hot}$)



$$\sum_{i=1}^2 \frac{q_{net,i}}{T_i} = \frac{q_{in,cold}}{T_{cold}} - \frac{q_{out,hot}}{T_{hot}} \leq 0 \rightarrow \frac{q_{in,cold}}{q_{out,hot}} \geq \frac{T_{cold}}{T_{hot}}$$

- **Carnot COP for refrigeration, air conditioning, chillers**

$$COP_{ref} = \frac{1}{\frac{q_{out}}{q_{in}} - 1} \leq \frac{1}{\frac{T_{hot}}{T_{cold}} - 1}$$

$$COP_{ref,Carnot} = \frac{1}{\frac{T_{hot}}{T_{cold}} - 1}$$

- **Carnot COP for heat pumps**

$$COP_{hp} = \frac{1}{1 - \frac{q_{in}}{q_{out}}} \leq \frac{1}{1 - \frac{T_{cold}}{T_{hot}}}$$

$$COP_{hp,Carnot} = \frac{1}{1 - \frac{T_{cold}}{T_{hot}}}$$

Maximum (COP)_{REF} for Refrigerator

- What is the maximum COP for a refrigerator and for a fridge?
- **Solution:**
- The maximum (COP)_{ref} is given by the Carnot (COP)_{ref,Carnot}

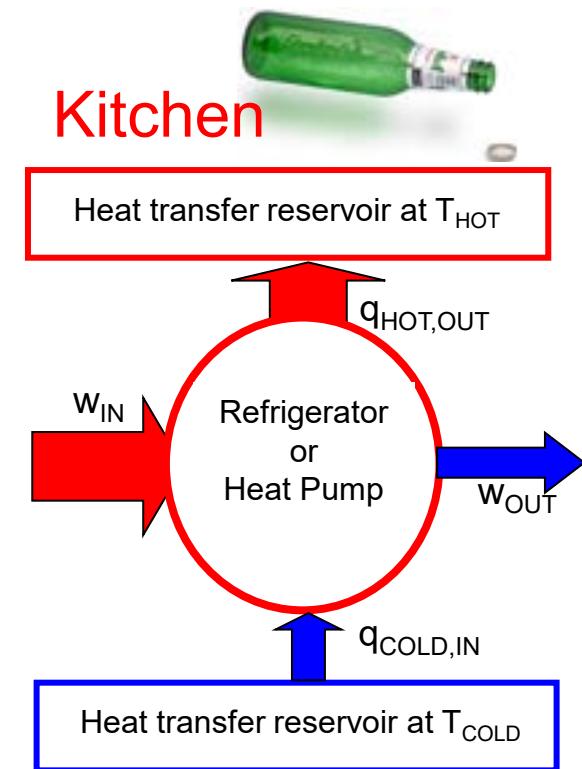
$$COP_{ref,Carnot} = \frac{1}{\frac{T_{hot}}{T_{cold}} - 1}$$

- T_{cold} is temperature inside the refrigerator or the fridge
- T_{hot} is temperature in the kitchen
- Assume $T_{hot} = 293K$

$$T_{cold,ref} = 277K, T_{cold,fridge} = 253K$$

$$COP_{ref,Carnot} = \frac{1}{\frac{293}{277} - 1} = 17.3$$

$$COP_{fridge,Carnot} = \frac{1}{\frac{293}{253} - 1} = 6.3$$



Refrigerator Inside

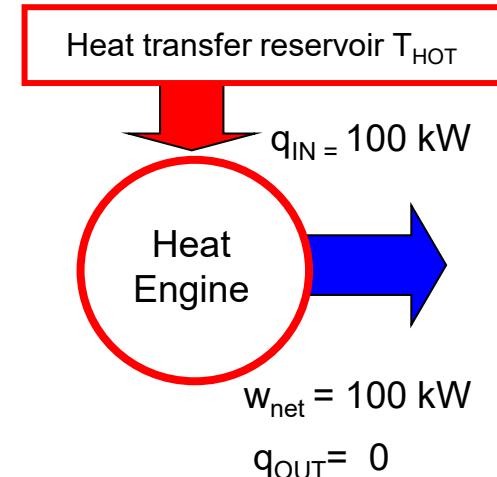


Second law statements revisited

- **Kelvin - Planck Statement**
 - It is impossible to construct an engine that, operating continuously, will produce no effect other than the extraction of heat from a single reservoir and the performance of an equivalent amount of work
- **Clausius Statement**
 - It is impossible to construct an engine that, operating continuously, will produce no effect other than the transfer of heat from a cooler to a hotter body
- The Kelvin – Planck and the Clausius statement are both alternative formulations of the second law of thermodynamics
- The second law states that entropy should increase in real processes, in a power cycle this is only possible if heat is rejected to a cold reservoir as the Kelvin – Planck statement states, this is the fundamental reason that the efficiency of the power engine never can be 100%
- The Clausius statement states the heat cannot flow spontaneously from cold to hot, this is also due to fact that the entropy should increase

Kelvin-Planck statement

- A heat engine that violates the Kelvin- Planck statement of the second law as there is only one heat reservoir and no heat transfer to a low temperature reservoir
- The thermal efficiency of a heat engine can never be 100% as there must be heat transfer from a high to a low temperature reservoir
- The maximum efficiency is the Carnot efficiency and depends on T_{hot} and T_{cold}
- The impossibility of having 100% efficiency is **not** due to friction or dissipative effects, its limitation applies to real and ideal engines

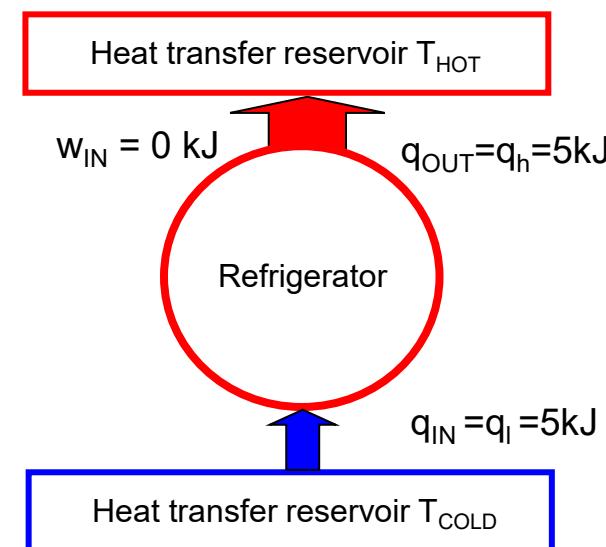


$$\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}}$$
$$= 1 - \frac{q_{out}}{q_{in}}$$

The efficiency is 100% if $q_{out} = 0$ in violation with the Kelvin – Planck statement

Clausius statement

- A refrigerator that violates the Clausius statement of the second law as there is no work input required to transfer heat from a low temperature reservoir to a high temperature reservoir
- Note heat can flow from cold to hot but only if power is applied (like in a fridge)
- Both the Kelvin – Planck and the Clausius statement of the second law are negative statements which can not be proved
- The second law is based on experimental observations
- Till now no experiment has been conducted that contradicts the second law (even Maxwell's Demon cannot violate the 2nd law)

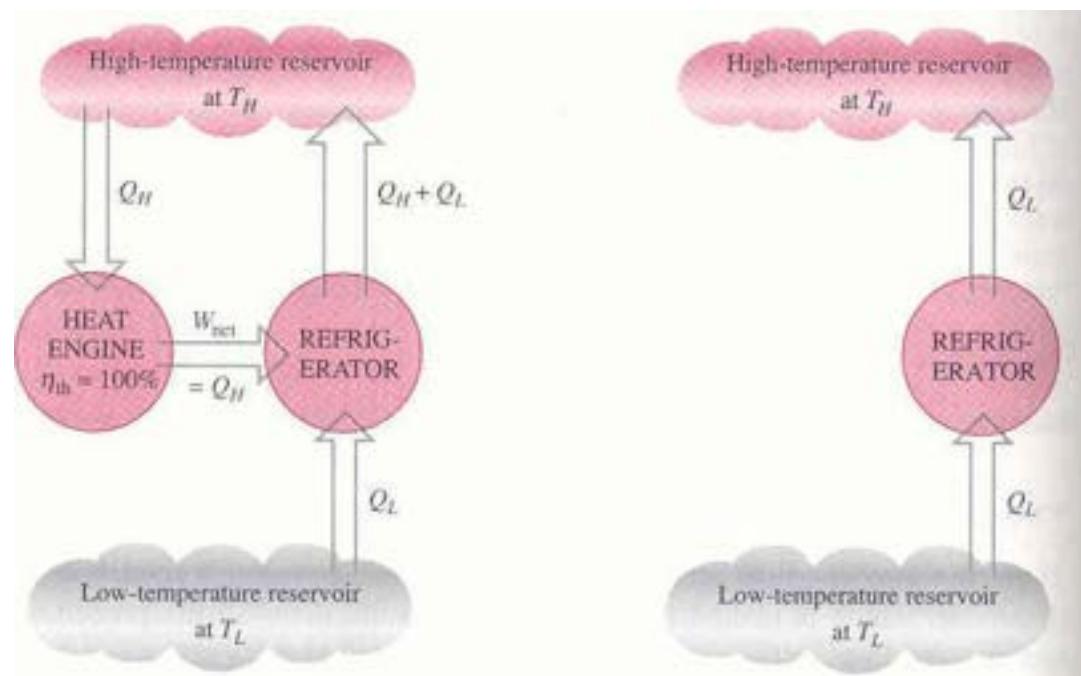


If W_{in} would be 0 kJ
the performance
would be infinite

$$COP_{ref} = \frac{Q_{in}}{W_{in}} = \frac{5}{0} \rightarrow \infty$$

Equivalence: Kelvin-Planck and Clausius statement

- Either expression can be used as the expression of the second law
- A heat engine with 100% efficiency (violation of the Kelvin Planck statement) powers a refrigerator
- The engine receives Q_H from T_H and converts it completely into power $Q_H = W_{\text{net,he}} = W_{\text{in,ref}}$
- The refrigerator losses energy to T_H equal to $W_{\text{in}} + Q_L = Q_H + Q_L$
- During the process T_H receives a net amount of heat of Q_L
- The combination can be seen as a refrigerator that transfers Q_L from T_L to T_H without requiring input (violation of the Clausius statement)



A refrigerator powered by a 100% efficient heat engine (left) and its equivalent refrigerator (right)

Perpetual - Motion machines

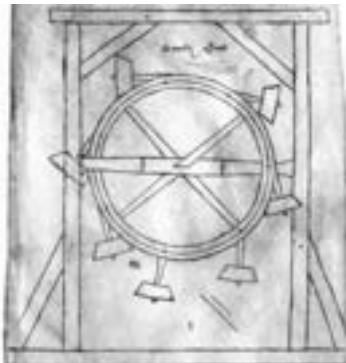
- A process can not take place unless it satisfies **both the first and the second laws of thermodynamics**
- Any device that violates either law is called **a perpetual – motion machine** (perpetuum mobile Latijn: Voortdurend (of eeuwig) bewegend)
 - A device that violates the first law (by creating energy) is called **a perpetual – motion machine of the first kind**
 - A device that violates the second law (no rejection of Q_{out}) is called **a perpetual – motion machine of the second kind**
- Despite numerous attempts, no perpetual – motion machine is known to have worked
- But this never stopped inventors from trying to create new ones (see examples next pages)



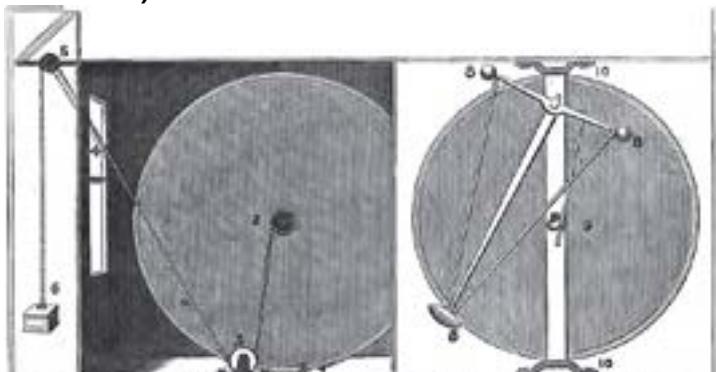
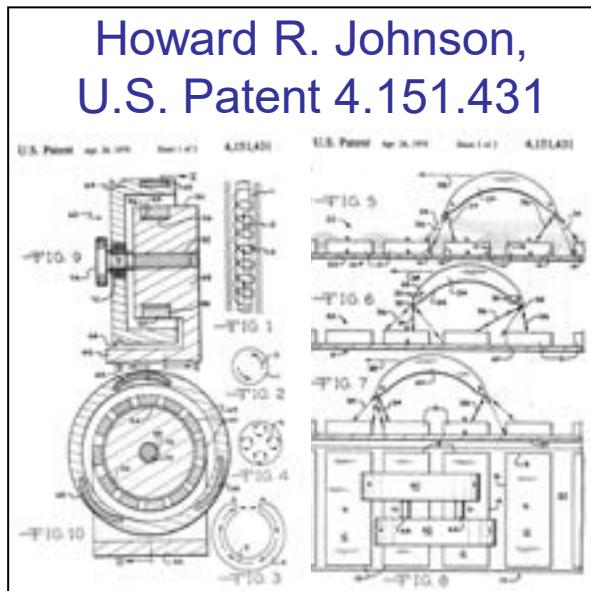
A perpetual – motion machine, an impossible cycle (M.C. Escher)

Perpetual - Motion machines: examples

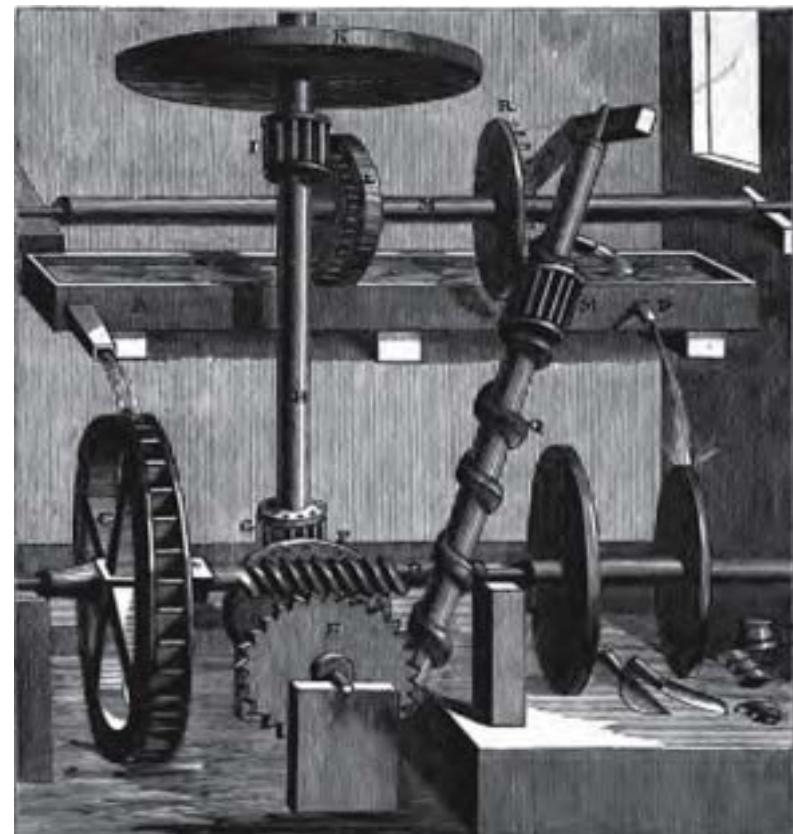
- Inventors will never stop try to create new perpetual motion machines



Perpetuum
Mobile of Villard
de Honnecourt
(about 1230)



Orffyreus Wheel, designed by Johann Bessler



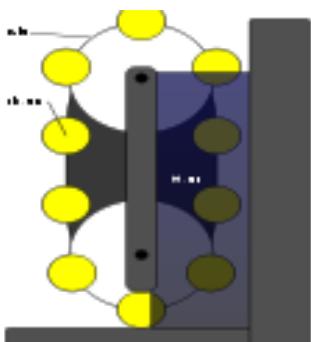
Robert Fludd's 1618 "water screw"
perpetual motion machine from a 1660
woodcut. This device is widely credited
as the first recorded attempt to describe
such a device in order to produce useful
work - driving millstones

Perpetual - Motion Machines: examples

- Inventors will never stop try to create new perpetual motion machines



The "Overbalanced Wheel" it was thought that the metal balls on the right side would turn the wheel because of the longer lever arm, but since the left side had more balls than the right side, the torque was balanced and the perpetual movement could not be achieved.



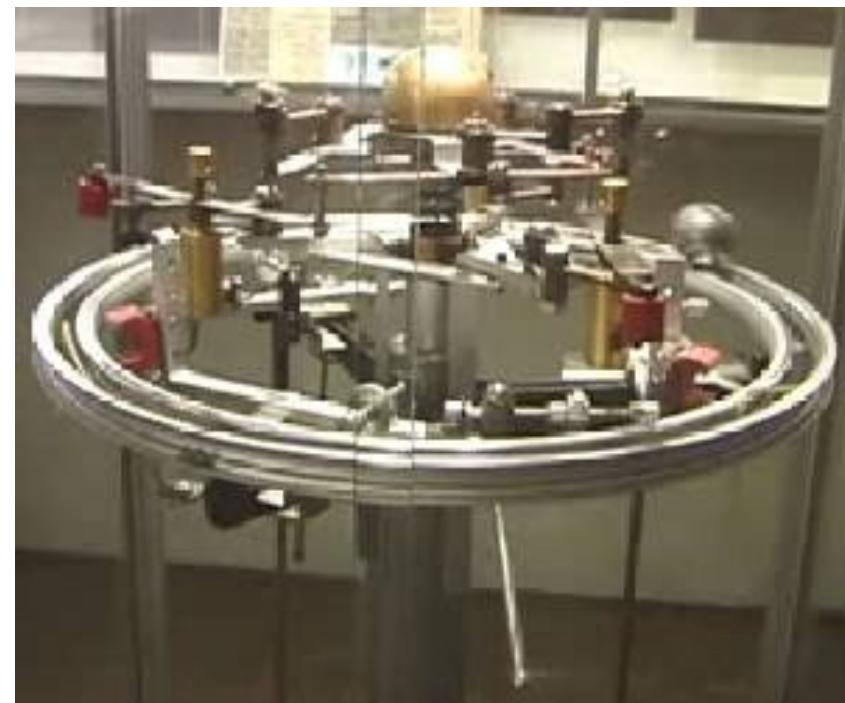
The "Float Belt" the yellow blocks indicate floaters. It was thought that the floaters would rise through the liquid and turn the belt. However pushing the floaters into the water at the bottom would require more energy than the floating could generate.



The "Capillary Bowl" it was thought that the capillary action would keep the water flowing in the tube, but since the cohesion force that draws the liquid up the tube in first place holds the droplet from releasing into the bowl, the flow is not perpetual.

Perpetual - Motion machines: examples

- The **Finsrud Wheel** is a moving sculpture built by Norwegian artist Reidar Finsrud (<http://www.reidar-finsrud.com/sider/mobile/foto.html>).
- **How it works:** It appears to use a combination of gravity, magnets, and pendulum effects, which modern physics would say is impossible, to generate continuous motion.
- Reidar says the machine does stop on occasions but that this is not on a daily basis. To start the machine the pendulums are swung by hand, this puts an external input energy into the system. It runs for about a month, until the glue is dried out, that holds the permanent magnets inside the footer. When a start up is required this takes about 15 minutes, this is due to the difficulty involved in getting all the parts moving in harmony.
- Short clip: http://www.galleri-finsrud.no/sider/download/finsrud_PM_02.WMV



Recapitulate class 6

- A **thermodynamic cycle** is composed of a series of processes which return to the initial state and works between a hot and a cold thermal reservoir
 - 1. **Heat power cycles** produce power from heat
 - 2. **Refrigeration / heat pump cycles** transport heat using power
- First law for a cycle: $w_{net} = q_{net}$
- Second law for a cycle: $\sum_{i=1}^n \frac{q_{net,i}}{T_i} \leq 0$ or $\oint \frac{\delta q_{net,i}}{T_i} \leq 0$
- Thermal efficiency for heat / power cycles: $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$
- Carnot (ideal) cycle
- Carnot (maximum) efficiency
$$\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$$
- Kelvin-Planck & Clausius statement (second law applied to cycles)

Energy flows in a heat engine (left) and in a refrigeration or heat pump cycle (right)

The diagram illustrates two thermodynamic cycles. On the left, a 'Heat Engine' (represented by a circle) receives heat q_{IN} from a 'Heat transfer reservoir T_{HOT} ' and rejects heat q_{OUT} to a 'Heat transfer reservoir T_{COLD} '. It also receives work w_{IN} and produces work w_{OUT} . On the right, a 'Refrigerator or Heat Pump' (also represented by a circle) receives work w_{IN} and rejects heat q_{IN} to a 'Heat transfer reservoir T_{COLD} '. It also receives heat q_{OUT} from a 'Heat transfer reservoir T_{HOT} ' and produces work w_{OUT} .

Next classes 7 – 11: Thermodynamic Power Cycles

- In class 1 to 6 we introduced all the (basic) tools we need to study thermodynamic systems that generate power or heat / cold
- Now it's time for the real job
- The thermodynamics power cycles !
- Class 7 & 8: **vapor power cycles**, cycles using **a working fluid that undergoes a phase transition** (mostly water) through the cycle (Rankine cycle)
- Class 10 & 11: **gas power cycles**, cycles using **gas as working fluid** through the whole cycle (Brayton cycle)
- **Refrigeration and heat pump cycles**, cycles moving heat opposite to the natural direction using power are treated in module 3



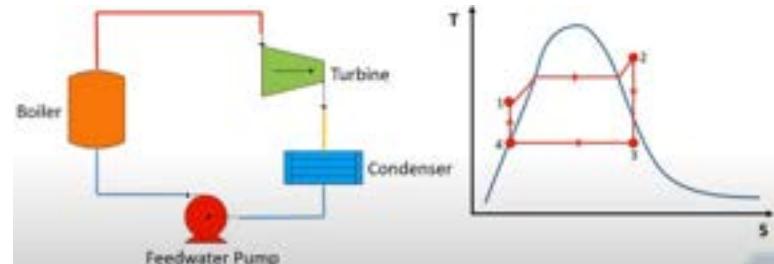
Jet engines are an example of gas power cycles



Power plants typically use vapor power cycles to generate electricity, e.g. the power plant in Geertruidenberg (NL)

Next class 7: Vapor Power Cycles - Simple

- **Vapor power cycles**, cycles using a working fluid that undergoes a phase transition (mostly water) through the cycle
 - Piston steam engine & some history
 - Steam turbine
 - Comparison to Carnot
 - Ideal and real Rankine cycles
 - Heat and power in- and output
 - Thermal efficiency
 - Design parameters
 - Mollier diagram for water
- Vapor power cycles are widely used in power plant to generate electricity, how does such a thermal power plant work?



Explanation about a simple Rankine cycle

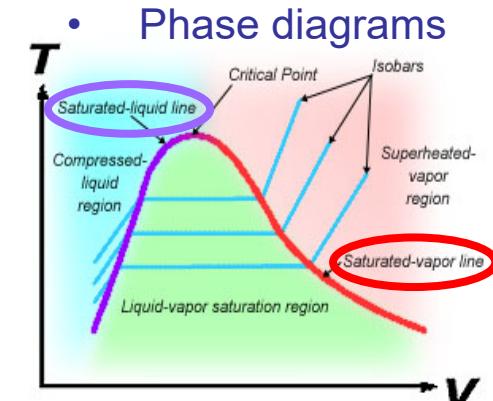
<https://www.youtube.com/watch?v=QFZN71MY71o&t=1s>



<https://www.youtube.com/watch?v=IdPTuwKEfmA>

Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal 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 $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)
- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdP$
- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$
- Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$
- Coefficient of performance $(COP)_{HP} = \frac{q_{HOT,OUT}}{w_{IN}}$ and $(COP)_{REF} = \frac{q_{COLD,IN}}{w_{IN}}$



Class 7

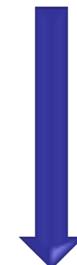
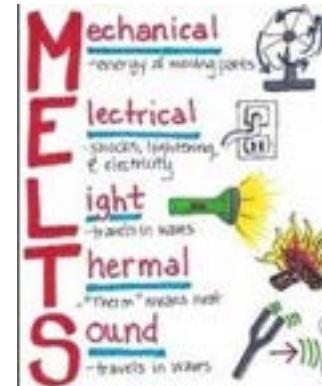
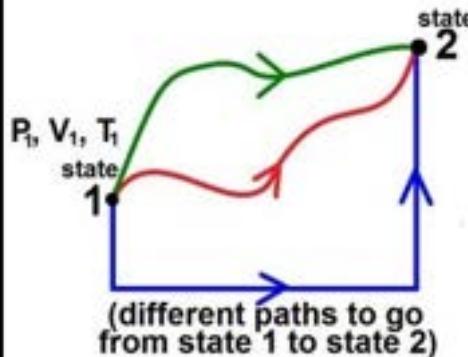
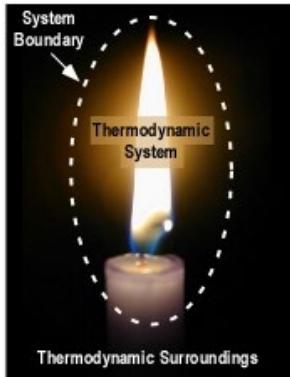
Vapor power cycles, simple

A field of mirrors concentrates solar energy onto a tower. This concentrated solar energy (heat) is used to drive a vapor power cycle. (PS20 and PS10 Solar Power Plant in Andalusia, Spain)

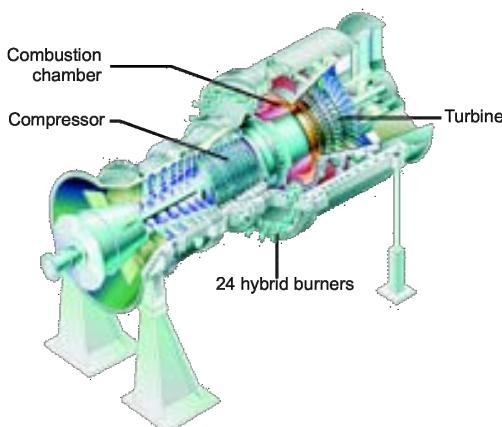


Roadmap Engineering Thermodynamics

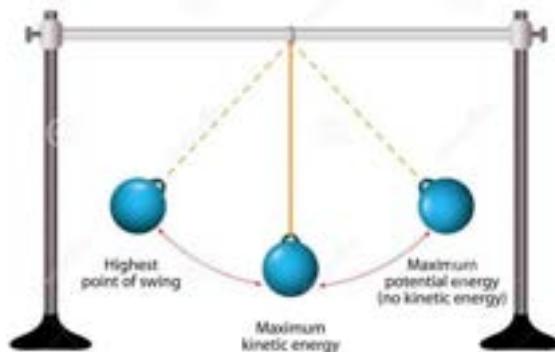
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



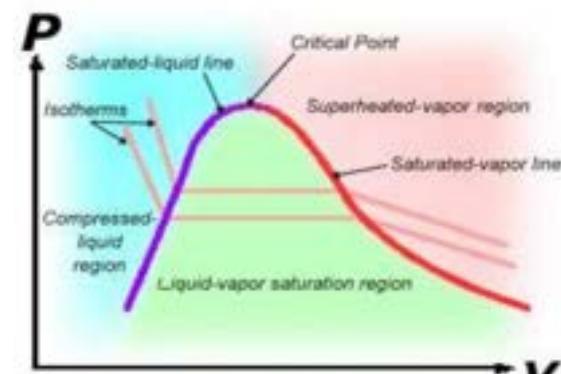
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

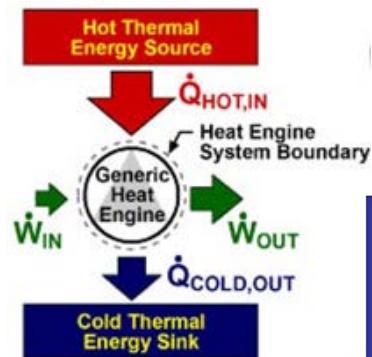


- Properties of Substances (Class 3, 9)

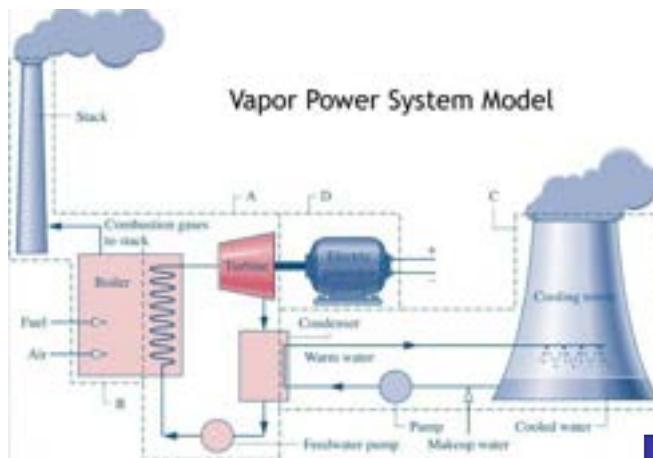


Roadmap Engineering Thermodynamics

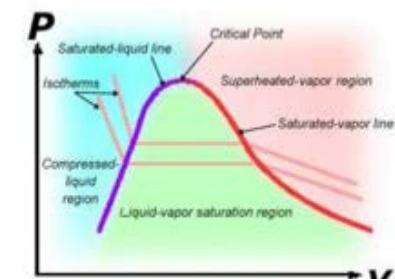
Thermodynamic cycles (Class 6)



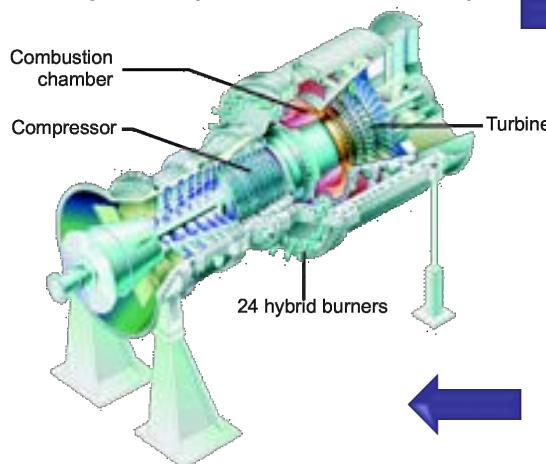
Vapor power cycles –
Rankine cycle (Class 7, 8)



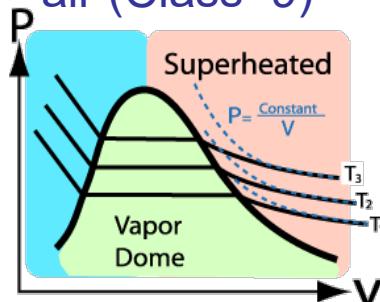
Properties of
water (Class 3)



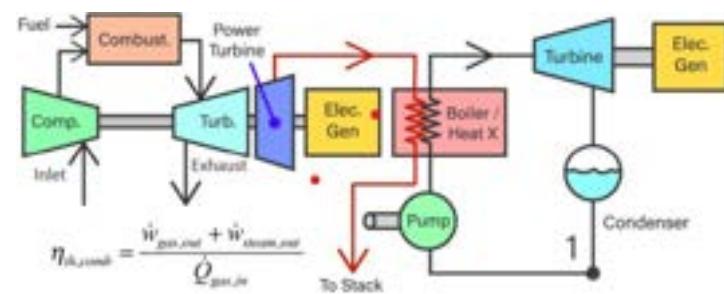
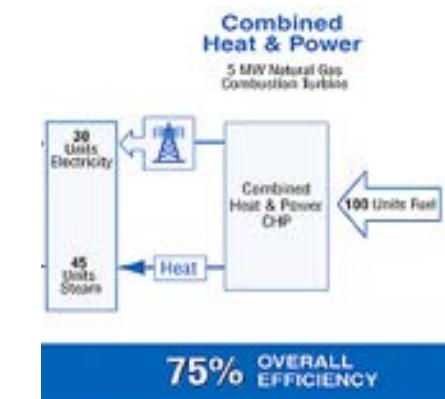
Gas power cycles – Brayton
cycle (Class 10, 11)



Properties of
air (Class 9)

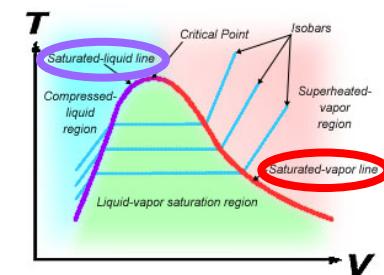


Combined cycles
Combined heat &
power (Class 8, 11)



Recapitulate class 1 - 5

- **Class 1: Introduction and basic concepts**
 - What is thermodynamics? → Science on using heat and power
 - Properties, open/closed/isolated system, states, processes, equilibrium
- **Class 2: Energy, work and heat transfer**
 - The energy of a system ($e=u+ke+pe$) can change due to work (w) and/or heat transfer (q) and/or mass flow (m) with flow work (Pv) over the system boundary
 - Enthalpy: $h = u + Pv$, entropy: s , efficiency
- **Class 3: Thermodynamic properties of water**
 - Phases, phase change, phase diagrams and tables to look up values
 - Saturated liquid, saturated vapor, saturated mixture, quality of the mixture (x), compressed liquid, superheated vapor
- $$x = \frac{v - v_l}{v_v - v_l}$$
- **Class 4: The first law of thermodynamics**
 - Conservation of energy and conservation of mass
 - Closed system: $du = \delta q + \delta w$
 - Open system: $q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$
- **Class 5: The second law of thermodynamics**
 - To describe the direction of spontaneous processes **entropy** (s in kJ/kgK) is introduced, it is a measure of disorder and entropy is maximal in equilibrium,
 - Entropy is not conserved, in the universe **entropy always increases (second law)**



Recapitulate class 6

- A **thermodynamic cycle** is composed of a series of processes which return to the initial state and works between a hot and a cold thermal reservoir
 - 1. **Heat power cycles** produce power from heat
 - 2. **Refrigeration / heat pump cycles** transport heat using power
- First law for a cycle: $w_{net} = q_{net}$
- Second law for a cycle: $\sum_{i=1}^n \frac{q_{net,i}}{T_i} \leq 0$ or $\oint \frac{\delta q_{net,i}}{T_i} \leq 0$
- Thermal efficiency for heat / power cycles: $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$
- Carnot (ideal) cycle
- Carnot (maximum) efficiency
$$\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$$
- Kelvin-Planck & Clausius statement
(second law applied to cycles)

Energy flows in a heat engine (left) and in a refrigeration or heat pump cycle (right)

The diagram illustrates two thermodynamic cycles. On the left, a 'Heat Engine' (represented by a circle) receives heat q_{IN} from a 'Heat transfer reservoir T_{HOT} ' and rejects heat q_{OUT} to a 'Heat transfer reservoir T_{COLD} '. It also receives work w_{IN} and produces work w_{OUT} . On the right, a 'Refrigerator or Heat Pump' (also represented by a circle) receives work w_{IN} and rejects heat q_{IN} to a 'Heat transfer reservoir T_{COLD} '. It also receives heat q_{OUT} from a 'Heat transfer reservoir T_{HOT} ' and produces work w_{OUT} .

Next classes 7 – 11: Thermodynamic Power Cycles

- In class 1 to 6 we introduced all the (basic) tools we need to study thermodynamic systems that generate power or heat / cold
- Now it's time for the real job
- The thermodynamics power cycles !
- Class 7 & 8: **vapor power cycles**, cycles using **a working fluid that undergoes a phase transition** (mostly water) through the cycle (Rankine cycle)
- Class 10 & 11: **gas power cycles**, cycles using **gas as working fluid** through the whole cycle (Brayton cycle)
- **Refrigeration and heat pump cycles**, cycles moving heat opposite to the natural direction using power are treated in module 3



Jet engines are an example of gas power cycles



Power plants typically use vapor power cycles to generate electricity, e.g. the power plant in Geertruidenberg (NL)

Content Class 7

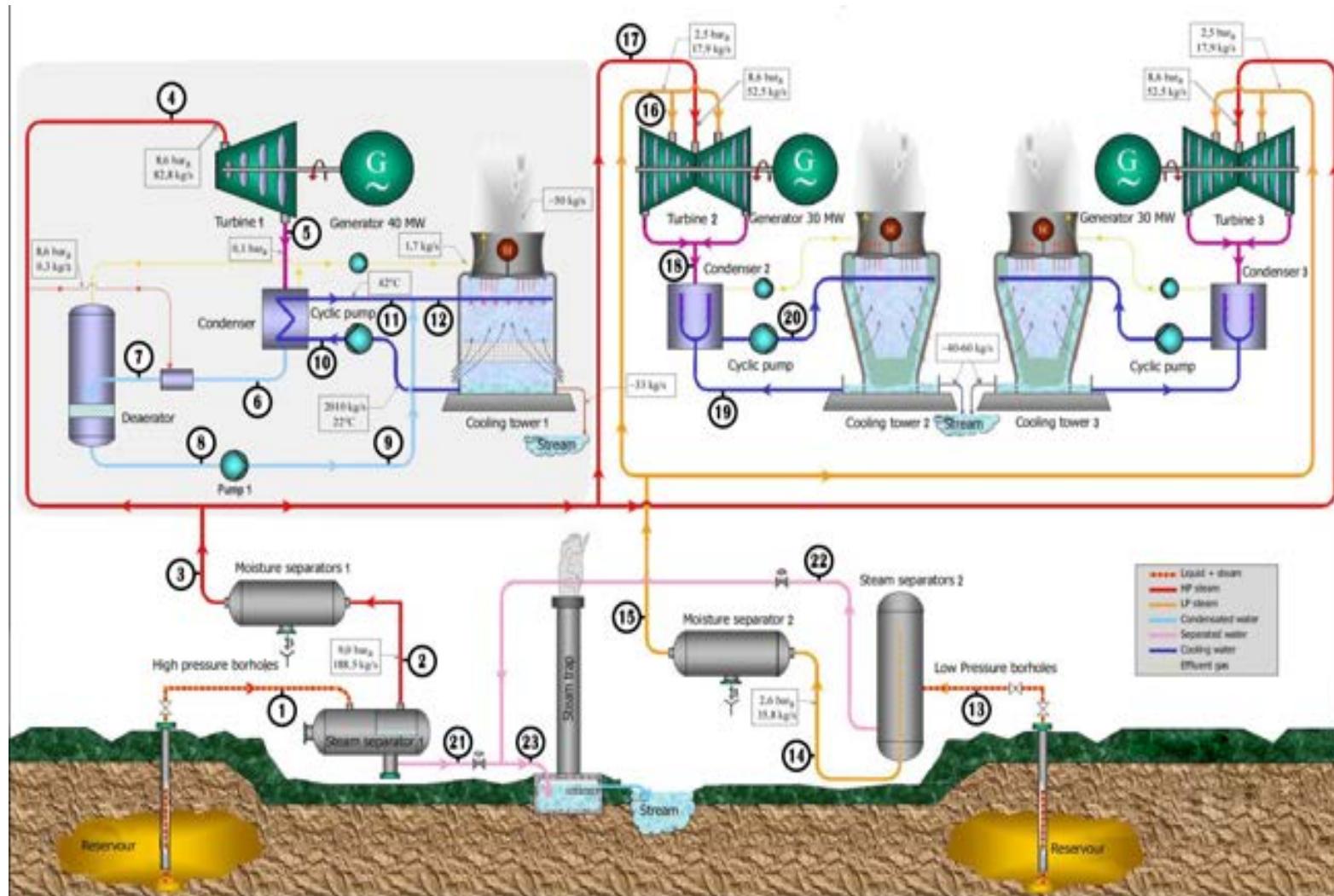
- **Vapor power cycles – Rankine cycles, simple**
- **Vapor power cycles** use a working fluid that undergoes a phase transition (mostly water) through the cycle, are studied
 - Piston steam engine & some history
 - Steam turbine
 - Comparison to Carnot
 - Ideal and real Rankine cycles
 - Heat and power in- and output
 - Thermal efficiency
 - Design parameters
 - Mollier diagram for water
- **Learning goal:** recognize a **simple** thermodynamic system to produce work, explain the configuration, analyse the thermodynamic aspects from the viewpoint of the first law of thermodynamics, interpret and evaluate the results and suggest improvements



<https://www.youtube.com/watch?v=IdPTuwKEfmA>

Example Vapor Power Cycle: Project 2

- Landsvirkjun geothermal power plant to be analysed in the project



Vapor power cycles

- To produce power a **thermodynamic cycle** is used
- In a thermodynamic gas cycle the working medium is in the gas phase throughout the whole cycle (chapter 9, class 10 & 11)
- In a **vapor power cycle** the working medium **changes phase** (chapter 10, class 7 & 8)
 - Liquid → Vapor → Liquid
- The vapor power cycle is externally heated, the heat is transferred to the fluid using a boiler or a heat exchanger
- Mostly vapor power cycles are closed cycles (an exception is the steam train)
- Vapor power cycles are first used in piston steam engines begin 1700
- Around 1900, vapor power cycles are also used in **steam turbine cycles**
- Today the biggest application of vapor power cycles is in **steam turbine cycles (Rankine cycles)** in power generation in power plants



A steam train uses a piston steam engine, some of them are still in use

The Aeolipile van Heron van Alexandrië

- Although the first steam engine was developed around 1700 already in antiquity the power of steam fascinated people
- An **aeolipile** (or **aeolipyle**, or **eolipile**), also known as a **Hero's engine**, is a simple bladeless radial steam turbine which spins when the central water container is heated. Torque is produced by steam jets exiting the turbine, much like a tip jet or rocket engine. In the 1st century AD, Hero of Alexandria described the device in Roman Egypt, and many sources give him the credit for its invention.
- The aeolipile Hero described is considered to be the first recorded steam engine or reaction steam turbine. The name – derived from the Greek word Αἴολος and Latin word *pila* – translates to "the ball of Aeolus", Aeolus being the Greek god of the air and wind.

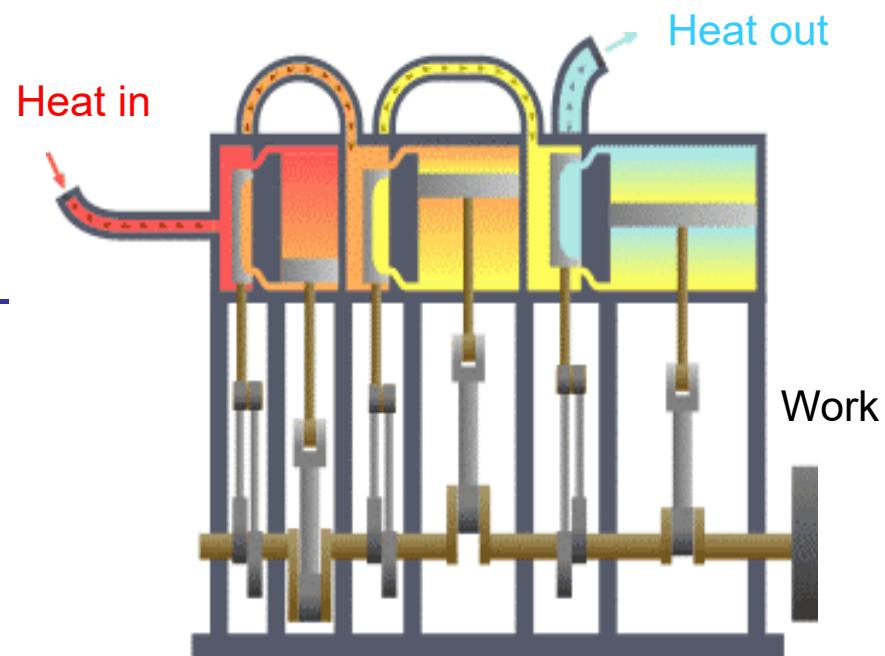


Some history, background information, not for the exam

<https://en.wikipedia.org/wiki/Aeolipile>

The piston steam engine

- A **piston steam engine** is a type of engine (or, more broadly a kind of machine) that uses the thermodynamic characteristics of water to produce work (power / electricity)
- The machine converts the energy of hot, pressurized steam into mechanical work, by expanding the steam in one or more cylinder / piston systems
- The piston will be squeezed by the expanding steam and generates volume work $\rightarrow \delta w = Pdv$
- Using a crank-connecting rod mechanism, the energy of the expansion is transferred to a flywheel
- Electricity can be produced using a generator



Animation from <http://en.wikipedia.org/wiki/Thermodynamics>

The Piston Steam Engine

- The invention of the (industrial) piston steam engine marked the beginning of the industrial revolution
- For the first time mechanical power was available to drive machines, where before manual power, draft animals, water and wind mills had to be used
- The first piston steam engine is developed by **Thomas Newcomen** in **1712** and used in the coal mines in England
- Historically piston steam engines are used for
 - Trains, boats and cars for propulsion
 - Pumping stations to move water for draining the polders in The Netherlands
 - Factories e.g. textile-industry here in Twente (Museum Twentse Welle)
- Nowadays the piston steam engine is almost completely replaced by the steam turbine (Rankine cycle)



Newcomen Steam Engine

- The **atmospheric engine** invented by Thomas Newcomen in 1712, today referred to as a **Newcomen steam engine** (or simply Newcomen engine), was the first practical device to harness the power of steam to produce mechanical work
- First used to pump water out of coal mines, starting in the early 18th century

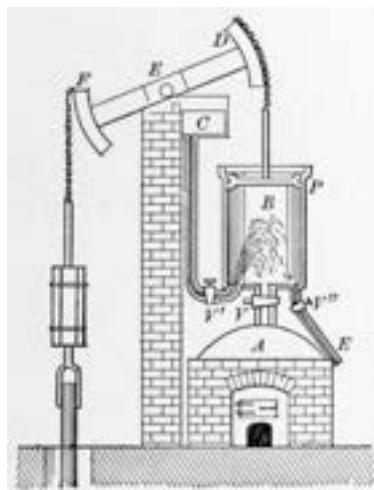
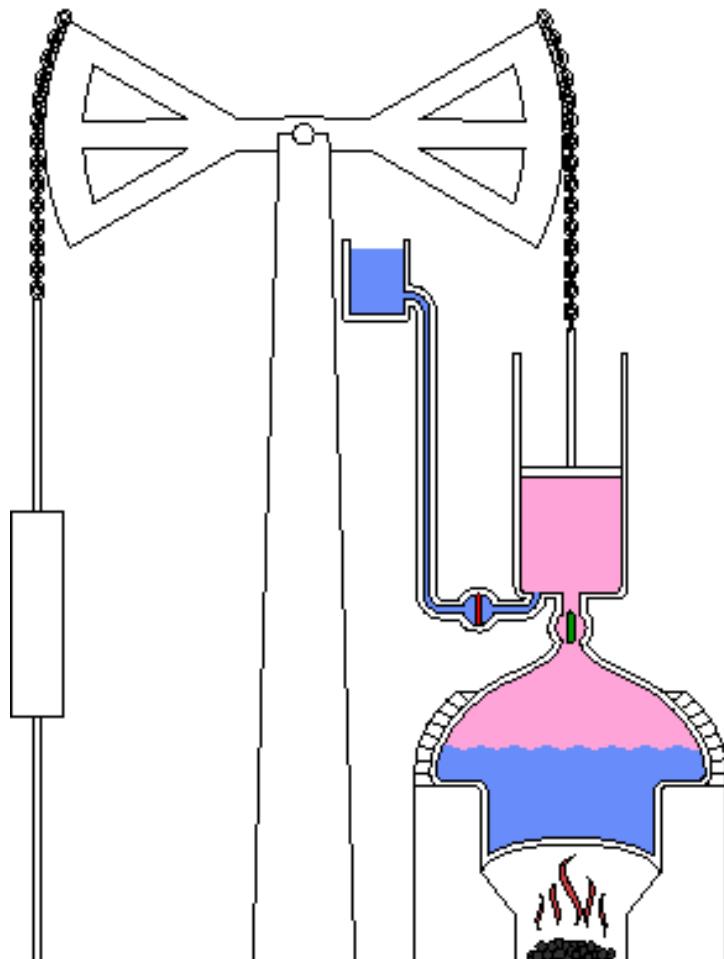


Diagram of the Newcomen steam engine and a Newcomens style engine at Elsecar Centre

Some history, background information, not for the exam



Animation of a schematic Newcomen steam engine
– Steam is shown pink and water is blue.
– Valves move from open (green) to closed (red)

James Watt and the Steam Engine

- James Watt's (1736 – 1819) later engine was an improved version of the Newcomen steam engine
- Although Watt is far more famous, Newcomen rightly deserves the first credit for the widespread introduction of steam power



James Watt's workshop



James Watt

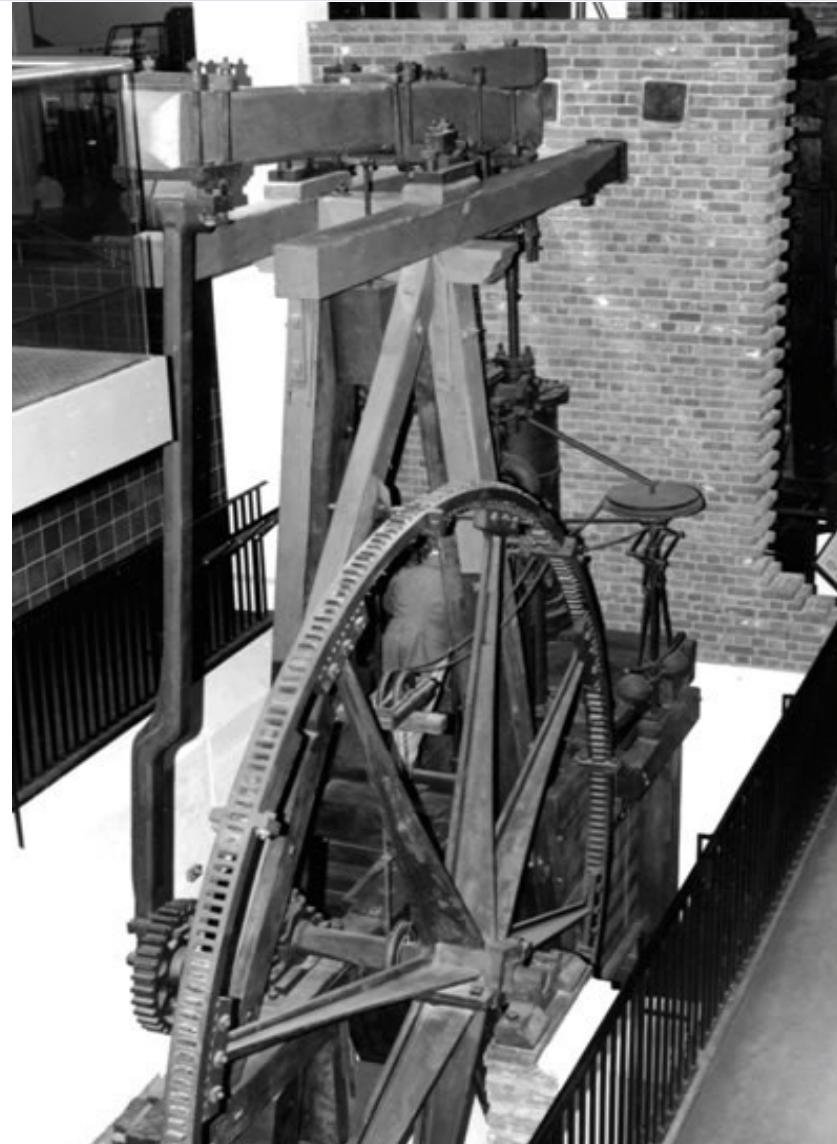
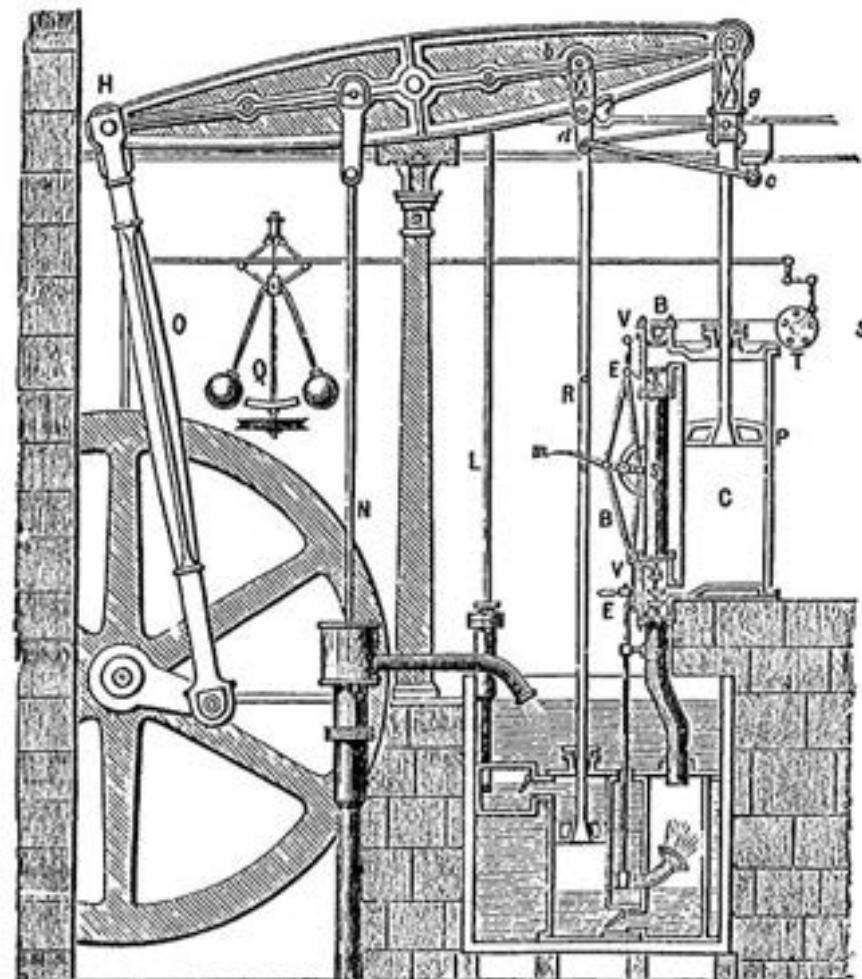


Photo: British Science Museum, London

Some history, background information, not for the exam

Boulton and Watt Steam Engine

- The Newcomen steam engine was very slow and inefficient
- In 1763 James Watt was asked to repair a Newcomen steam engine
- He made a number of improvements and modifications and transformed the engine to a more efficient one
 - He added the condenser
 - He used the up as well as the down stroke of the piston
 - He added a crank to transform the translation motion into rotation
- Used in 1777 in a mine in Cornwall



Steam engine designed by Boulton & Watt.
Engraving of a 1784 engine

Some history, background information, not for the exam

Cruquius Stoomgemaal, The Netherlands

- In the Netherlands steam engines were used to move water for draining
- '**Stoomgemaal Cruquius**', build in 1849, had a piston diameter of 3.66m
- This diameter made it the largest steam engine in the world
- Pumping-engine '**De Cruquius**' is one of the three pumping-engines used for draining 'De Haarlemmermeer' between 1849 and 1852
- It is used for draining till 1933 when it is replaced by a more modern engine
- It is named after the Dutch engineer *Nicolaus Samuelis Cruquius*, born as Nicolaas Kruik, in 1678 in Vlieland (NL)

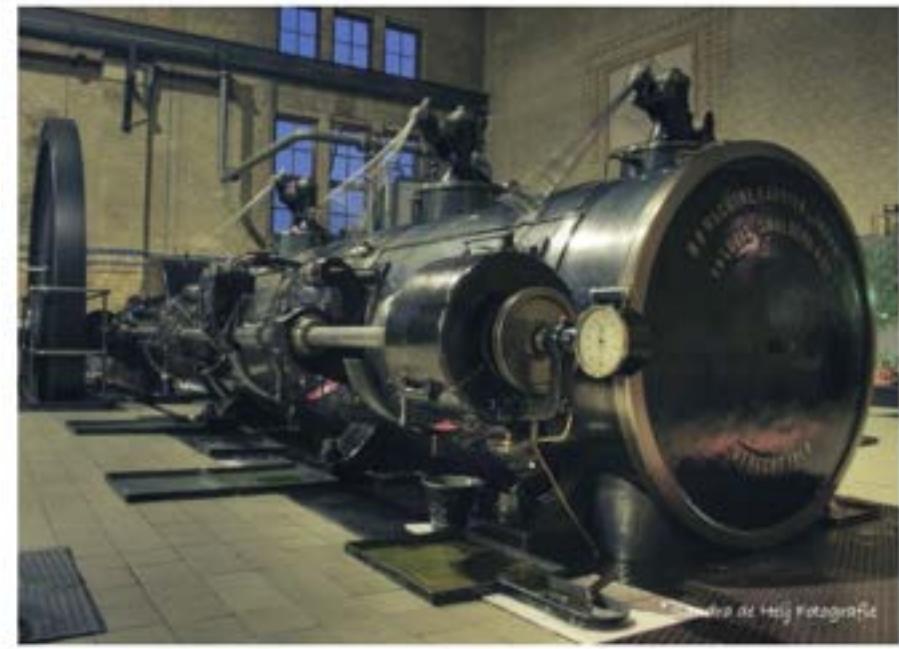


Background information, not for the exam

Woudagemaal in The Netherlands

- The steam engine seems to be old fashioned but is still in use
- The **Ir. D.F. Woudagemaal** is the largest steam engine in the world that is still used
- Its function is to lower the water level in Friesland (het FZP)
- In 1966 its function is taken over by the J.L. Hooglandgemaal in Stavoren
- The Ir. D.F. Woudagemaal however, is still used if the capacity of the new pumping-engine is too low (last times at the storm at 2-9 January 2012 and Christmas 2012)
- The pumping-engine is positioned in Tacozijl (close to Lemmer) and is placed on the **UNESCO – world heritage list** in 1998

Background information, not for the exam



Steam Locomotive: De Arend

- **De Arend:** First Steam Locomotive running in The Netherlands

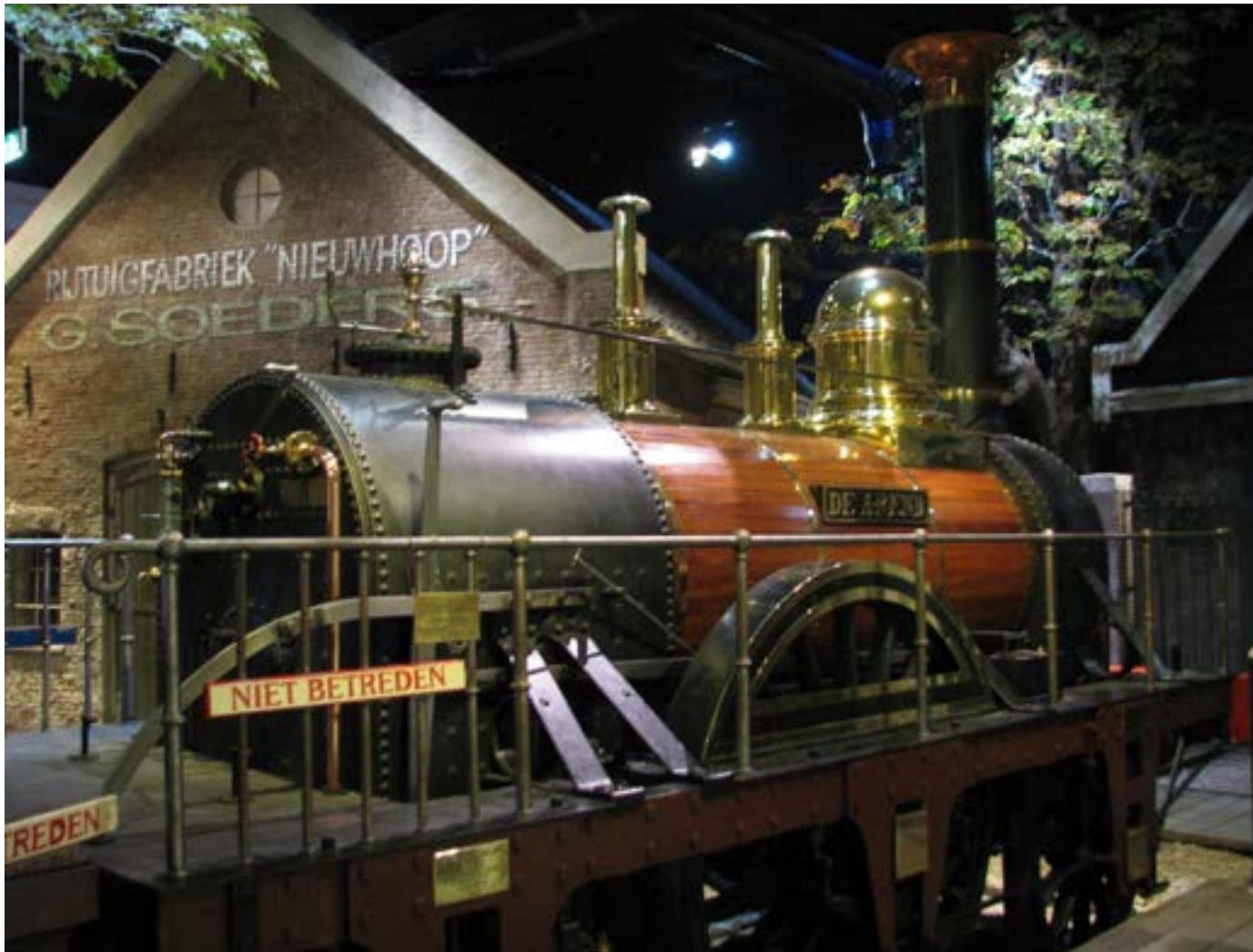


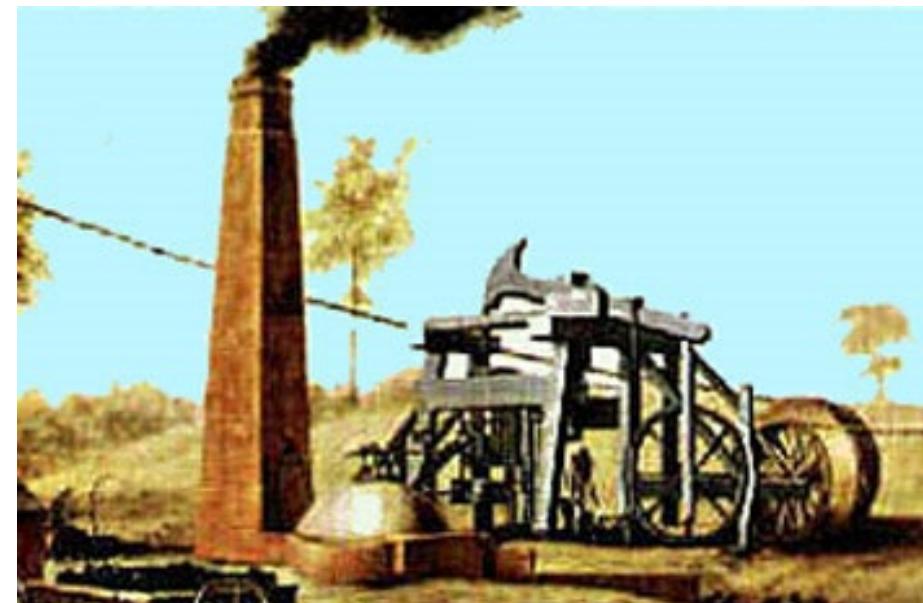
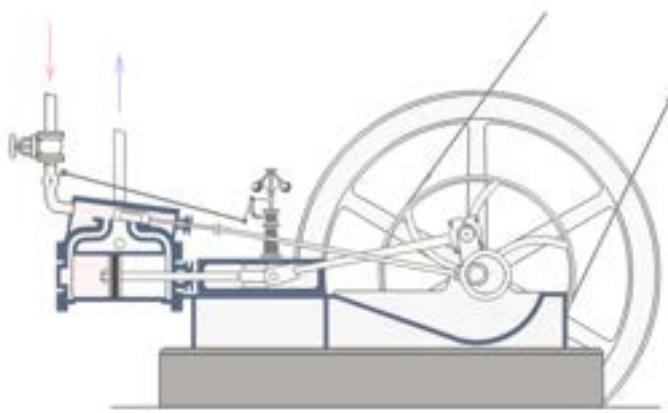
Photo taken in *Het Spoorwegmuseum* in Utrecht, The Netherlands

Some history, background information, not for the exam

- **Route:** Amsterdam ↔ Haarlem
- **First ride:** 20 September 1839

Historical Importance of Steam Power

- It might be clear that the invention of the industrial piston steam engine was very important and had a large impact on society
- The steam engine is marked as the beginning of the industrial revolution
- The theory of heat (thermodynamics) would later be formulated in an attempt to make the first steam engines more efficient
- The concept of entropy was only discovered in 1865 (150 years later) by Clausius to close the theory
- Nowadays steam power is mostly used in steam turbines to produce electricity



Some history, background information, not for the exam

http://www.zaans-industrieel-erfgoed.nl/pages_4/rep_no_engeland_tyne.html

Steam Turbine

- A **steam turbine** is a mechanical device that extracts thermal energy from pressurized steam, and converts it into rotary motion, its modern manifestation was invented by Sir Charles Parsons in 1884
- It has almost completely replaced the reciprocating piston steam engine primarily because of its greater thermal efficiency and higher power-to-weight ratio
- Because the turbine generates rotary motion, it is particularly suited to be used to drive an electrical generator – a large amount of all electricity generation in the world is by use of steam turbines



A rotor of a modern steam turbine, used in a power plant

Steam Power Plant

- Nowadays most of the electricity is generated in power plants that use **steam turbines in vapor power cycles**
- Vapor power cycles using steam turbine are called **Rankine cycles**, named after William John Macquorn Rankine (1820 – 1872)



Steam power plant for power generation

The British Steam Car

- Application of a steam turbine in a modern vehicle



Background information,
not for the exam

The British Steam Car

- **The British Steam Car; Official Land Speed Record Holder**
- On 25 August 2009, Team Inspiration of the British Steam Car Challenge broke the long-standing record for a steam vehicle set by a Stanley Steamer in 1906, setting a new speed record of 225.055 km/h at the Edwards Air Force Base, in the Mojave Desert of California. This was the longest standing automotive record in the world. It had been held for over 100 years.
- The car was driven by Charles Burnett III. FIA land speed records are based on an average of two runs (called 'passes') in opposite directions, taken within an hour of each other – in this case the maximum speeds reached were 219.037 km/h on the first run and 243.148 km/h on the second. As of August 25 the record is subject to official confirmation by the FIA.
- On August 26, 2009 the British Steam Car, driven this time by, the grandson of Sir Malcolm Campbell, broke a second record by achieving an average speed of 238.679 km/h over two consecutive runs over a measured kilometer. This was also recorded and again, has since been ratified by the FIA.

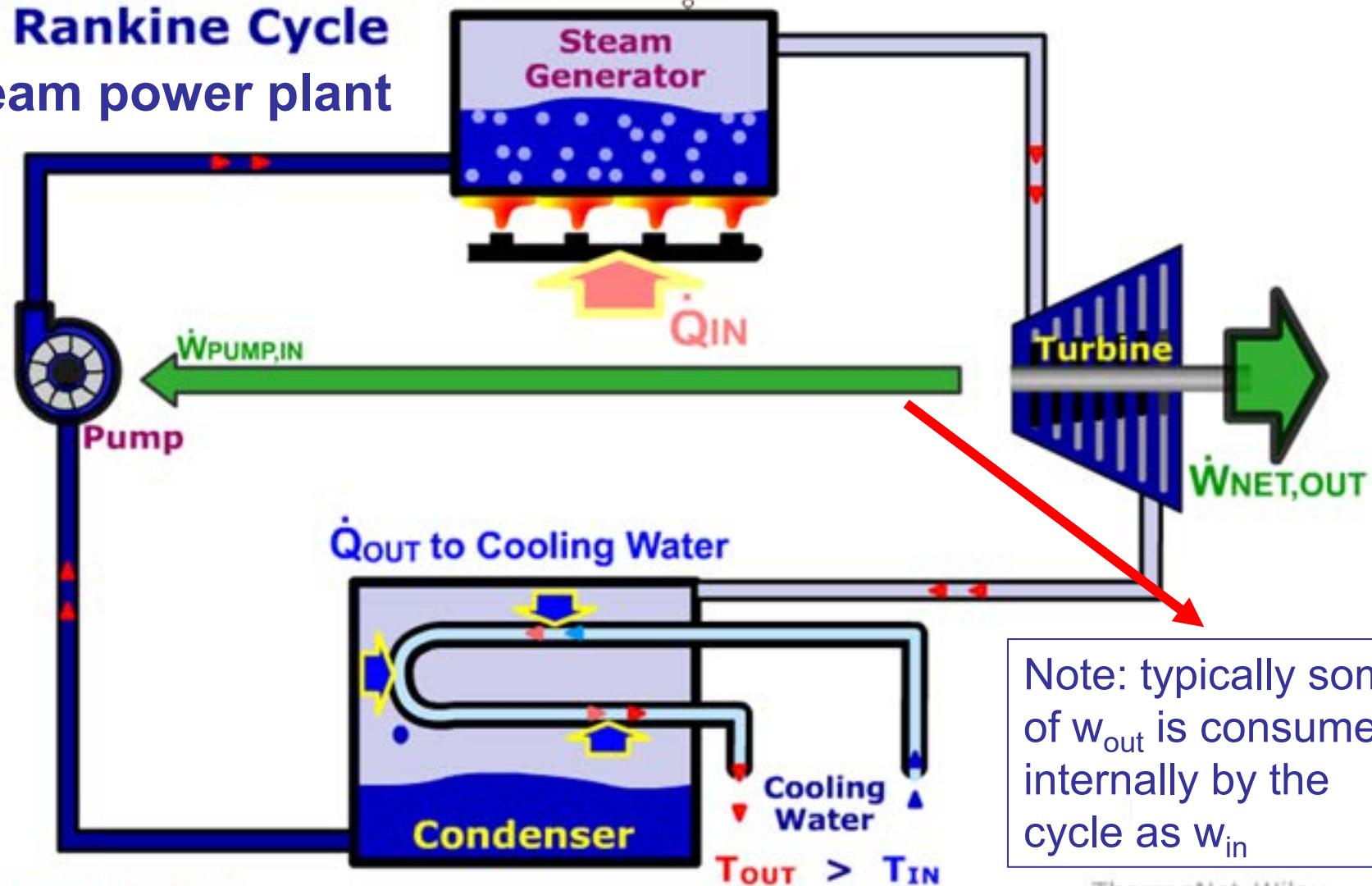


Background information, not for the exam

The Rankine Cycle

Rankine Cycle

Steam power plant



ThermoNet:Wiley

Principle of the Ideal Rankine Cycle

Principle of the ideal Rankine cycle (reversible)

- **1 → 2 isentropic compression (w_{in})**

Fluid enters the pump and is compressed to a higher pressure, the pump is assumed to be adiabatic and ideal (reversible, isentropic) work is taken from the turbine

- **2 → 3 isobaric heat addition (q_{in})**

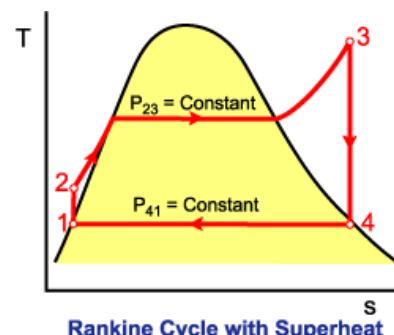
At high constant pressure heat is added to the fluid in the boiler, the fluid starts boiling and vaporizes (phase change), it results in hot high-pressure vapor

- **3 → 4 isentropic expansion (w_{out})**

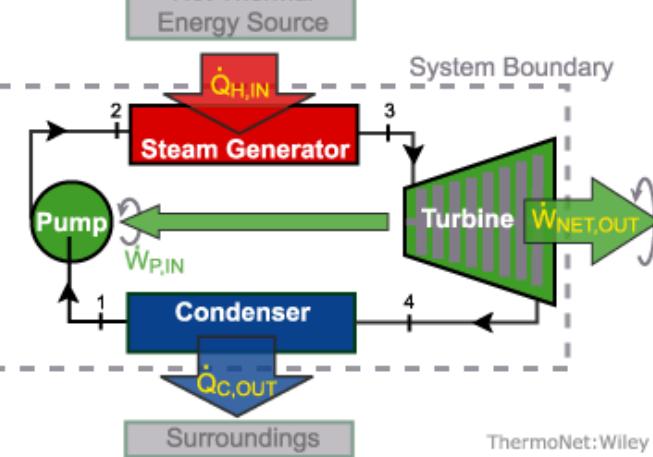
The hot vapor is expanded in the turbine producing work, at the turbine outlet the working fluid is still in the gas phase or it is a mixture at low temperature and pressure, the turbine is assumed to be adiabatic and ideal (reversible, isentropic)

- **4 → 1 isobaric heat rejection (q_{out})**

Heat rejection at constant low pressure, in the condenser the vapor / mixture is cooled and condensed to fluid again (phase change)



Components for Rankine Cycle



ThermoNet: Wiley

Rankine Cycle

- The external source of hot thermal energy is not important for the analysis of a Rankine cycle
- The heat source can be coal, nuclear, wood, solar, geothermal, etcetera
- Only the **amount of energy** (Q_{in}) transferred to the working fluid is important
- A boiler or heat exchanger is used to transfer the heat to the working fluid



A solar power plant, uses solar radiation to produce the steam



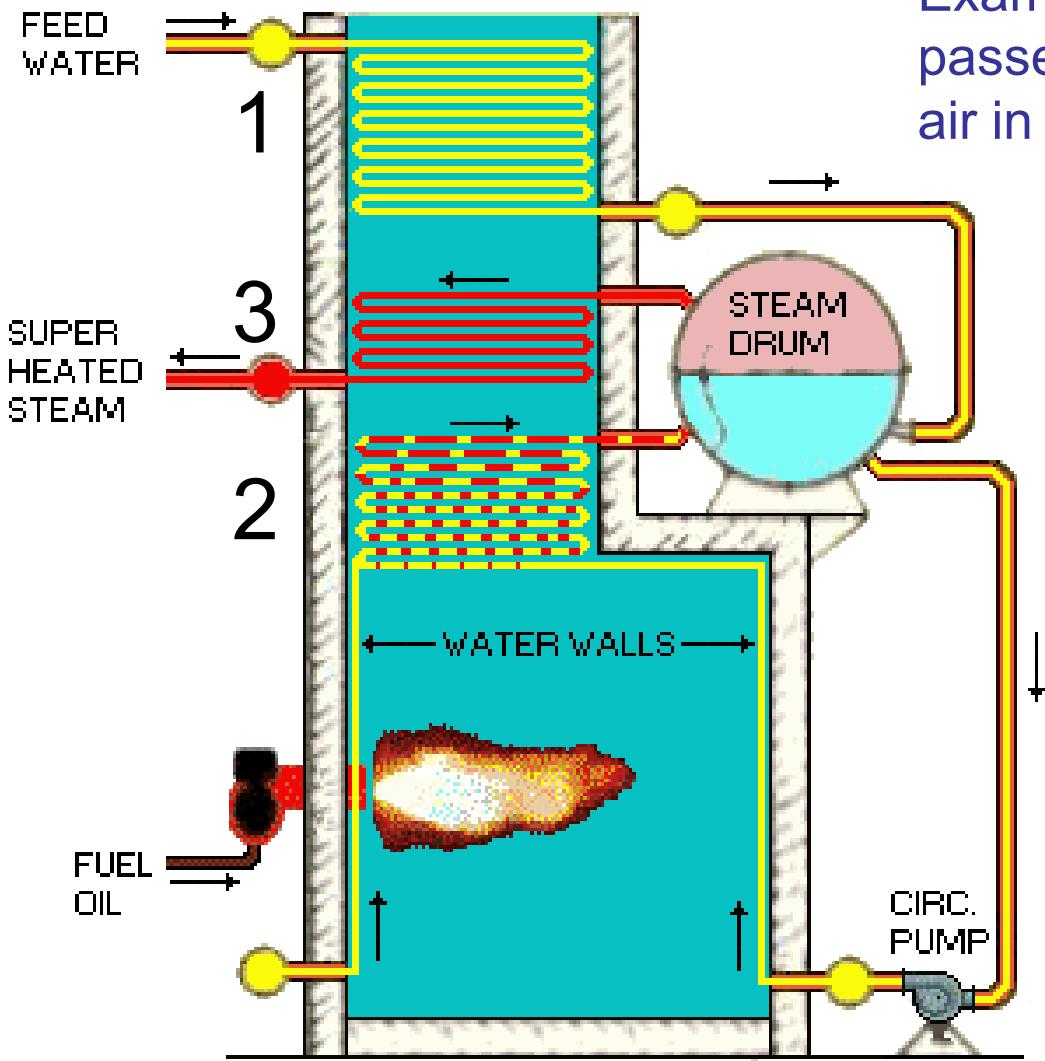
The biomass power plant of Twence in Hengelo uses biomass to produce heat

Huge cooling towers are characteristic for nuclear power plants, a nuclear reactor produces the heat



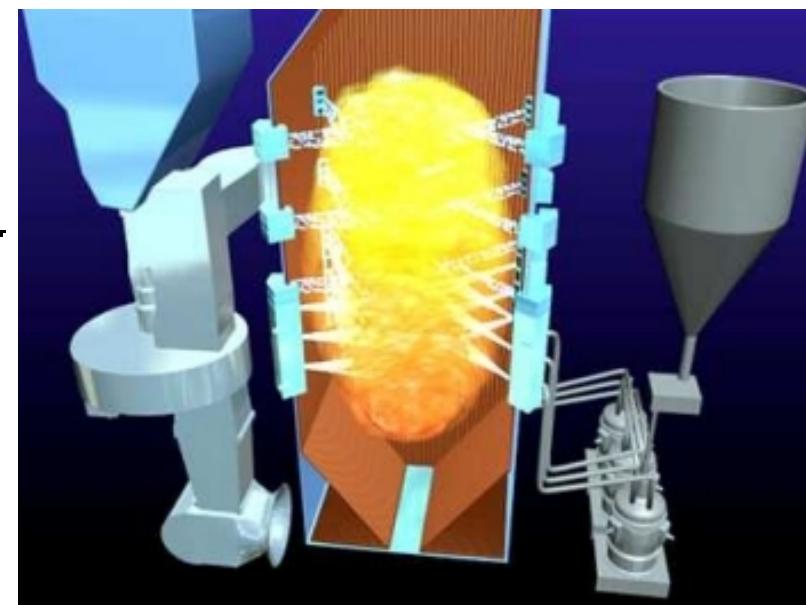
A geothermal power plant uses heat from a geothermal source

Steam Boiler Construction



- Example of a steam boiler, the steam passes three times through the heated air in the boiler

1. Preheating
2. Evaporating
3. Superheating

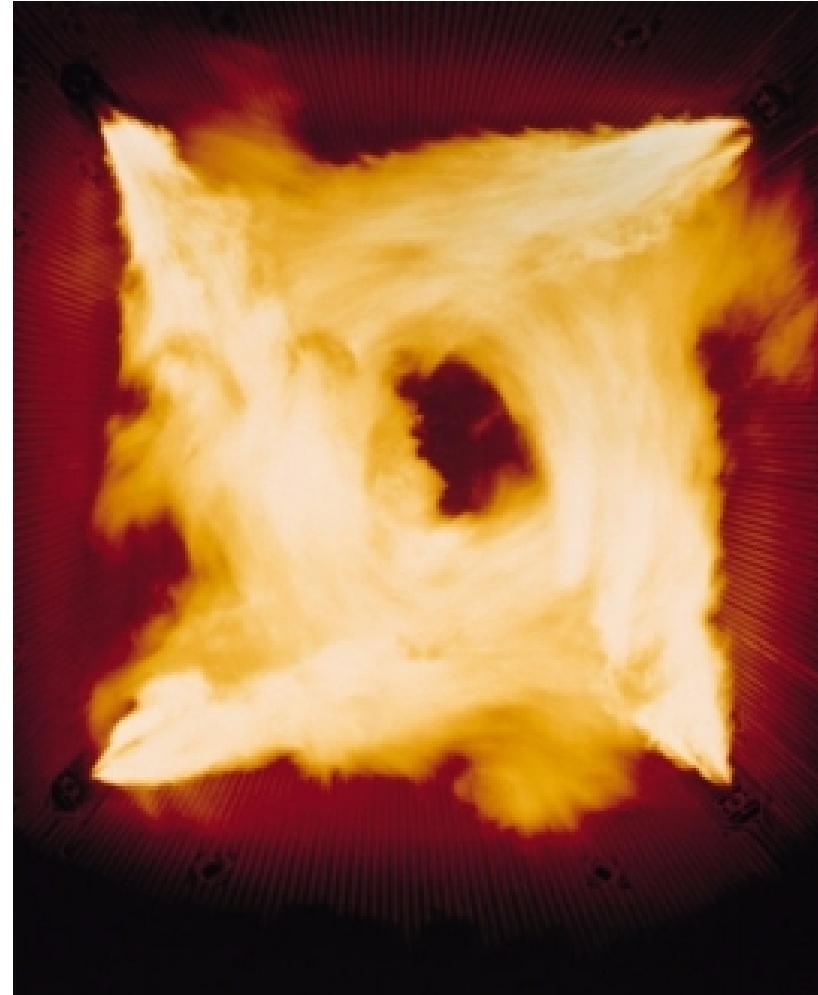


Tangentially coal fired furnace

Steam Boiler



Rentech vertical boiler



Tangentially fired furnace

Steam Turbine



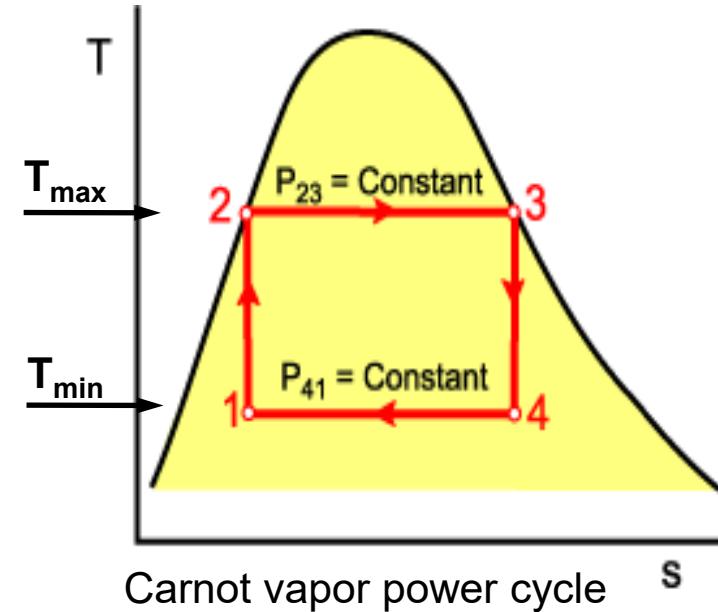
Alstom Steam Turbine double action rotor



Alstom Steam turbine

Comparison of Rankine to Carnot Cycle

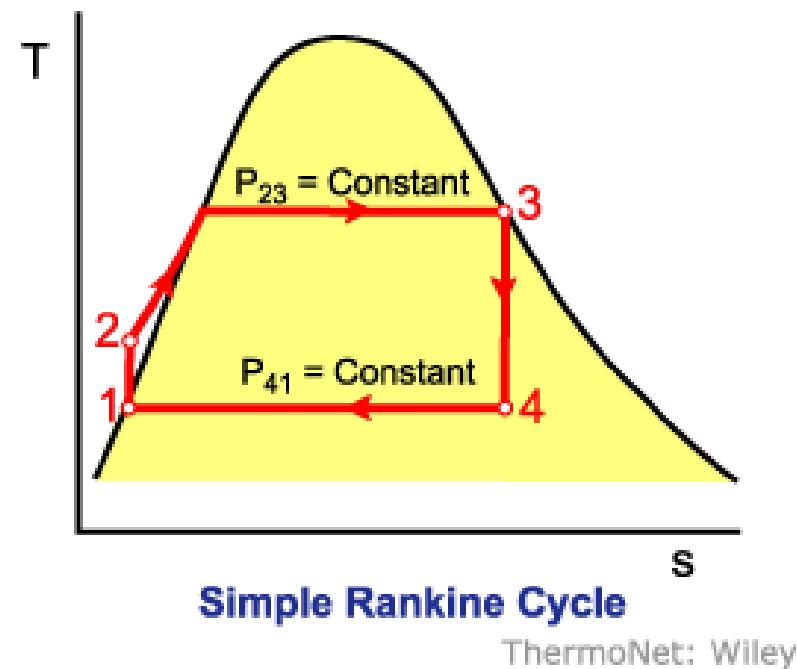
- The ideal vapor power cycle is a Carnot vapor power cycle
- It is a cycle operating between two heat reservoirs (see class 6)
- The maximum efficiency of a thermodynamic cycle operating between two temperature reservoirs T_{\max} and T_{\min} is $\rightarrow \eta_{carnot} = 1 - \frac{T_{\min}}{T_{\max}}$
- Following the theory of Carnot the ideal Rankine cycle would be the one shown in the diagram consisting of isentropic compression (1-2), isobaric heat addition (2-3), isentropic expansion (3-4) and isobaric heat rejection (4-1)
- However in process 1→2 the pressure of a 2-phase mixture needs to be increased
- This is mechanically difficult to do in a reliable process
- So the cycle needs to be modified



Comparison of Rankine to Carnot Cycle

- Simple Rankine power cycle without superheating
- The cycle following the theory of Carnot is modified by changing the position of point 1
- The mixture is completely condensed to the saturated water phase
- The advantage is that this is a pure liquid which is easily and to compress using a pump (the disadvantage is that more heat should be rejected)
- This is mechanically more reliable, thermodynamically easier to implement and uses less work (note: $w_{\text{pump}} \ll w_{\text{turbine}}$)
- However the efficiency is lower than the efficiency of the Carnot cycle as the heat rejected increases while the heat input doesn't change

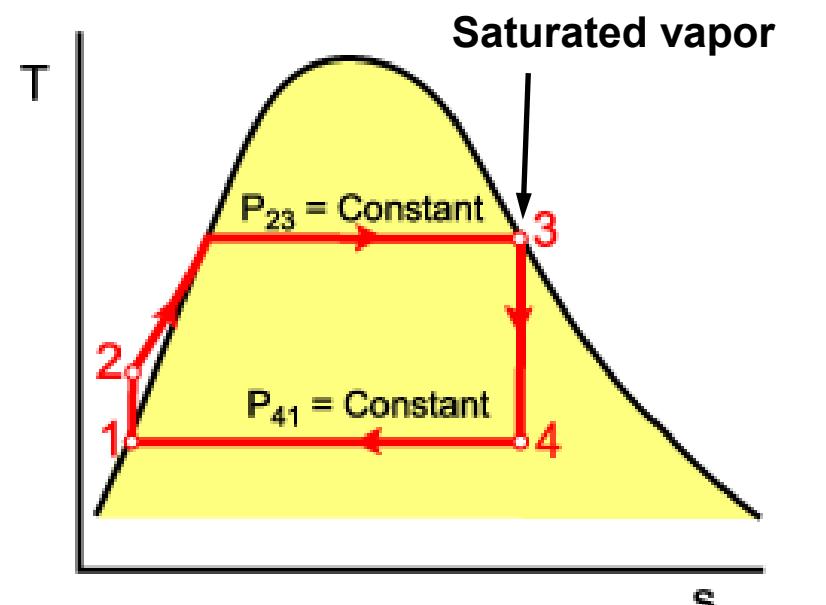
$$\eta_{th} = \frac{\dot{W}_{out} - \dot{W}_{in}}{\dot{Q}_{in}} = \frac{\dot{Q}_{in} - \dot{Q}_{out}}{\dot{Q}_{in}}$$



ThermoNet: Wiley

Simple Ideal Rankine Cycle without Superheat

- The simple Rankine cycle without superheating was representative for early fossil fuel steam engines, but it was still not very reliable and efficient
- It should be improved further to make it more reliable and efficient
- The expansion process (3 – 4) ends in the 2-phase region, during the expansion process the fluid becomes a mixture and consists of vapor with an increasing amount of water droplets
- These water droplets causes erosion and reliability problems in the turbine (see Materials Science)
- On the other hand the temperature of point 2 & 3, the highest temperature in the cycle is not very high resulting in a low efficiency
- The solution is superheating, heat the saturated vapor to higher temperatures so that point 3 shifts to the right and up

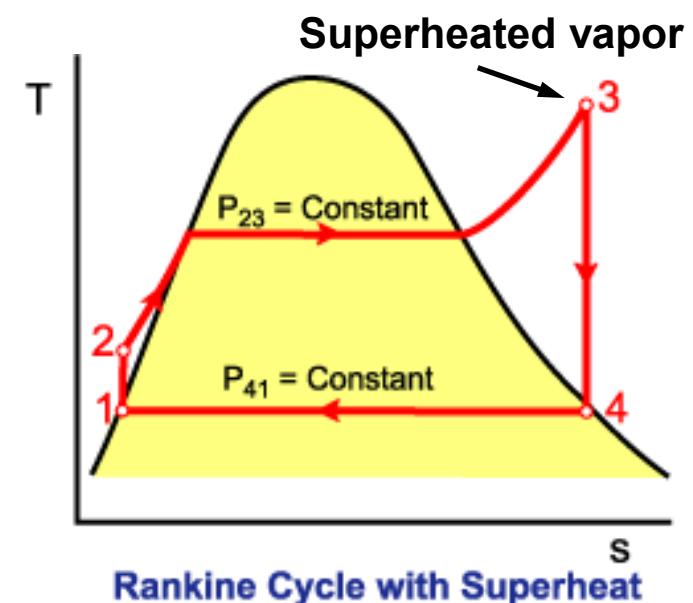


Simple Rankine Cycle

ThermoNet: Wiley

Ideal Rankine Cycle with Superheat

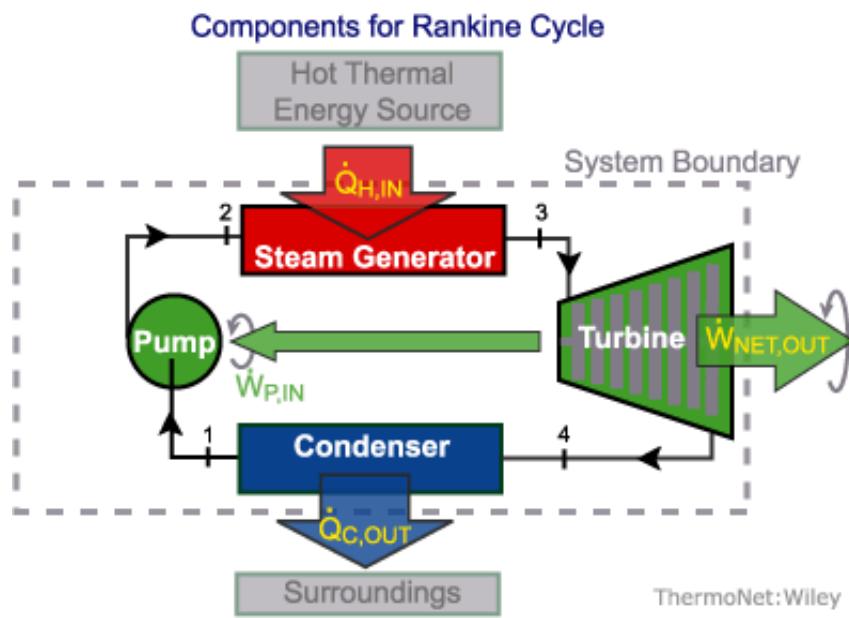
- The ideal Rankine cycle with superheating
- Superheating reduces turbine erosion and reliability problems as the working fluid in the turbine is mostly in the vapor phase
- At the end of the expansion process it may end up in the mixture region some droplets in the turbine are allowed
- The temperature after the boiler or heat exchanger gets higher than the saturation temperature, the vapor gets superheated after the fluid has vaporized completely
- The advantage is that the fluid during the expansion process is mostly in the vapor phase and the highest temperature is higher than without superheat
- Fossil plants have more superheat than nuclear or solar power plants or geothermal plants due to the higher temperature of the heat source (the temperature in a combustion process is higher than the temperature of nuclear, solar or thermal heat)



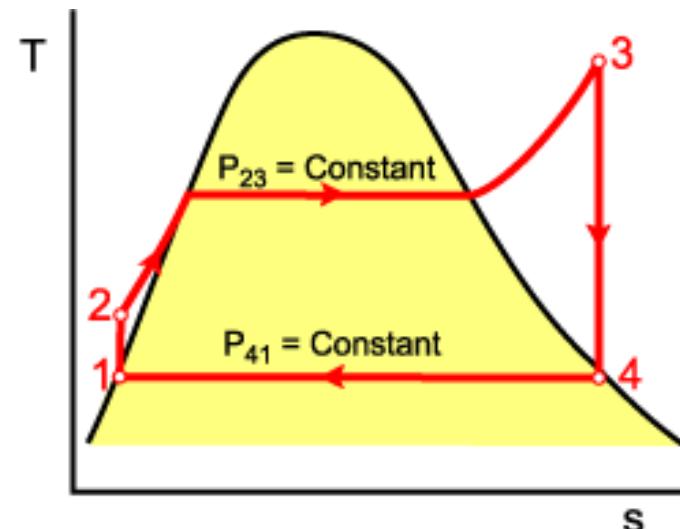
Ideal Rankine Cycle

- The 4 basic components and processes of the Rankine cycle

Process	Component	q	w	Constant
$1 \rightarrow 2$	Pump	0	w_{IN}	s
$2 \rightarrow 3$	Steam generator (boiler, superheater)	q_{IN}	0	P
$3 \rightarrow 4$	Turbine	0	w_{OUT}	s
$4 \rightarrow 1$	Condenser	q_{OUT}	0	P



ThermoNet:Wiley



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Ideal Rankine Cycle Analysis

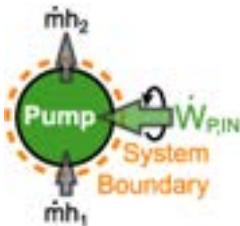
- We have seen that a Rankine cycle consist of 4 basic processes occurring in a series of open devices
- For each device is assumed
 - There is no change in kinetic and potential energy
 - In an **ideal** cycle devices are adiabatic and reversible → isentropic ($s = \text{constant}$, $ds = 0$)
 - The liquid phase is incompressible ($v = \text{constant}$, $dv = 0$)
- Remember for each process the energy balance is given by

$$\begin{aligned}\dot{Q}_{in} + \dot{W}_{in} + \dot{m}(h + \cancel{ke} + \cancel{pe})_{in} &= \dot{Q}_{out} + \dot{W}_{out} + \dot{m}(h + \cancel{ke} + \cancel{pe})_{out} \\ \Rightarrow (\dot{Q}_{in} + \dot{W}_{in}) - (\dot{Q}_{out} + \dot{W}_{out}) &= \dot{m}(h_{out} - h_{in}) \\ \Rightarrow (q_{in} + w_{in}) - (q_{out} + w_{out}) &= h_{out} - h_{in} = \Delta h\end{aligned}$$

- Each device is analyzed separately to analyse the total cycle

Ideal Rankine Cycle Analysis

- Process 1 → 2, **isentropic pressure increase by ideal pump (compression)**



- Apply the energy balance to the pump

$$(q_{in} + w_{in}) - (q_{out} + w_{out}) = \Delta h$$

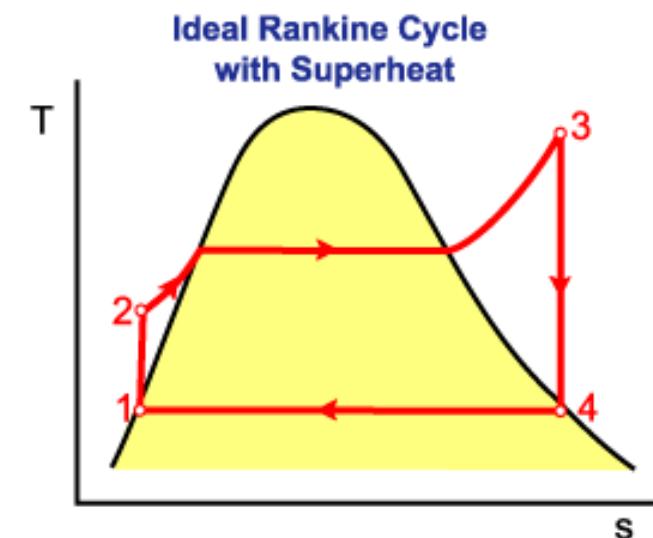
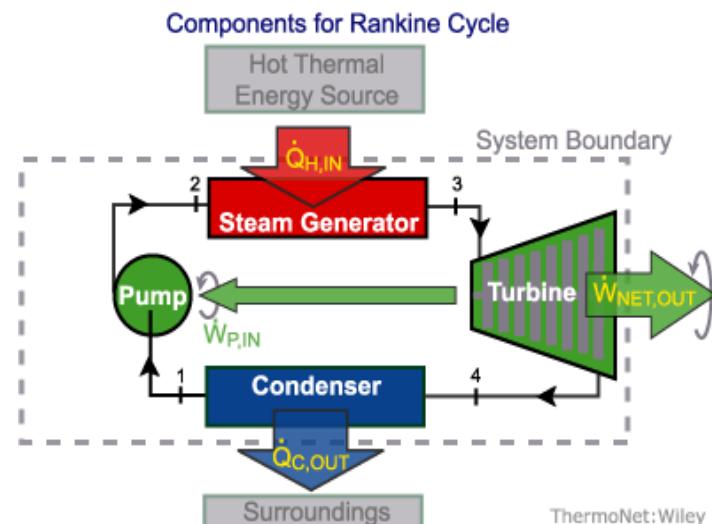
$$w_{pump,in} = h_{out} - h_{in} = h_2 - h_1$$

- Recalling: $dh = Tds + vdP = vdP$ as for an isentropic process $ds = 0$
- For an incompressible liquid $v = \text{constant}$ so integrating $dh = vdP$ gives $\Delta h = v\Delta P$
- Resulting in

$$w_{pump,in} = v(P_{out} - P_{in})$$

$$w_{pump,in} = v(P_2 - P_1) \quad [\text{kJ/kg}]$$

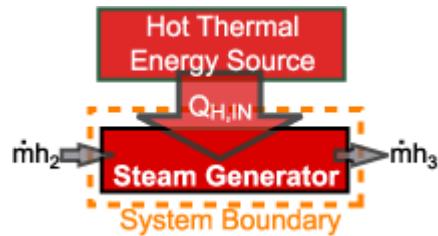
The formula for the pump work is often forgotten at the exam



ThermoNet: Wiley

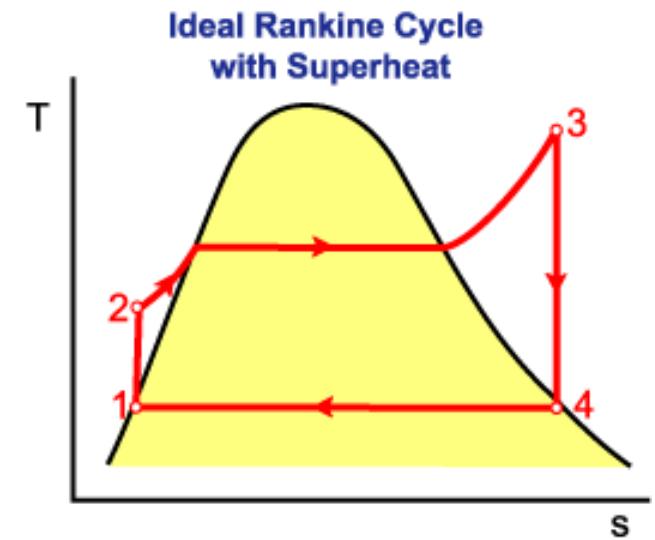
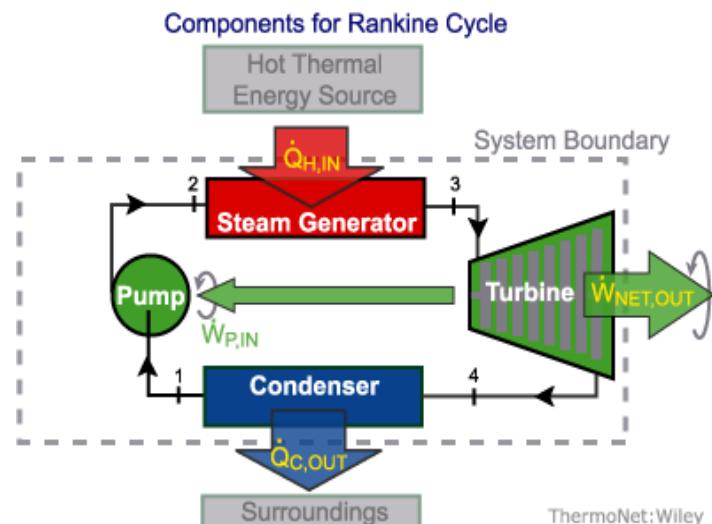
Ideal Rankine Cycle Analysis

- Process 2 → 3, isobaric heat transfer in boiler



- Apply the energy balance to the boiler

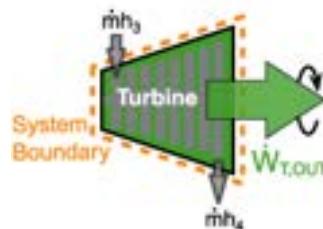
$$(q_{in} + w_{in}) - (q_{out} + w_{out}) = \Delta h$$
$$q_{in,boiler} = h_{out} - h_{in} = h_3 - h_2$$



ThermoNet: Wiley

Ideal Rankine Cycle Analysis

- Process 3 → 4, isentropic pressure decrease in ideal turbine (expansion)



- Apply the energy balance to the turbine

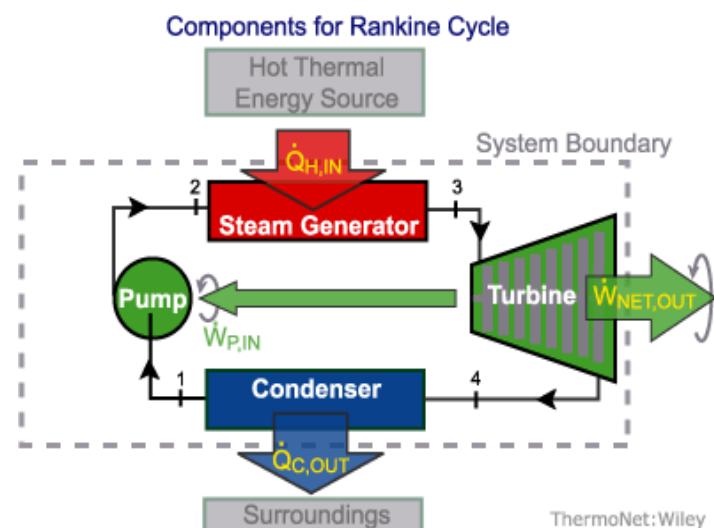
$$(q_{in} + w_{in}) - (q_{out} + w_{out}) = \Delta h$$

$$w_{out,turbine} = h_{in} - h_{iut} = h_3 - h_4$$

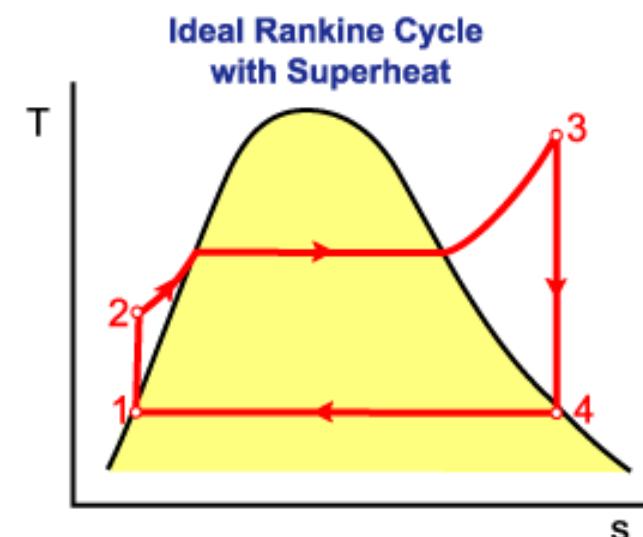
- The pump need work the compress the fluid, considering that the pump consumes some of the work the net work leaving the system is

$$w_{net} = w_{out,turbine} - w_{pump,in}$$

$$w_{net} = (h_3 - h_4) - (h_2 - h_1)$$



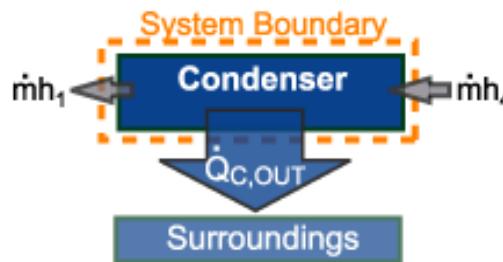
ThermoNet: Wiley



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Ideal Rankine Cycle Analysis

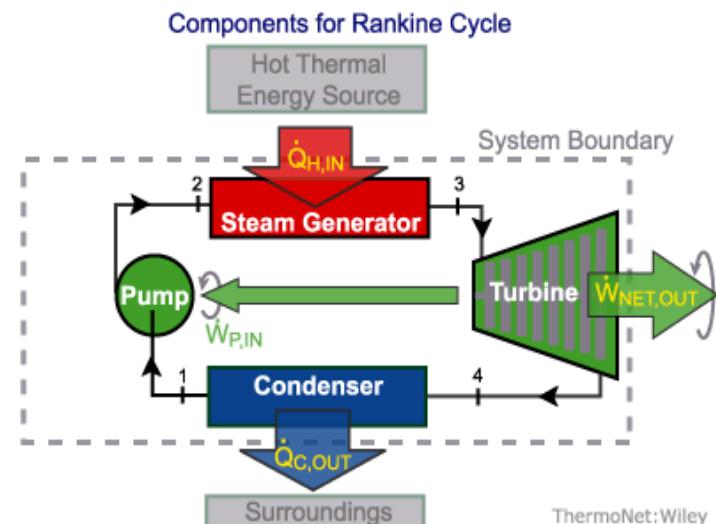
- Process 4 → 1, isobaric heat transfer in condenser



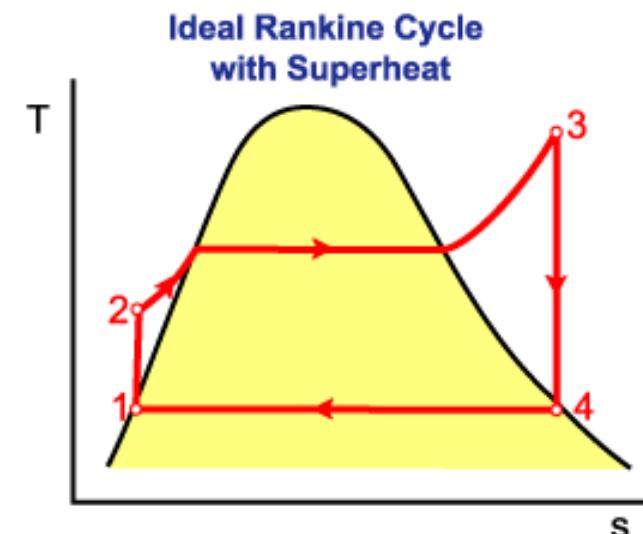
- Apply the energy balance to the condenser

$$(q_{in} + w_{in}) - (q_{out} + w_{out}) = \Delta h$$

$$q_{out,condenser} = h_{in} - h_{out} = h_4 - h_1$$



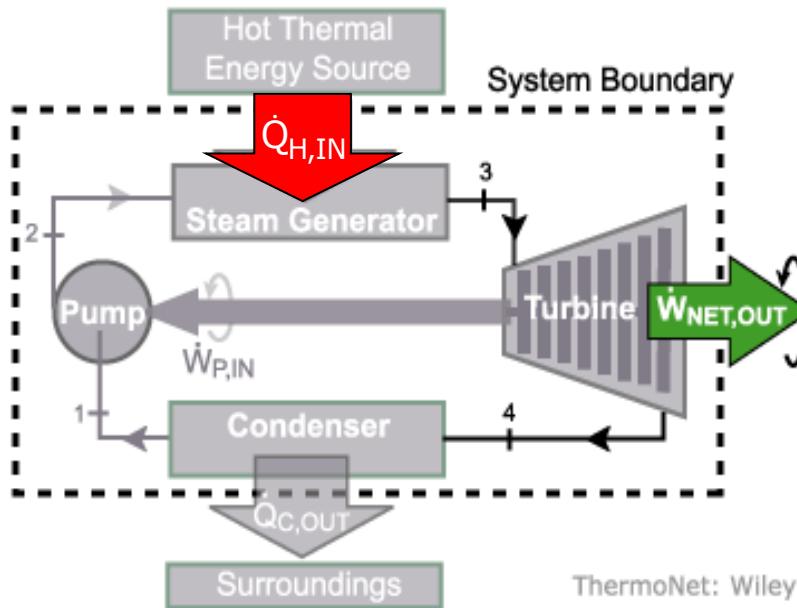
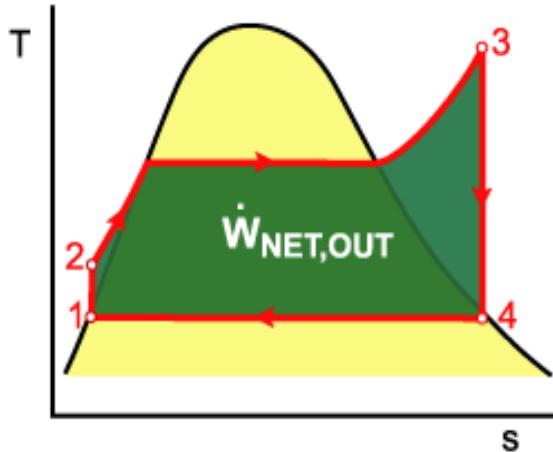
ThermoNet: Wiley



ThermoNet: Wiley

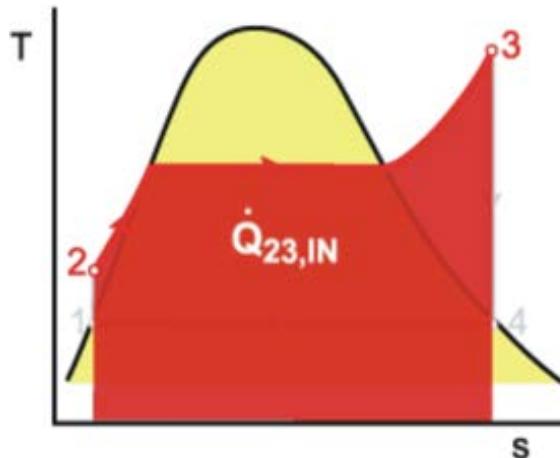
Rankine Cycle Efficiency

- Net work output



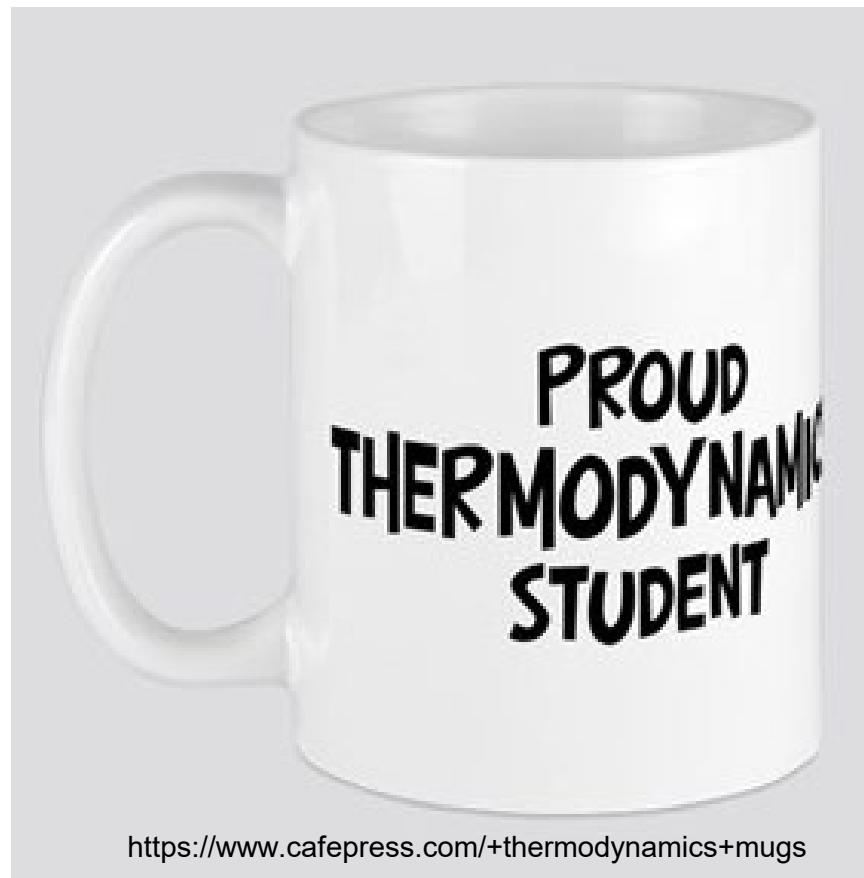
ThermoNet: Wiley

- Heat added



$$\eta_{Rankine} = \frac{w_{out,turbine} - w_{pump,in}}{q_{in}}$$
$$= \frac{w_{net}}{q_{in}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$

BREAK



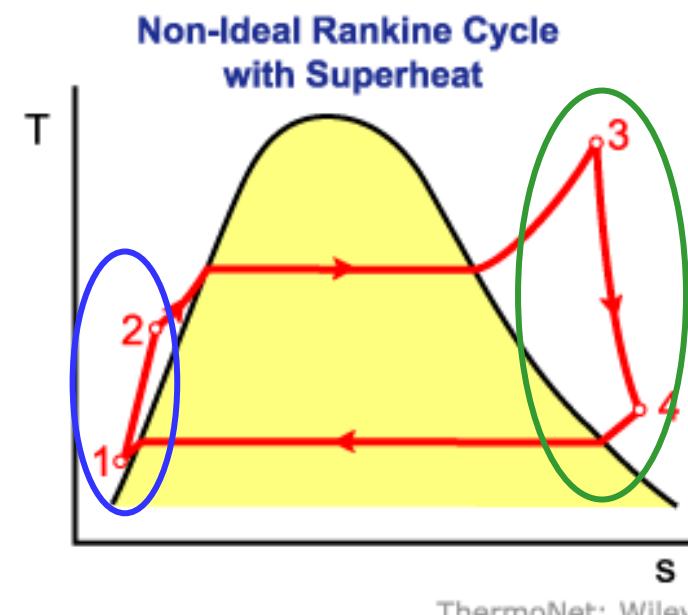
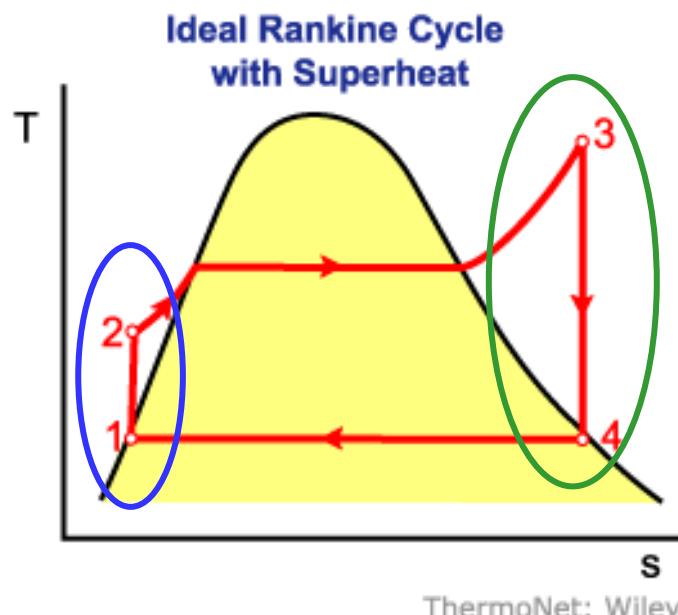
<https://www.cafepress.com/+thermodynamics+mugs>

Non-Ideal Rankine Cycle

- For a real (non-ideal) Rankine cycle isentropic efficiencies for the pump and the turbine must be included

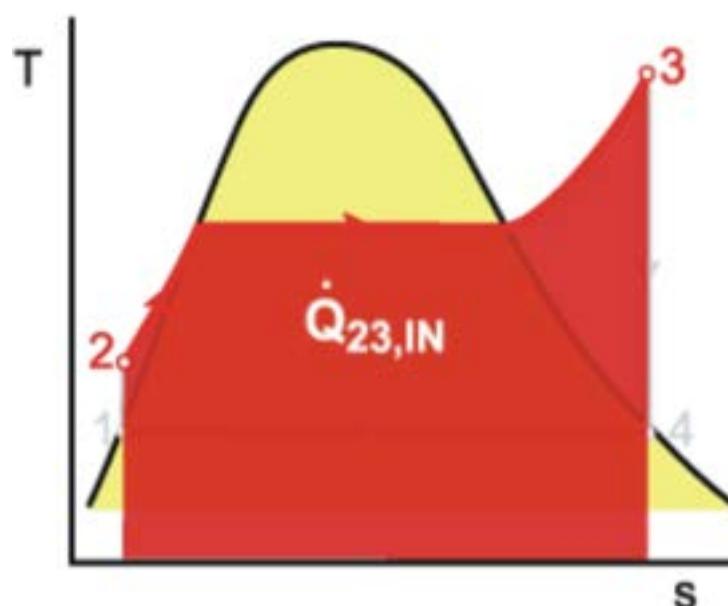
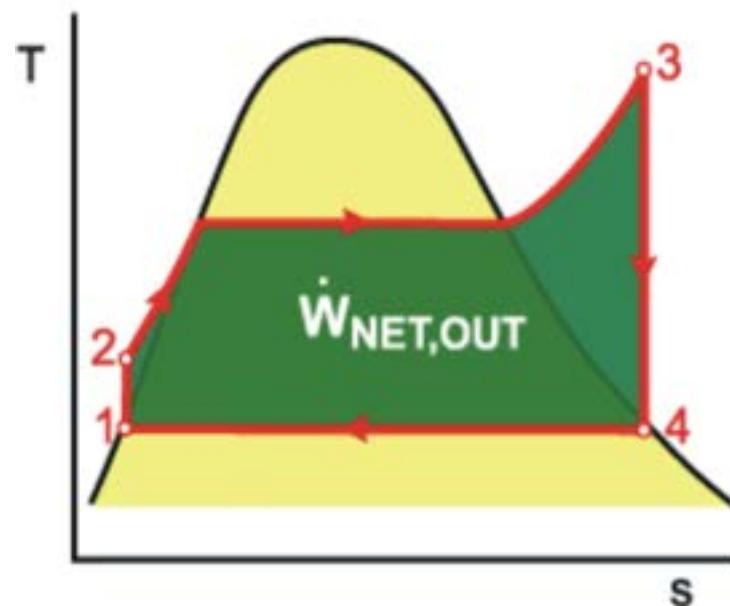
$$\eta_{s,pump} = \frac{h_{out,s} - h_{in}}{h_{out,a} - h_{in}} = \frac{v_{ICL}(P_{out} - P_{in})}{h_{out,a} - h_{in}} \quad \text{and} \quad \eta_{s,turbine} = \frac{h_{in} - h_{out,a}}{h_{in} - h_{out,s}}$$

- The entropy in the pump and the turbine increases, resulting in shifting point 2 and 4 to the right



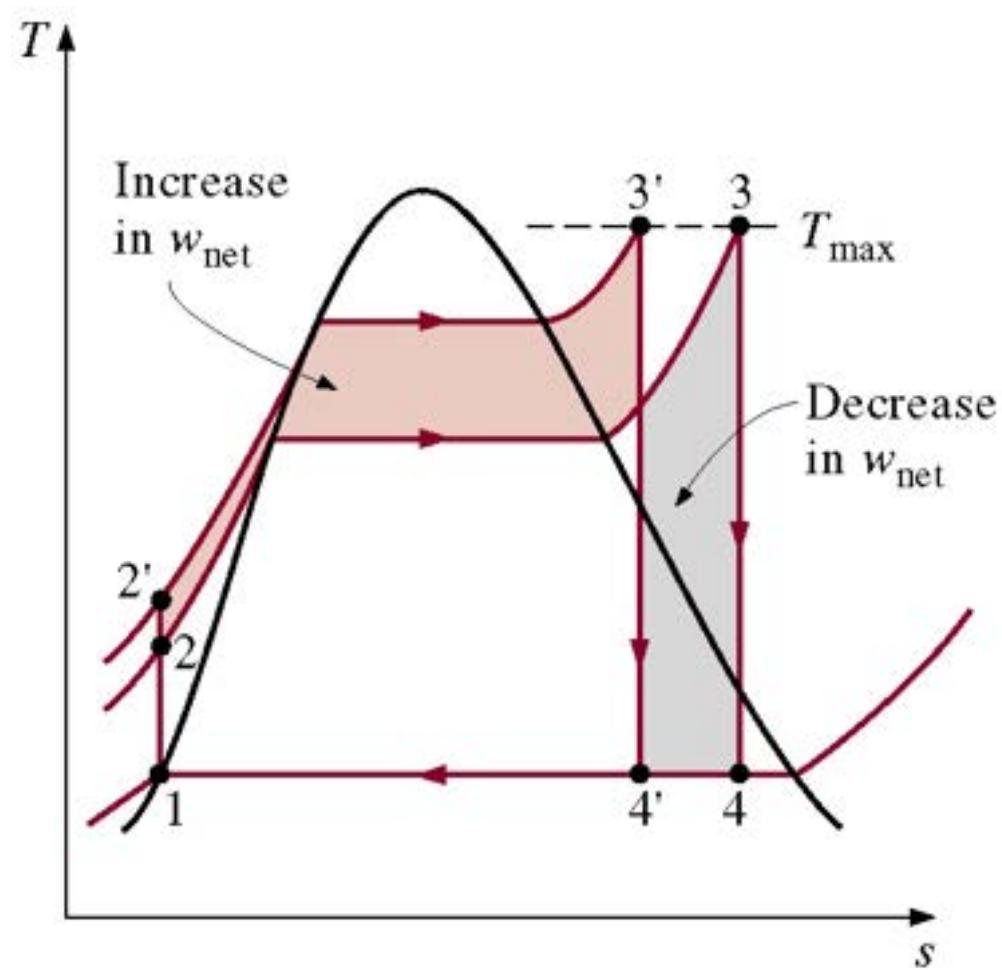
Design parameters Rankine Cycle

- How can the efficiency of the basic Rankine cycle be increased?
- Remember the net work output is the area enclosed in the graph, the net heat input is the area below the curve 2 – 3
- The area can be enlarged by
 - Changing the turbine input pressure
 - Changing the turbine inlet temperature
 - Changing the condenser temperature/pressure



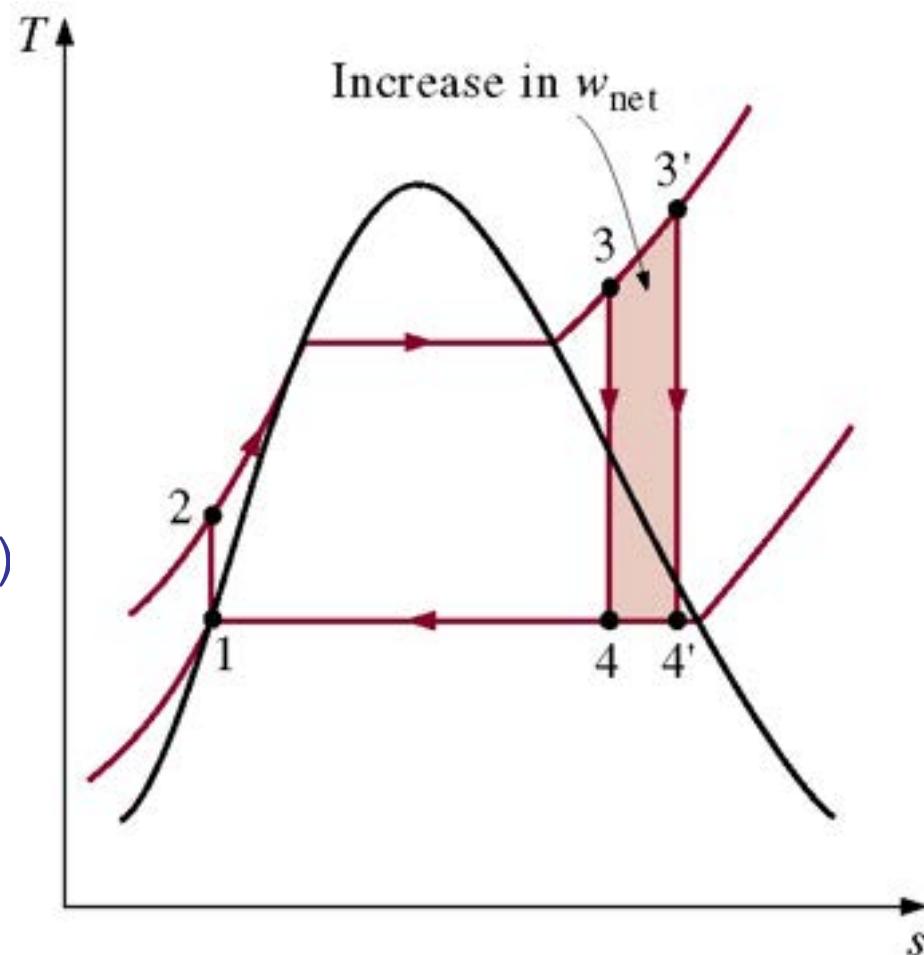
Design parameters Rankine Cycle

- The effect of increasing the boiler pressure on the ideal Rankine cycle
- **Power output:** hardly any change
- **Heat input:** hardly any change but a large part of the heat is added at a higher temperature
- **Efficiency:** increases (because the heat is added at a higher temperature)
- The **quality** of the saturated mixture at the turbine exit decreases (more liquid, less vapor), this is unfavorable for the turbine



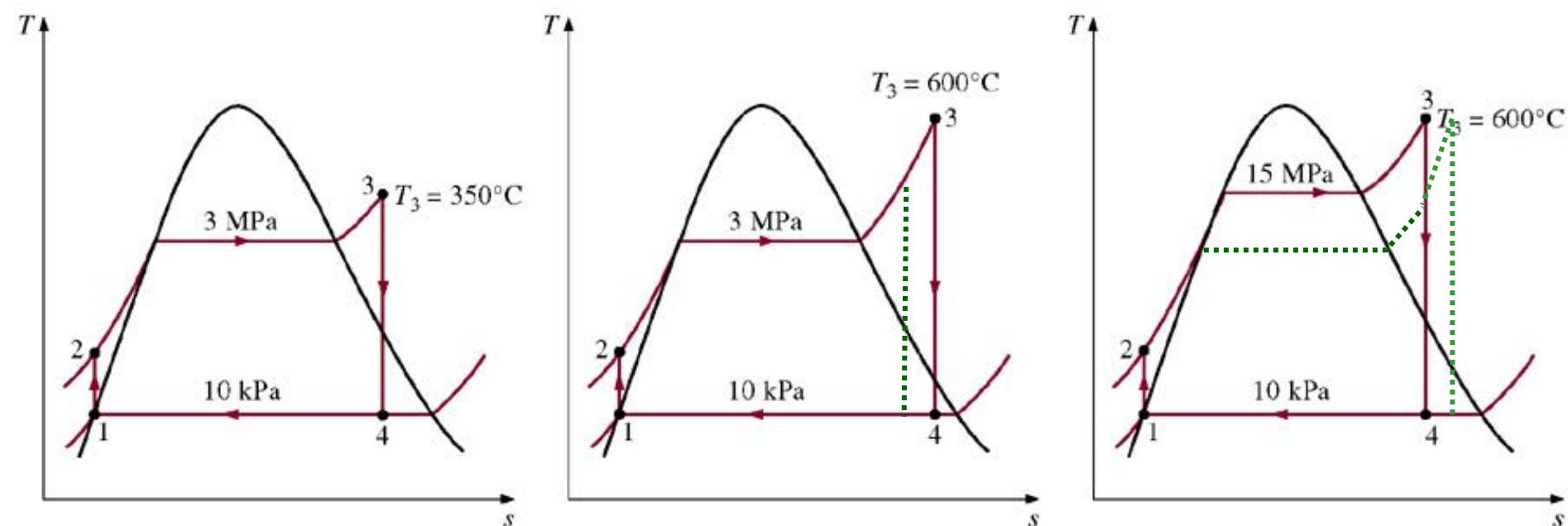
Design parameters Rankine Cycle

- The effect of superheating the vapor to higher temperatures on the ideal Rankine cycle
- Power output:** increases
- Heat input:** increases but it is an advantage that this extra heat is added at a high temperature
- Efficiency:** increases
- The **quality** of the saturated mixture at the turbine exit increases (less liquid, more vapor) this is favorable for the turbine
- Note: the temperature in the system is limited to about 620°C by the material properties (see Material Sciences)



Design parameters Rankine Cycle

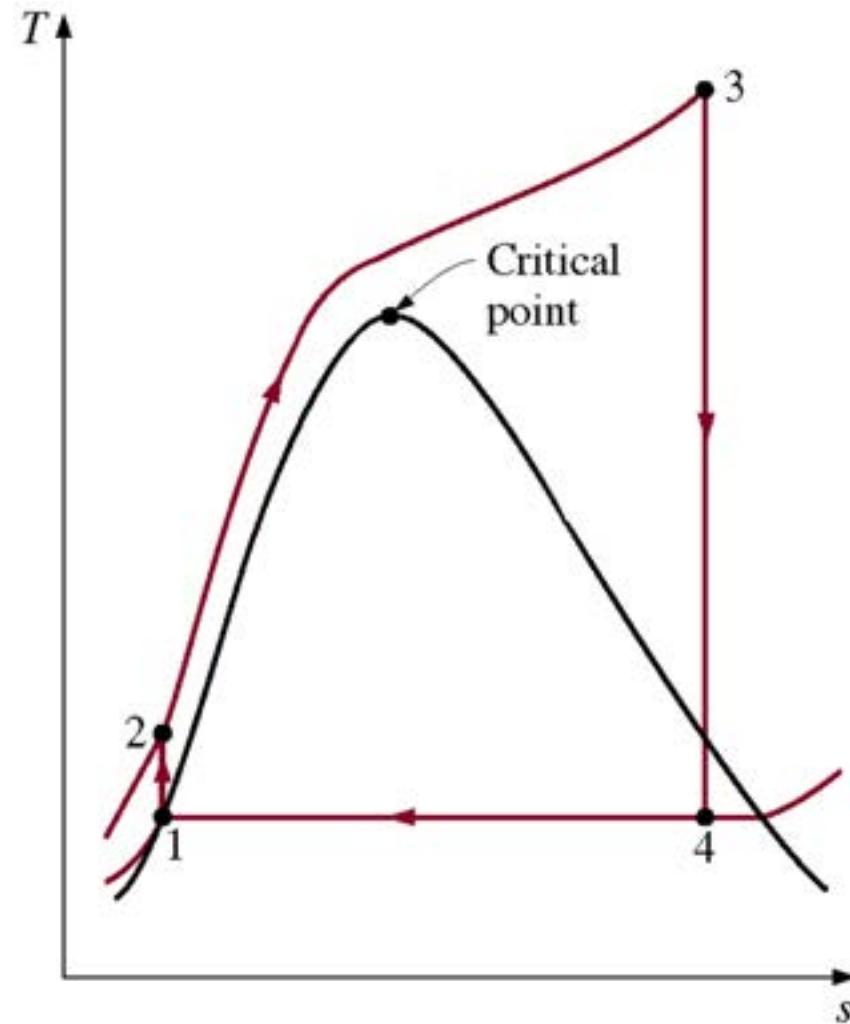
- The effect of increasing the boiler pressure and superheating the vapor to higher temperatures on the ideal Rankine cycle
 - Pressure 3 Mpa → 15 MPa
 - Temperature 350°C → 600°C



- The combination of the pressure and temperature at the turbine inlet determines the quality of the mixture at the turbine outlet
- To find the best design both must be considered

Design parameters Rankine Cycle

- The supercritical Rankine cycle
- An extreme situation, the boiler pressure goes to supercritical pressures, the curve rises above the critical point
- This results in high efficiencies as the temperature at which the heat is added is high
- On the other hand the requirements for the materials are higher



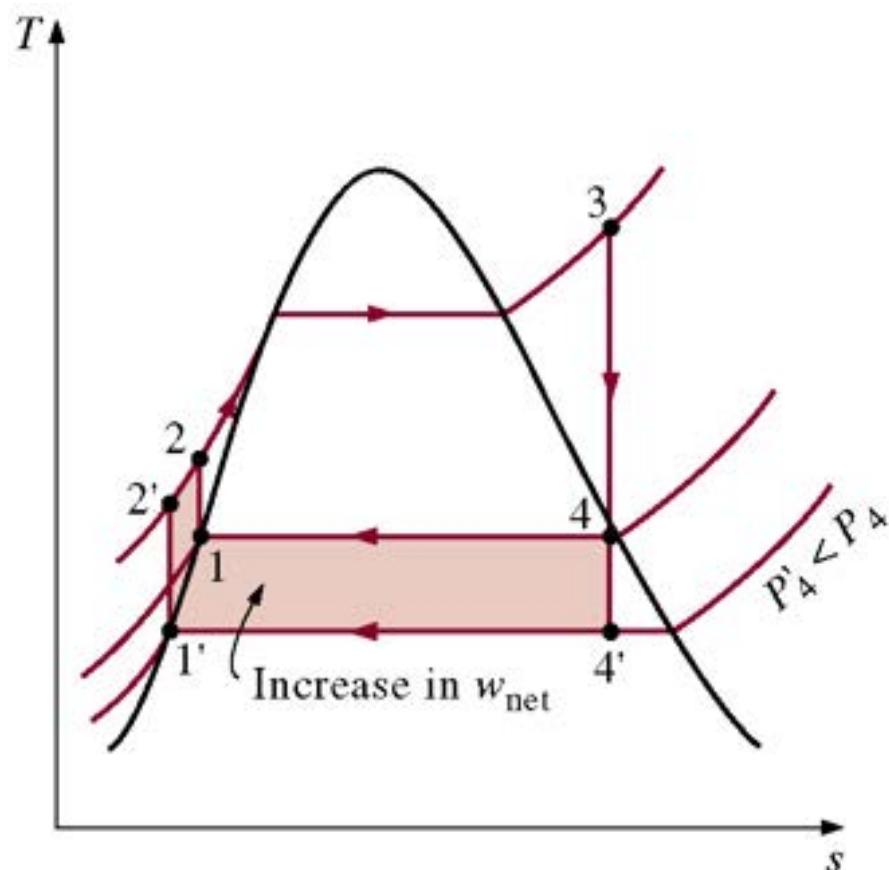
Design parameters Rankine Cycle

- The effect of lowering the condenser pressure on the ideal Rankine cycle

- Power output:** increases
- Heat input:** no change
- Efficiency:** increases as the power output increases and the heat output decreases while the heat input does not change

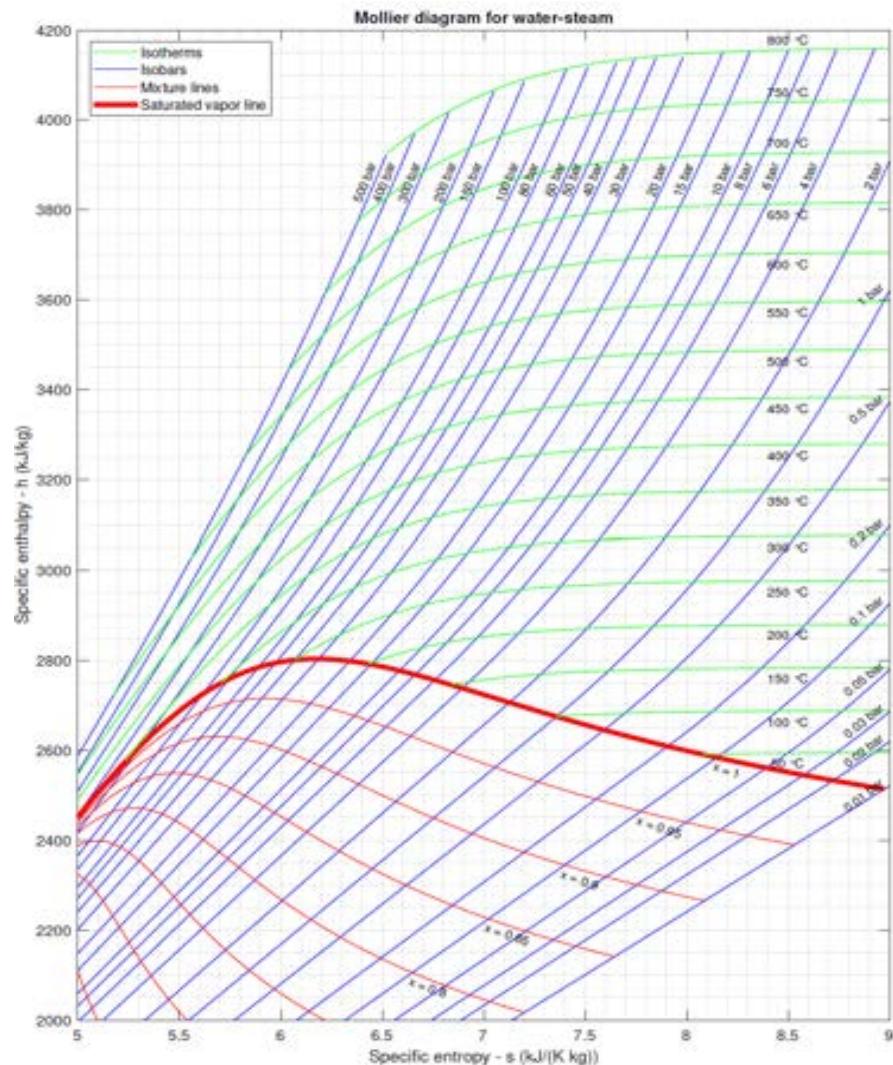
$$\eta_{th} = \frac{\dot{W}_{out} - \dot{W}_{in}}{\dot{Q}_{in}} = \frac{\dot{Q}_{in} - \dot{Q}_{out}}{\dot{Q}_{in}}$$

- The **quality** of the saturated mixture at the turbine exit decreases (more liquid, less vapor), which is unfavorable for the turbine
- Note: the condenser pressure is related to the condenser temperature which always must be higher than the temperature of the environment



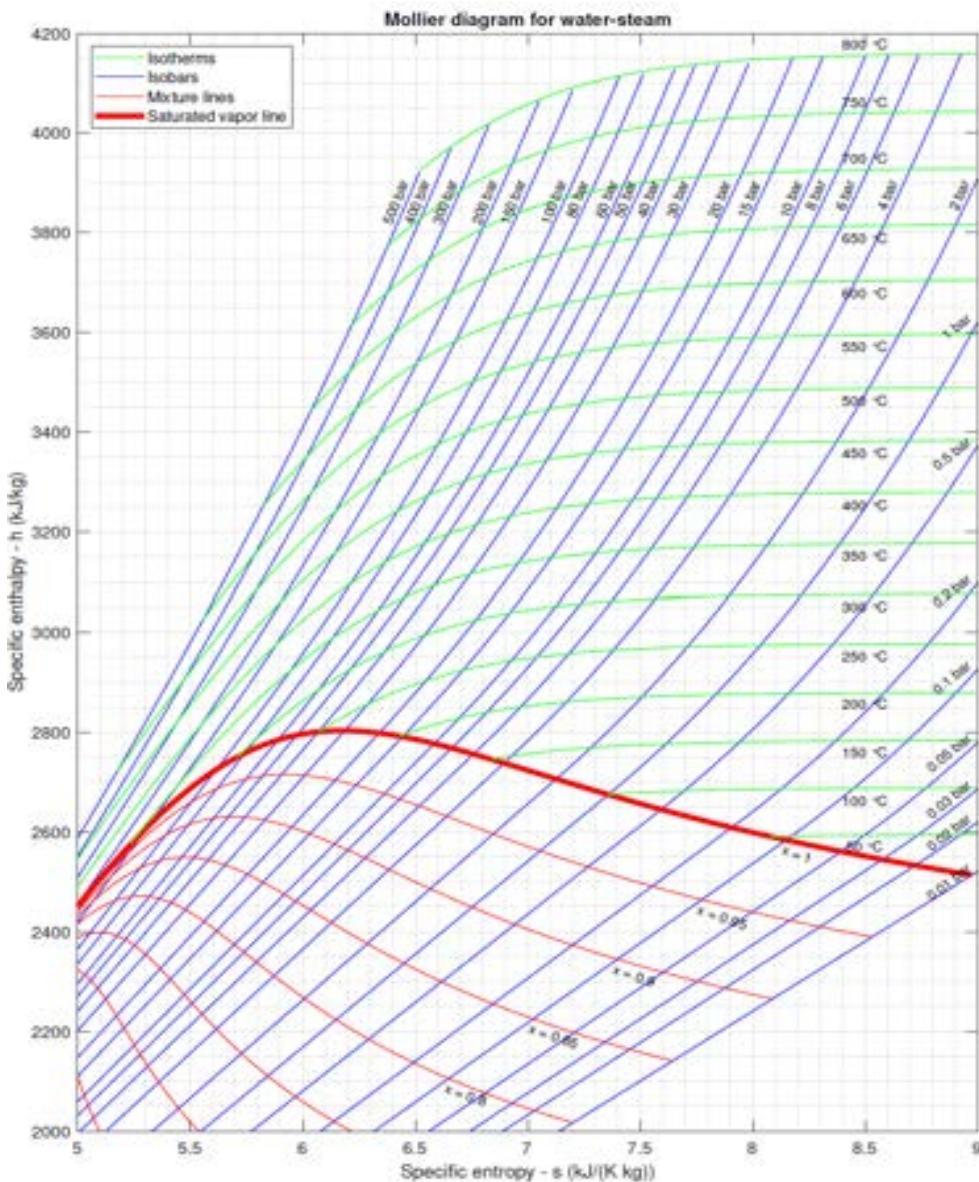
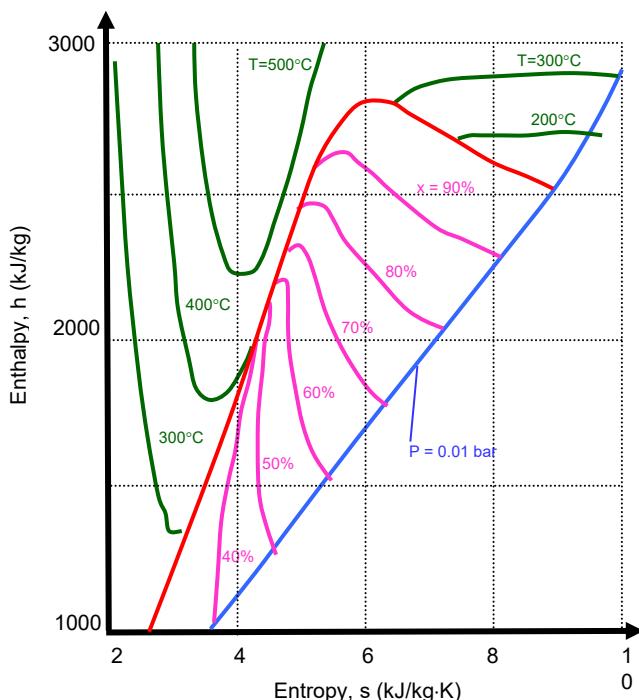
Mollier Diagram Water for Rankine Cycle

- 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)?



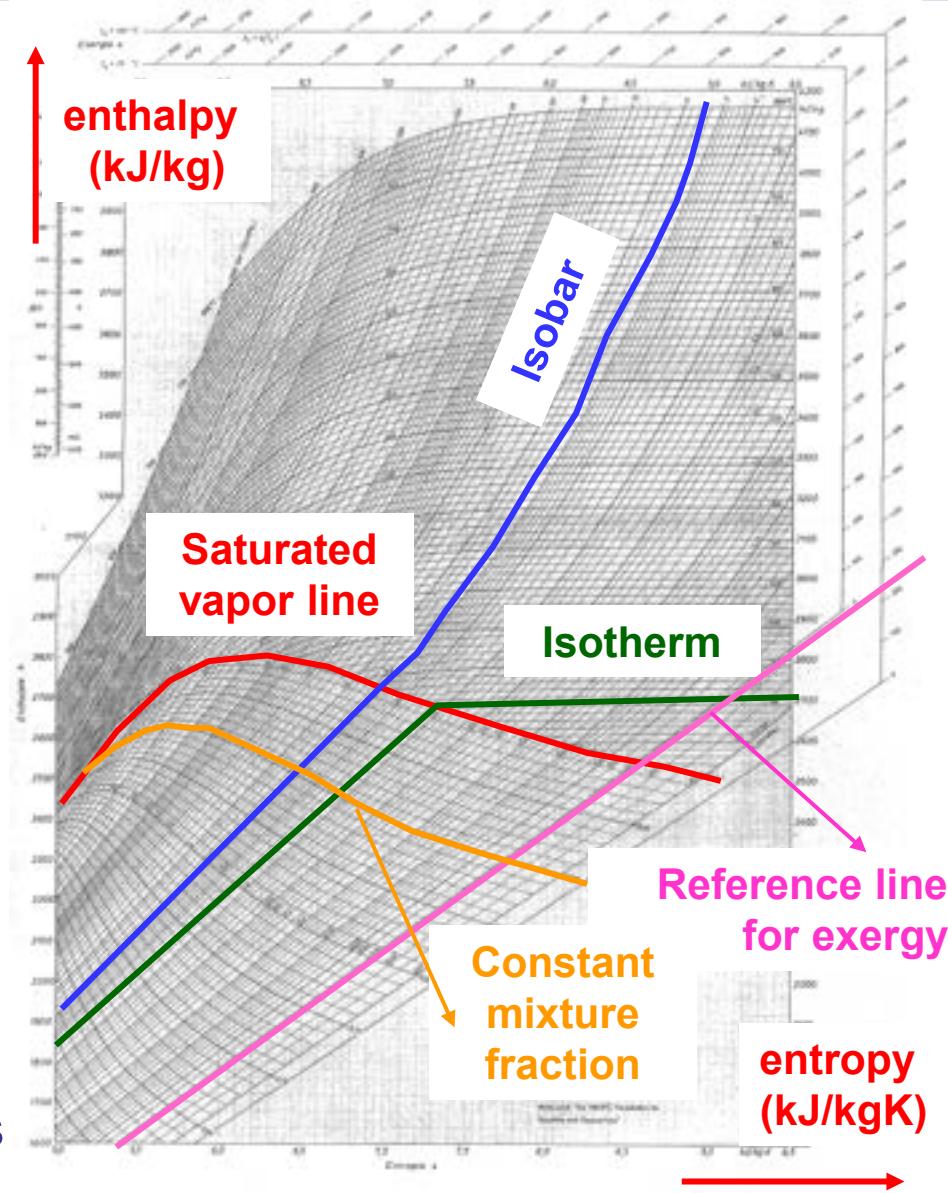
Mollier Diagram Water for Rankine Cycle

- 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



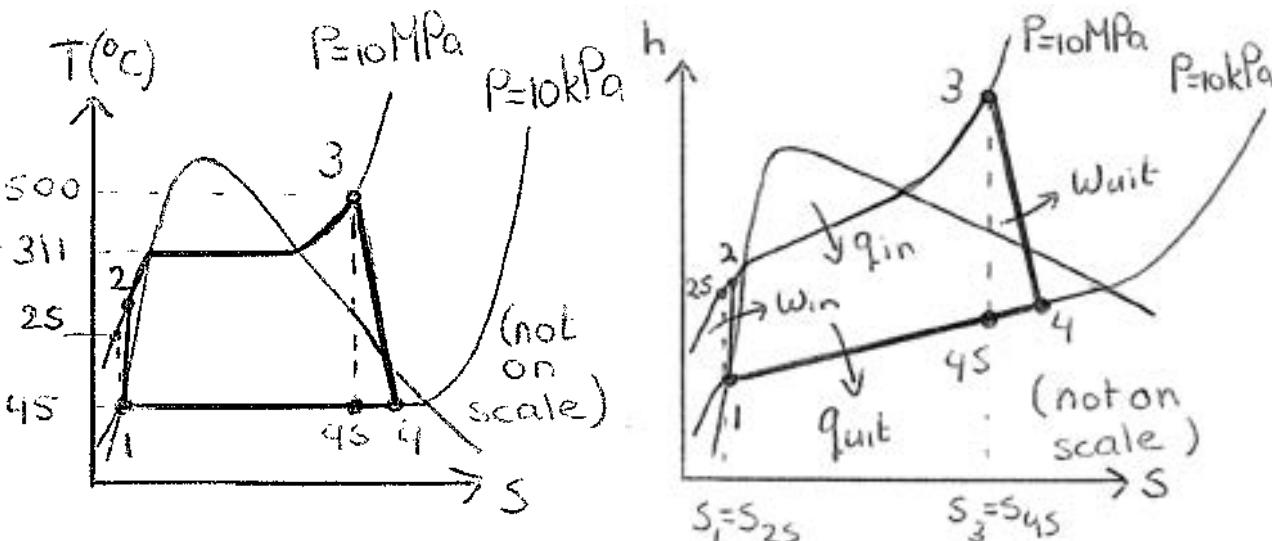
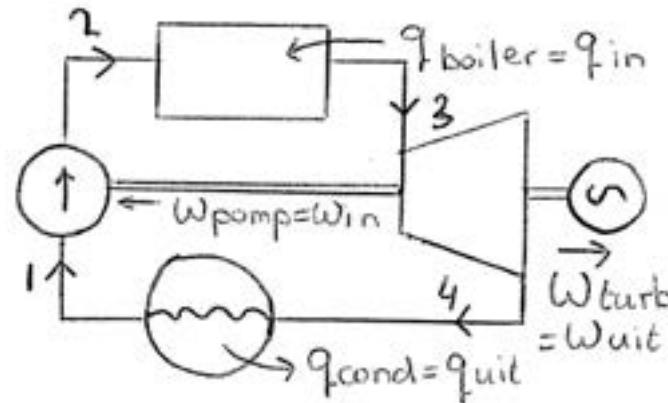
Mollier Diagram Water for Rankine Cycle

- 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
 - Reference line for exergy
- 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



Example analysis Rankine Cycle

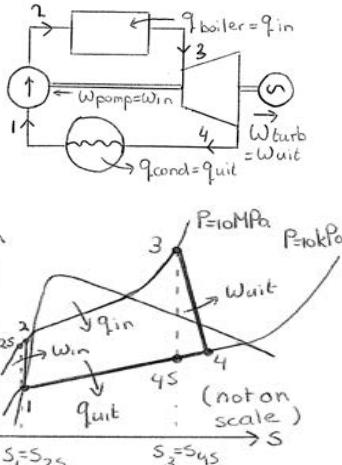
- Steam power plant on Rankine cycle between $P_3=10\text{ MPa}$ and $P_4=10\text{ kPa}$
- Temperature of the steam at the turbine inlet is $T_3=500^\circ\text{C}$
- Isentropic efficiencies of the pump and the turbine are 0.8, mass flow is 5 kg/s
- Draw schematically the set up of the cycle
- Draw the T-s and h-s diagram
- Give for every point two characteristics
(with two characteristics the point can be found)
- Calculate heat and work in- and output
- Calculate the net power output and the efficiency



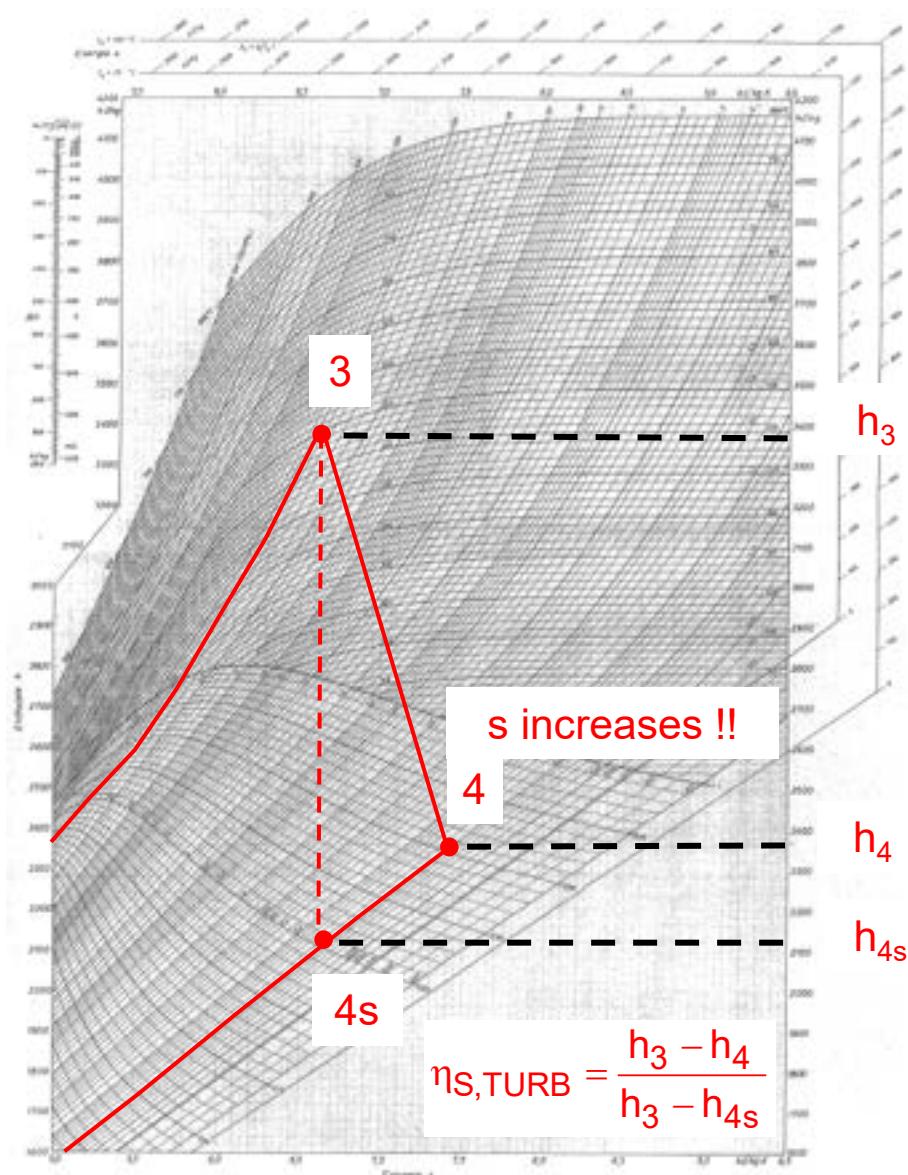
	First	Second
1	10kPa	$T_{\text{sat}}@10\text{ kPa}$
2s	10MPa	$s_{2s}=s_1$
2	10MPa	$\eta = 0.8$
3	10MPa	500°C
4s	10kPa	$s_{4s}=s_3$
4	10kPa	$\eta = 0.8$

Example analysis Rankine Cycle

- Rankine cycle



	First	Second
1	10kPa	$T_{sat}@10kPa$
2s	10MPa	$s_{2s} = s_1$
2	10MPa	$\eta = 0.8$
3	10MPa	500°C
4s	10kPa	$s_{4s} = s_3$
4	10kPa	$\eta = 0.8$



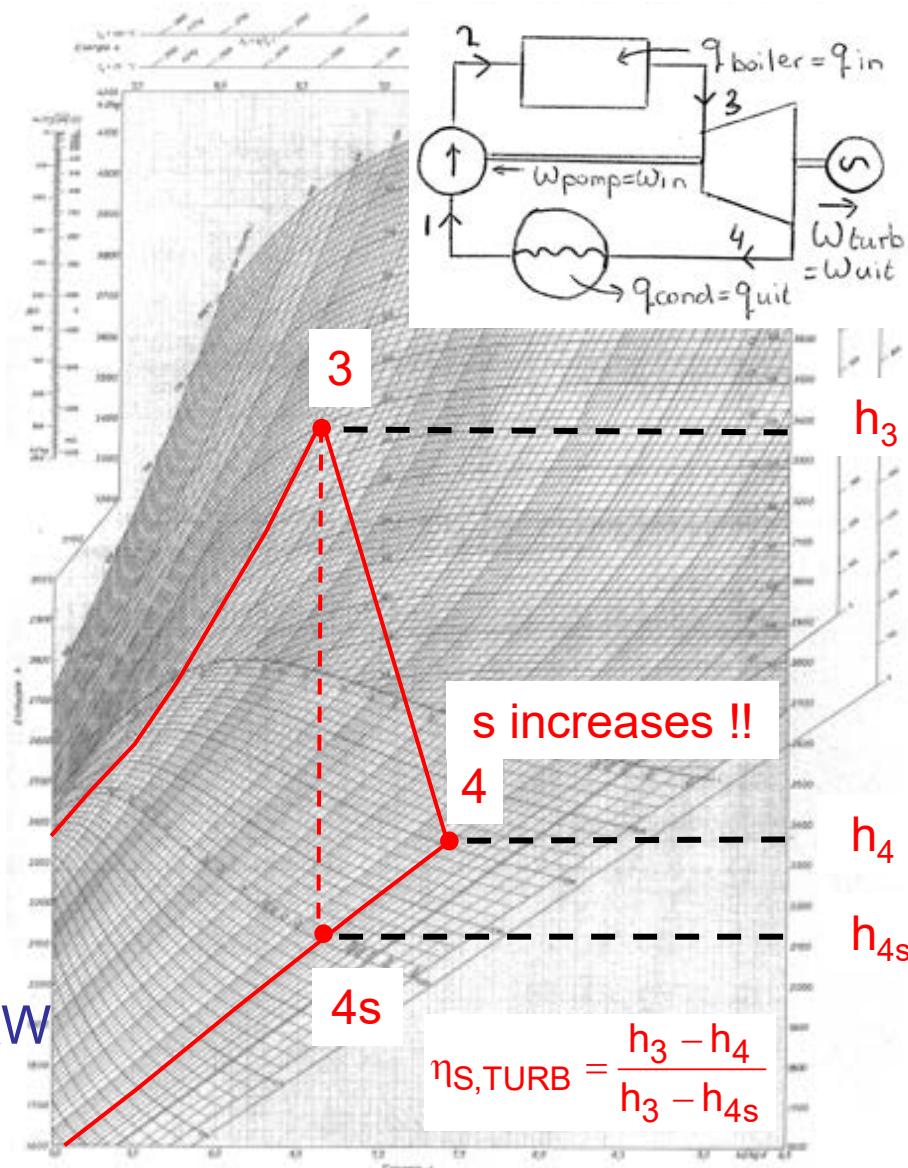
Example analysis Rankine Cycle

- Find the h value of every point

	P (kPa)	T (°C)	h (kJ/kg)	phase
1	10	45	192	Sat L
2s	10000		193	Com L
2	10000		193.3	Com L
3	10000	500	3375	Sup V
4s	10	45	2125	X=0.81
4	10	45	2375	X=0.91

- $w_{in} = h_2 - h_1 = 1.3 \text{ kJ/kg}$
- $q_{in} = h_3 - h_2 = 3181.7 \text{ kJ/kg}$
- $w_{out} = h_3 - h_4 = 1000 \text{ kJ/kg}$
- $q_{out} = h_4 - h_1 = 2183 \text{ kJ/kg}$
- See $w_{in} + q_{in} = w_{out} + q_{out}$ (first law)
- $\dot{W}_{net} = \dot{m}(w_{out} - w_{in}) = 5 \cdot 998.7 = 4993.5 \text{ kW}$

$$\eta_{RANKINE} = \frac{w_{out} - w_{in}}{q_{in}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2} = 31\%$$



Example analysis Rankine Cycle

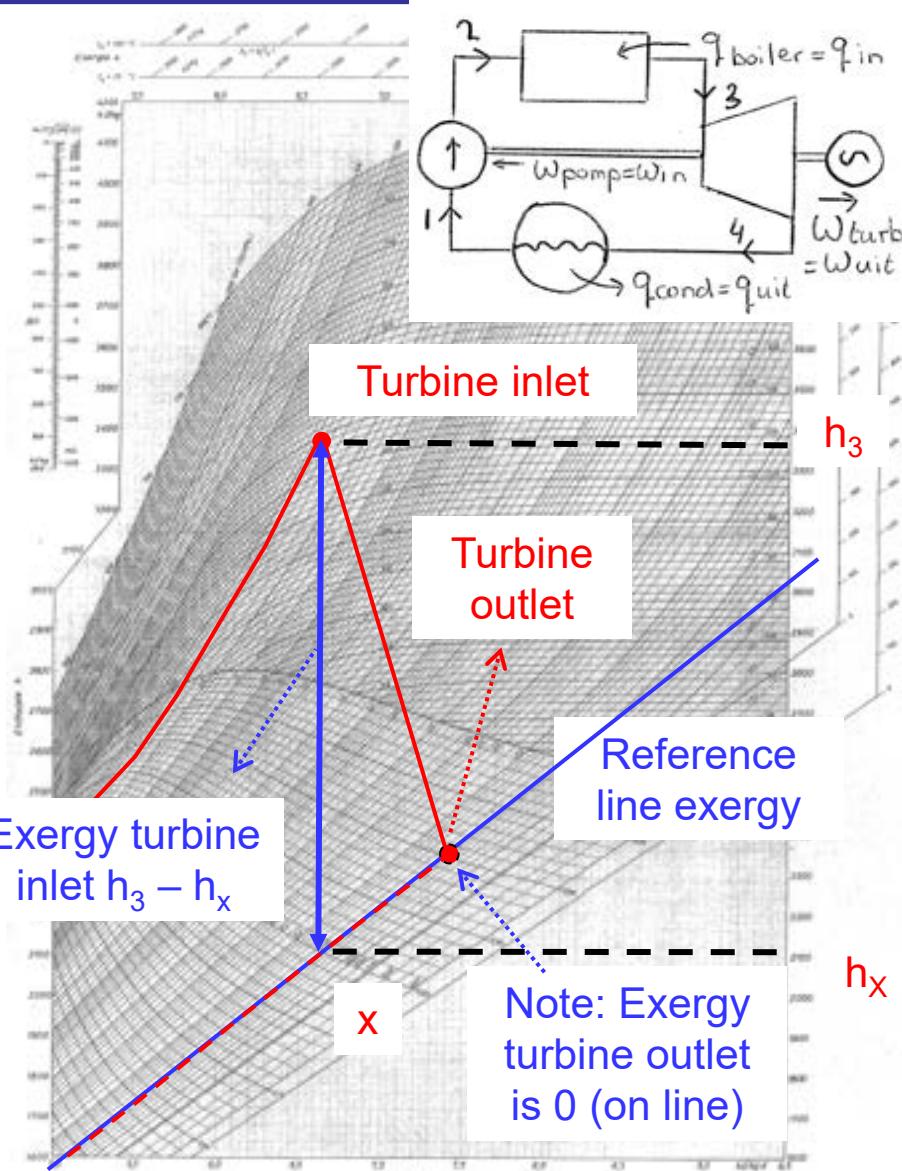
- Consider the Rankine cycle from the previous example and analyze it using second law analysis (exergy analysis)
- What is the second law efficiency?
- What is the exergy of the steam at the turbine outlet and the turbine inlet as determined from the diagram?

$$\eta_{SECOND\ LAW} = \frac{\eta_{RANKINE}}{\eta_{CARNOT}} \quad \eta_{RANKINE} = 0.31$$

$$\eta_{CARNOT} = 1 - \frac{T_{COLD}}{T_{HOT}} = 1 - \frac{45 + 273}{500 + 273} = 0.59$$

$$\eta_{SECOND\ LAW} = \frac{0.31}{0.59} = 0.52 \rightarrow 52\%$$

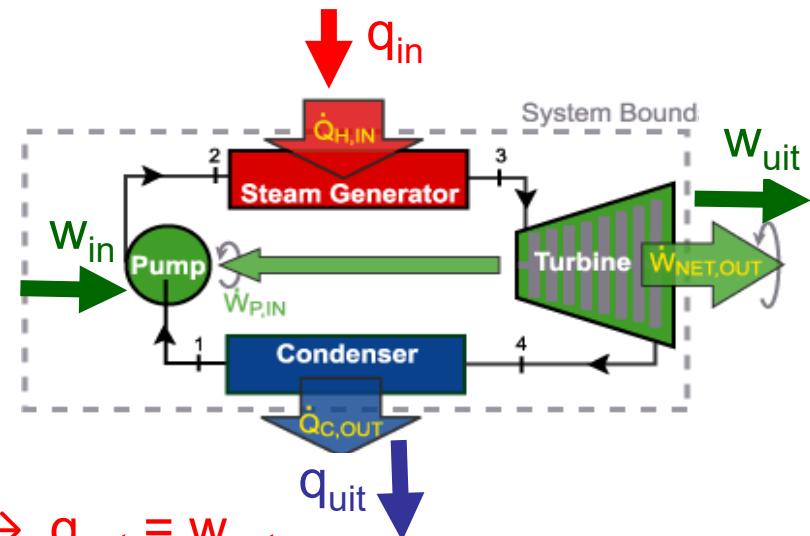
- Exergy inlet: $\Psi_{in} = h_3 - h_x = 3375 - 2100 = 1275 \text{ kJ/kg}$
- Exergy outlet: $\Psi_{out} = 0 \text{ kJ/kg}$



Exergy and second law analysis is not part of the exam, this is material for the project

Example: Rankine Cycle, check 1st & 2nd law

- Consider the steam cycle
- Energies in and out
 - $w_{in} = 1 \text{ kJ/kg}$
 - $q_{in} = 3182 \text{ kJ/kg}$ at $T_{in} = 311^\circ\text{C}$
 - $w_{out} = 1000 \text{ kJ/kg}$
 - $q_{out} = 2183 \text{ kJ/kg}$ at $T_{uit} = 45^\circ\text{C}$



- Check the first law: $q_{in} - q_{out} = w_{out} - w_{in} \rightarrow q_{net} = w_{net}$

$$\left. \begin{aligned} q_{net} &= q_{in} - q_{out} = 3182 - 2183 = 999 \text{ kJ/kg} \\ w_{net} &= w_{out} - w_{in} = 1000 - 1 = 999 \text{ kJ/kg} \end{aligned} \right\} \rightarrow q_{net} = w_{net} \text{ Correct !}$$

- Check the second law: $\sum_{i=1}^n \frac{q_{net,i}}{T_i} \leq 0$ (Clausius inequality: $\frac{\delta q_{net}}{T} \leq ds$)

$$\sum_{i=1}^n \frac{q_{net,i}}{T_i} = \underbrace{\frac{q_{in}}{T_{in}} - \frac{q_{out}}{T_{out}}}_{ds_{in} - ds_{out}} = \frac{3185}{584} - \frac{2183}{318} = 5.45 - 6.86 = -1.41 \text{ kJ/kgK} \leq 0 \text{ kJ/kgK} \rightarrow \text{Right !}$$

- Both laws are valid for this cycle 1: energy is conserved ($e_{in} = e_{out}$)
2: entropy is created ($ds_{out} > ds_{in}$)

Recapitulate class 7

- **Vapor power cycles (Rankine cycles):** cycles using a working fluid that changes phase throughout the cycle

- Piston steam engine & steam turbine
- Ideal and real Rankine cycles

- Heat and power in- and output:

$$w_{pump,in} = v(P_{out} - P_{in}) = v(P_2 - P_1)$$

$$q_{in,boiler} = h_{out} - h_{in} = h_3 - h_2$$

$$w_{out,turbine} = h_{in} - h_{iut} = h_3 - h_4$$

$$q_{out,condenser} = h_{in} - h_{out} = h_4 - h_1$$

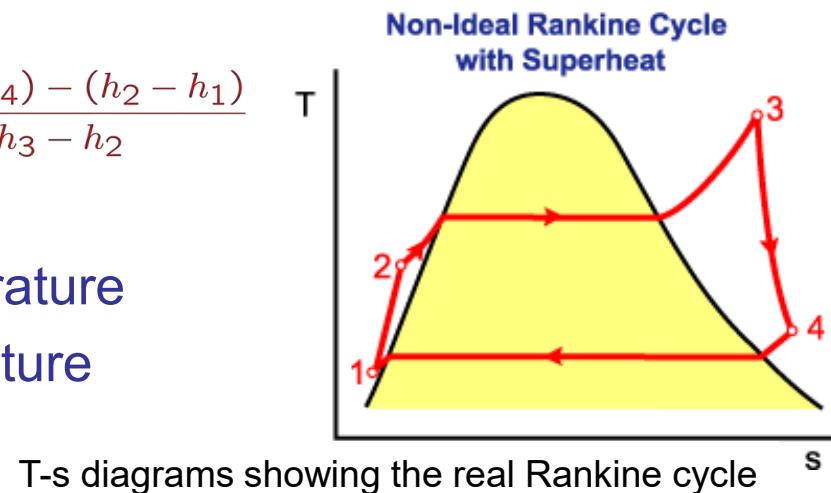
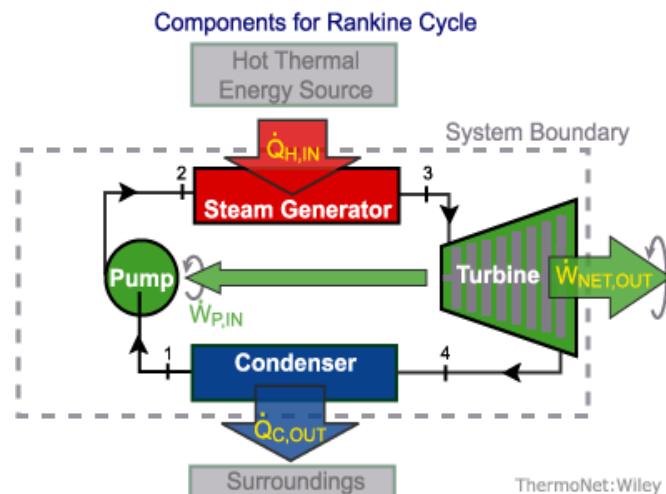
$$w_{net} = w_{out,turbine} - w_{pump,in} = (h_3 - h_4) - (h_2 - h_1)$$

- Thermal efficiency:

$$\eta_{Rankine} = \frac{w_{turbine,out} - w_{pump,in}}{q_{in,boiler}} = \frac{w_{net,out}}{q_{in,boiler}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$

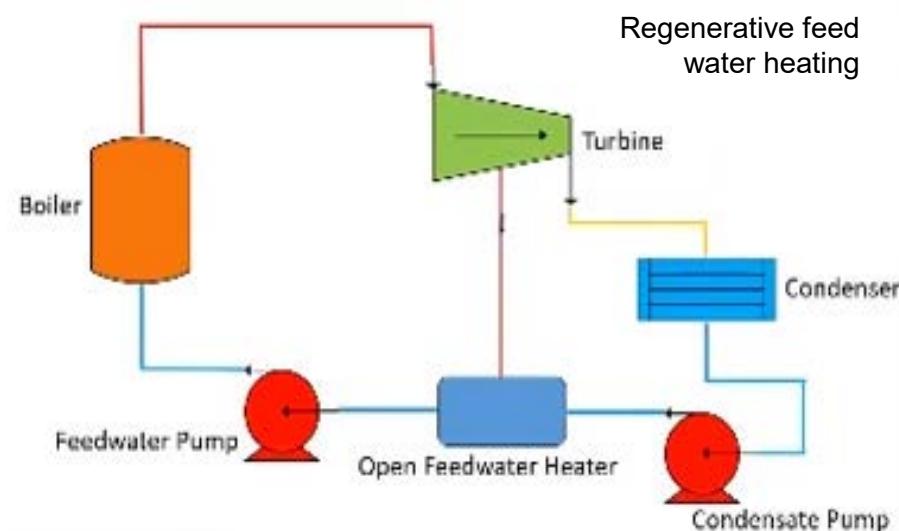
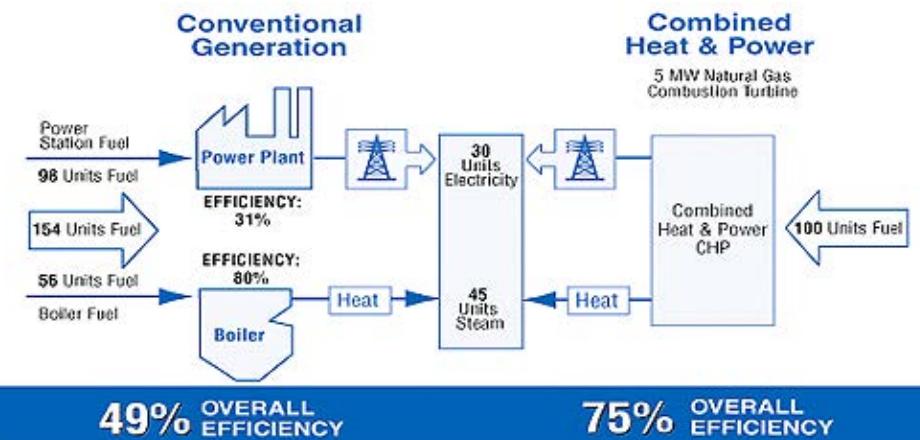
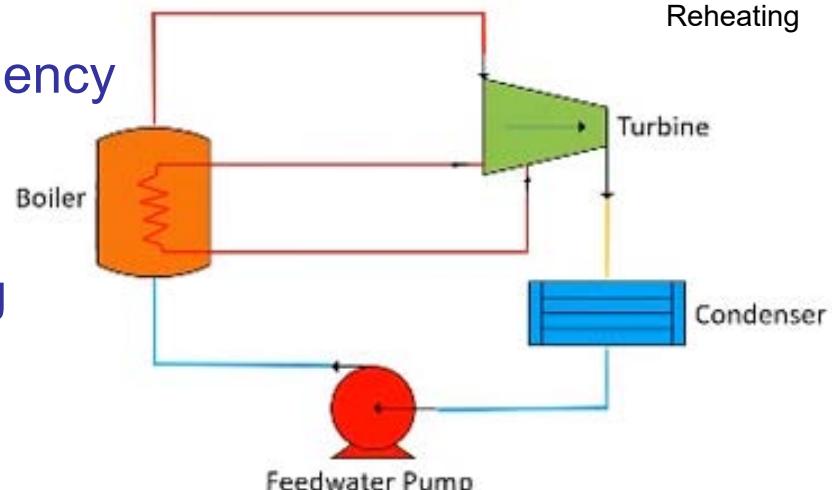
- Design parameters

- Turbine inlet pressure and temperature
- Condenser pressure and temperature
- Mollier diagram for water



Next class 8: Vapor Power Cycles - Advanced

- Designing a simple Rankine cycle
- Adding extra devices → improves efficiency
 - Extra heater → reheating
 - Open & closed feedwater heater
→ regenerative feedwater heating
- Combined heat & power generation
- Examples of real power plants

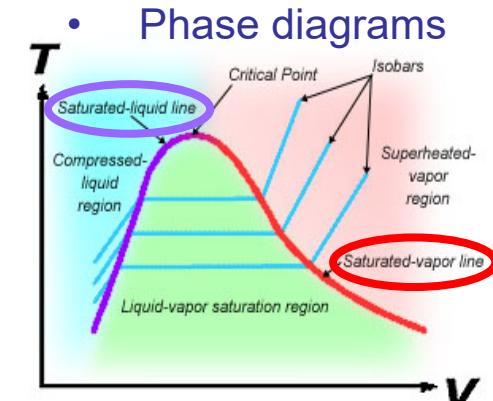


Combined heat and power reduces the energy loss

Types or Rankine cycles
<https://www.youtube.com/watch?v=QFZN71MY71o&t=1s>

Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal 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 $du = \delta q - \delta w \rightarrow \Delta u = q - w$
 - 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 $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)
- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdP$
- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$
- Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$
- Coefficient of performance $(COP)_{HP} = \frac{q_{HOT,OUT}}{w_{IN}}$ and $(COP)_{REF} = \frac{q_{COLD,IN}}{w_{IN}}$



Class 8

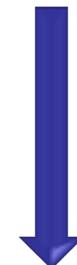
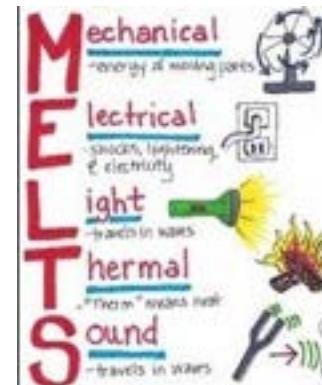
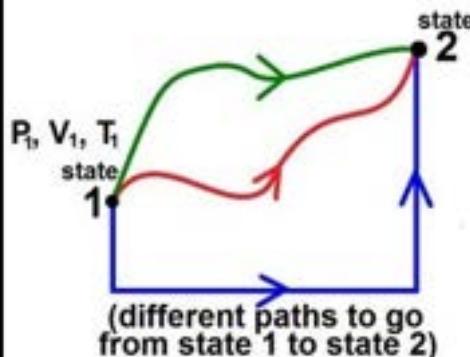
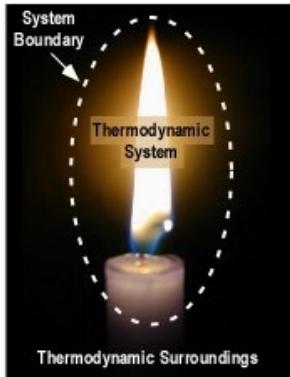
Vapor power cycles, advanced

Steam rising from the Nesjavellir geothermal power station, the largest geothermal power plant in Iceland. It uses geothermal energy that has absorbed inside the earth's magma.

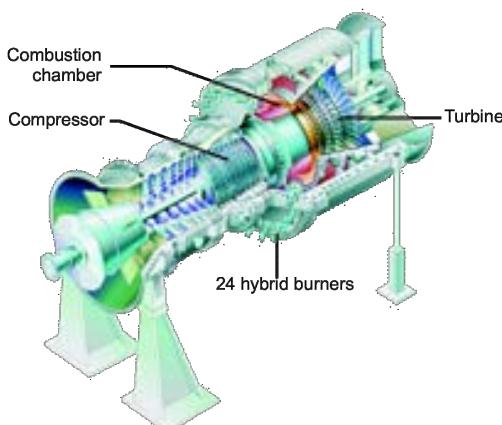


Roadmap Engineering Thermodynamics

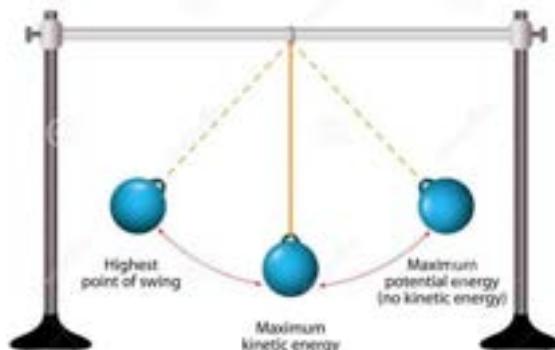
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



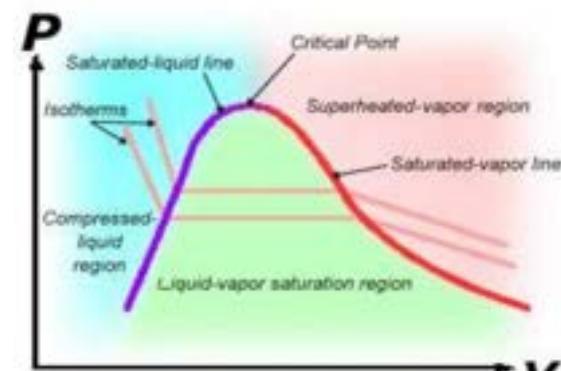
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

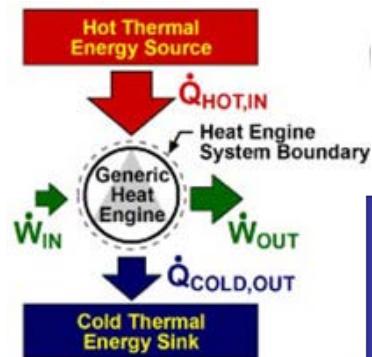


- Properties of Substances (Class 3, 9)

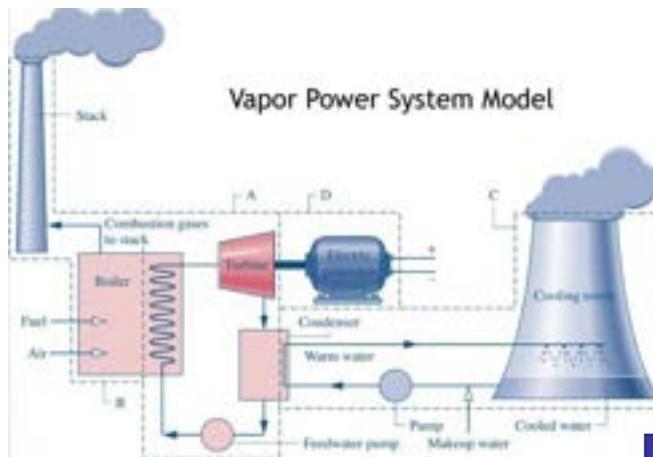


Roadmap Engineering Thermodynamics

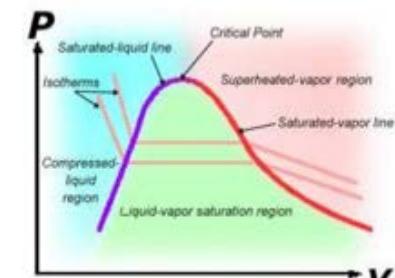
Thermodynamic cycles (Class 6)



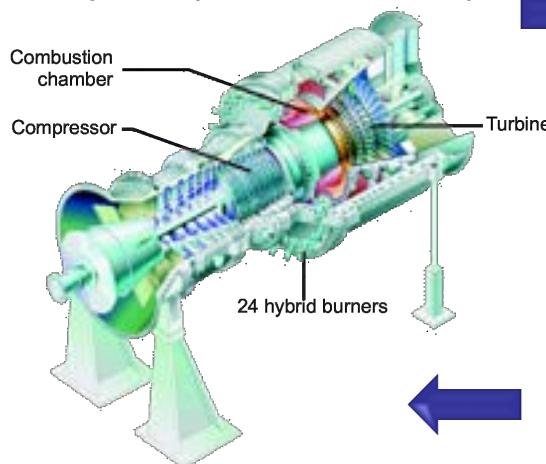
Vapor power cycles – Rankine cycle (Class 7, 8)



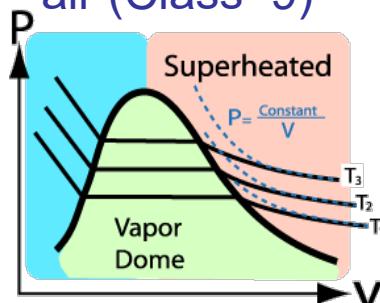
Properties of water (Class 3)



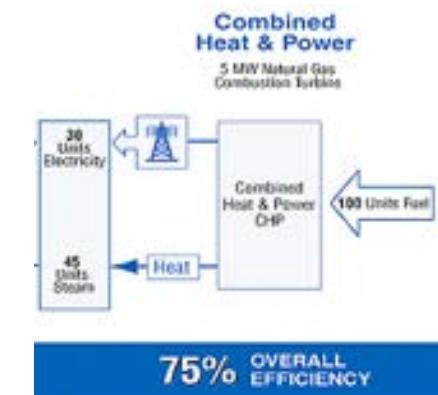
Gas power cycles – Brayton cycle (Class 10, 11)



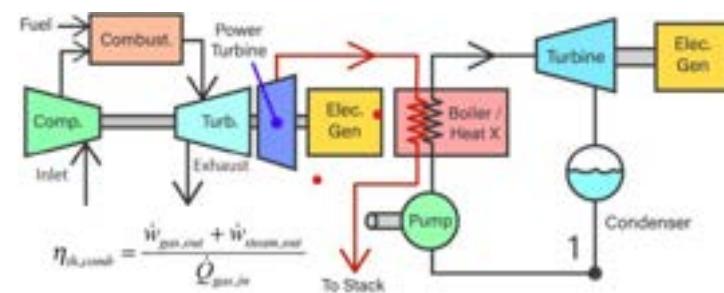
Properties of air (Class 9)



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



75% OVERALL EFFICIENCY



Recapitulate Class 7

- **Vapor power cycles (Rankine cycles):** cycles using a working fluid that changes phase throughout the cycle

- Piston steam engine & steam turbine
- Ideal and real Rankine cycles

- Heat and power in- and output:

$$w_{pump,in} = v(P_{out} - P_{in}) = v(P_2 - P_1)$$

$$q_{in,boiler} = h_{out} - h_{in} = h_3 - h_2$$

$$w_{out,turbine} = h_{in} - h_{iut} = h_3 - h_4$$

$$q_{out,condenser} = h_{in} - h_{out} = h_4 - h_1$$

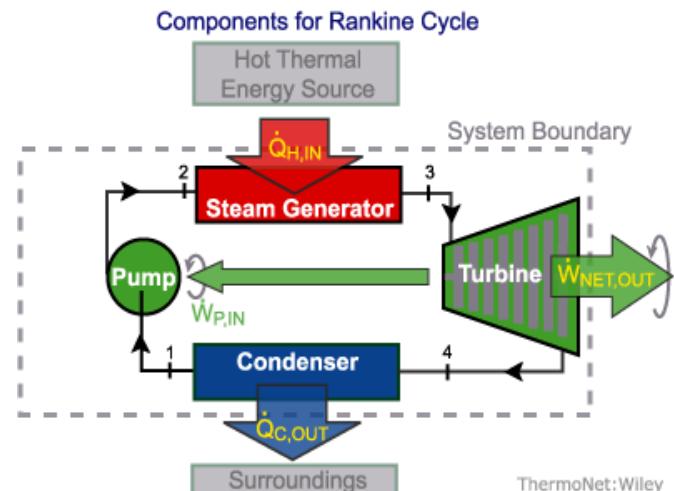
$$w_{net} = w_{out,turbine} - w_{pump,in} = (h_3 - h_4) - (h_2 - h_1)$$

- Thermal efficiency:

$$\eta_{Rankine} = \frac{w_{turbine,out} - w_{pump,in}}{q_{in,boiler}} = \frac{w_{net,out}}{q_{in,boiler}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$

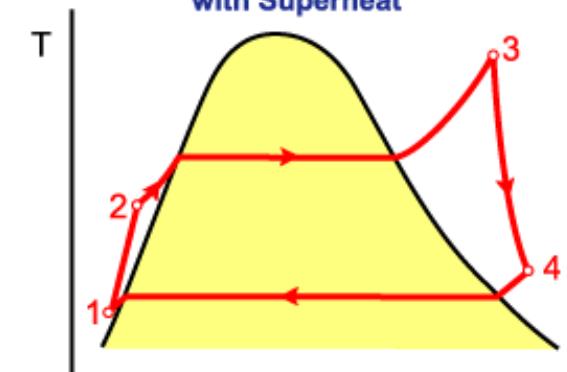
- Design parameters

- Turbine inlet pressure and temperature
- Condenser pressure and temperature
- Mollier diagram for water



ThermoNet:Wiley

Non-Ideal Rankine Cycle with Superheat



T-s diagrams showing the real Rankine cycle

Content Class 8

- Vapor power cycles – Rankine cycles, advanced
- Designing a simple Rankine cycle
- Adding extra devices → improves efficiency
 - Extra heater → reheating
 - Open & closed feedwater heater → regenerative feedwater heating
- Combined heat & power generation
- Examples of real power plants



Reheat steam turbine

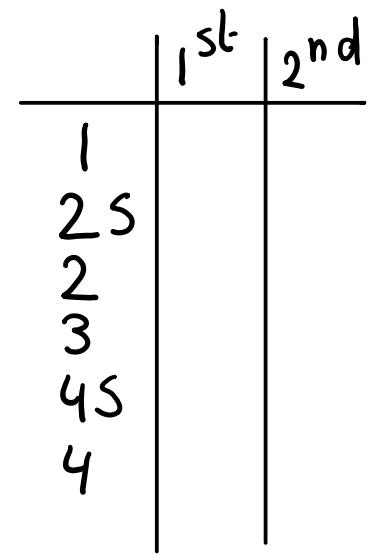
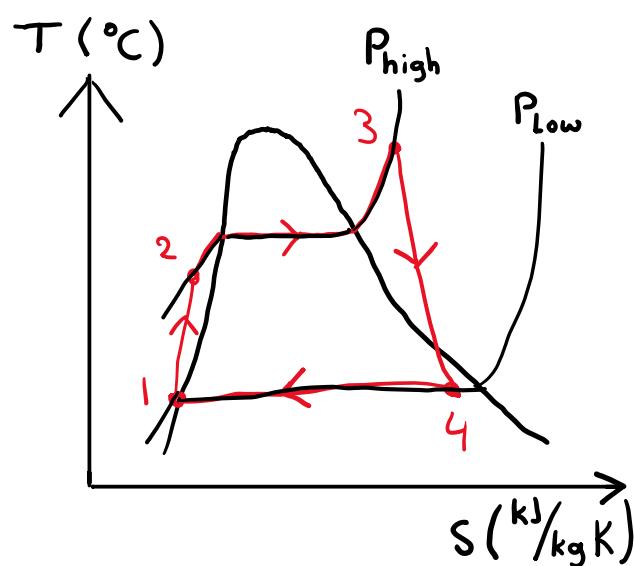
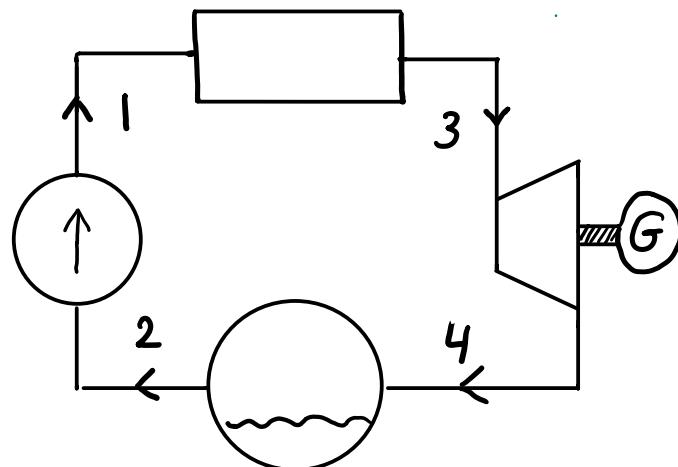
Feedwater heater tubes



- Learning goal: recognize a **complicated** thermodynamic system to produce work, explain the configuration, analyse the thermodynamic aspects from the viewpoint of the first law of thermodynamics, interpret and evaluate the results and suggest improvements

How to design a simple Rankine power cycle

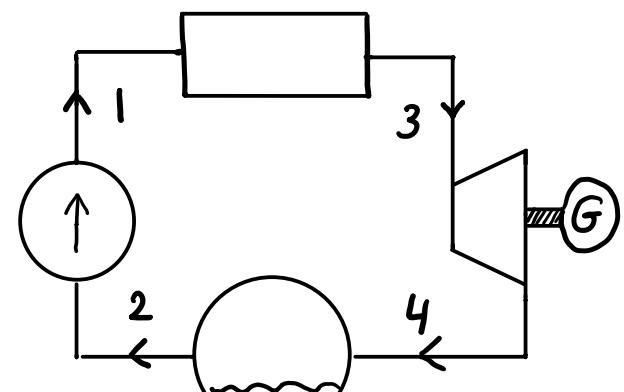
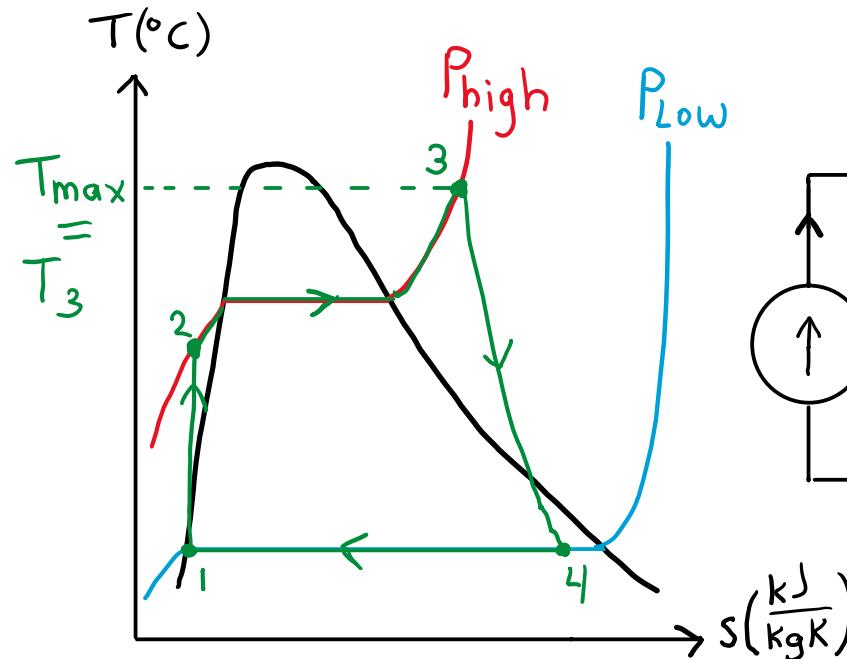
- In class 7 we learned how a vapor power cycle looks like, how it works and how to analyse the cycle
- The next step is to design your own cycle for a given power requirement
- How do you do that?
- The simple Rankine cycle consists of four components: pump, boiler or heat exchanger, turbine and condenser
- Draw the flow diagram with the 4 components and sketch a Ts - diagram
- Make a table and determine 2 properties needed to find the energies (h-values) for every point



How to design a simple Rankine power cycle

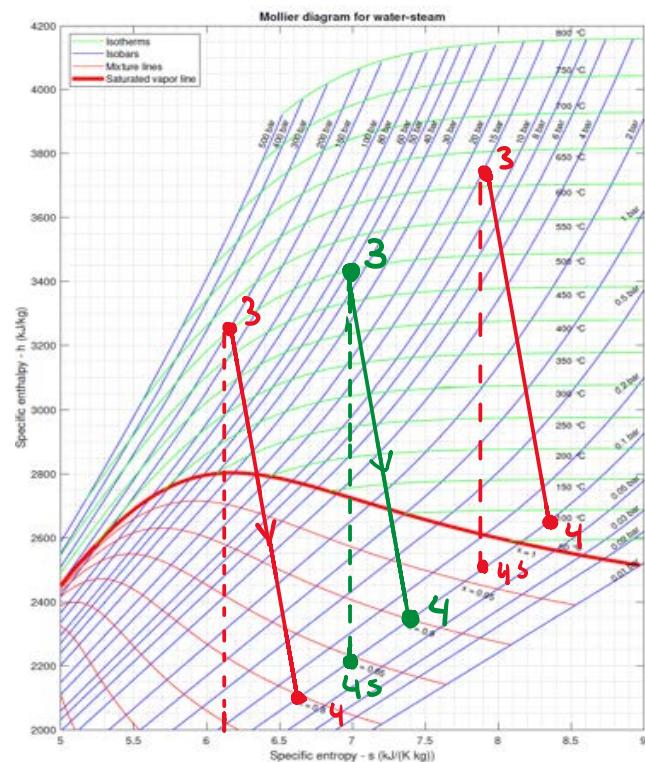
- For the two properties it is common to choose / assume
 - Isentropic efficiencies for the pump and the turbine (point 2 and 4)
 - A high pressure for the cycle (point 2 and 3)
 - A low pressure for the cycle (point 1 and 4)
 - A maximum temperature in the cycle (at the turbine inlet, point 3)
 - Saturated liquid at the condenser outlet (point 1)
- Add data to the table and the Ts - diagram

	1 st	2 nd
1	P_L	$x = 0$
2S	P_H	$S_{2S} = S_1$
2	P_H	$\eta_{s,p}$
3	P_H	T_{max}
4S	P_L	$S_{4S} = S_3$
4	P_L	$\eta_{s,t}$



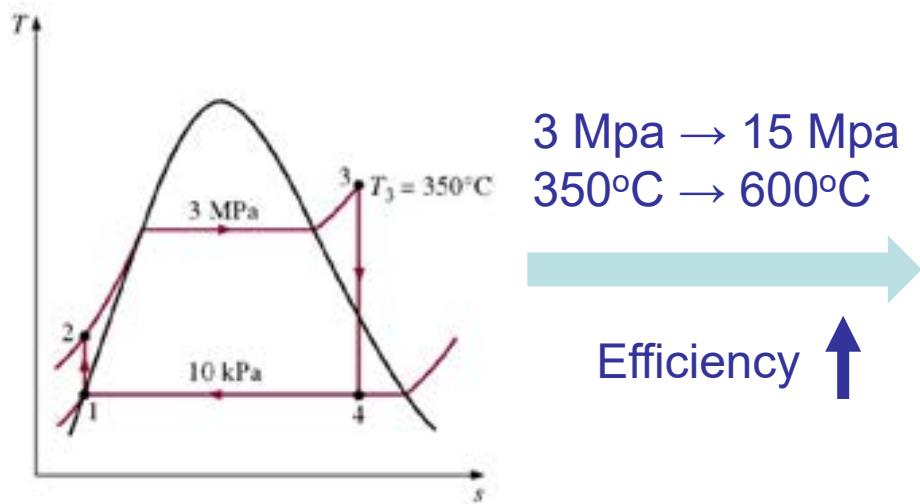
How to design a simple Rankine power cycle

- Isentropic efficiencies depend on how good the pump and the turbine are manufactured, cannot be changed they come with the device and are in the order of 70 to 90%
- The low pressure should be such that the temperature in the condenser is higher than the temperature of the environment to which the heat of the condensation process is rejected (note: the pressure in the condenser determines the temperature, saturation P & T)
- The combination of the pressures and the turbine inlet temperature should be such that the quality of the fluid at the turbine outlet is acceptable
- This can be trial and error but sketching in a hs - diagram makes it much easier to see
- The line 3 – 4 can be shifted left – right
- The green line is a good combination of P & T, the red ones are less good as the quality at the outlet is too low or T is too high



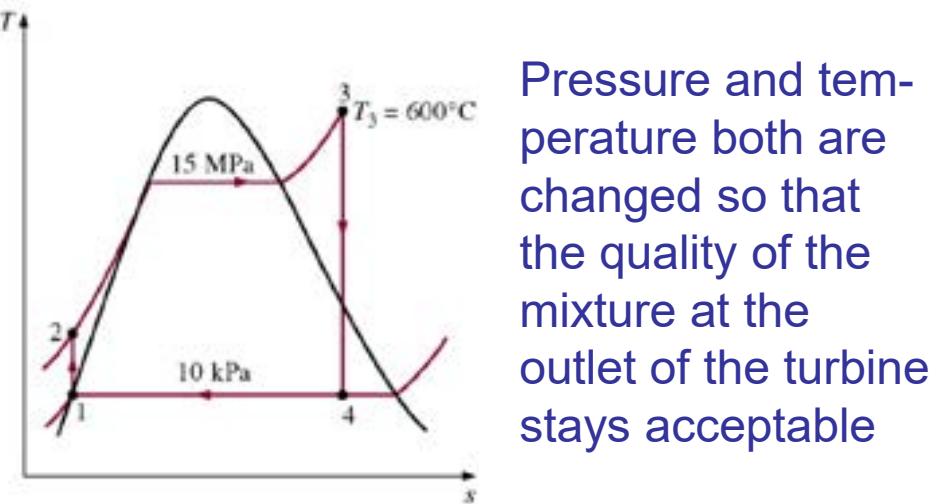
How to design a simple Rankine power cycle

- Choosing the turbine inlet temperature and the low and high pressures is the most challenging part
- You can use these parameters to optimize the output and / or the efficiency
- We have seen (class 7) that the efficiency of the simple cycle can be improved by
 - Increasing the turbine inlet pressure
 - Increasing the turbine inlet temperature
 - Decreasing the condenser temperature / pressure



3 Mpa → 15 Mpa
350°C → 600°C

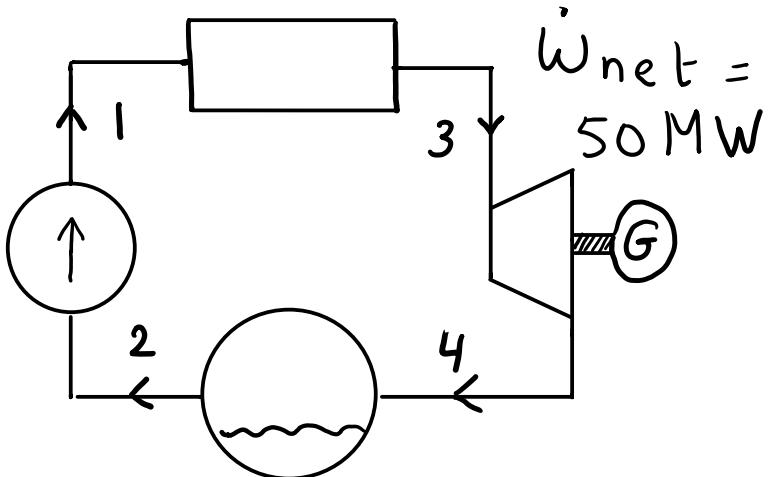
Efficiency ↑



Pressure and temperature both are changed so that the quality of the mixture at the outlet of the turbine stays acceptable

How to design a simple Rankine power cycle

- Example: design a cycle that delivers 50 MW net power output
- Isentropic efficiencies are assumed to be 80%
- Low pressure is 0.1 bar = 100 kPa, saturation temperature for 100 kPa is 45 degrees C, this is high enough to be able to transfer the heat of the condensation process to the environment (assumed to be 20 degree C)
- High pressure is 50 bar = 5000 kPa
- Turbine inlet temperature is 500 Degree C
- Put a values in the table and check if you have two properties for every point



	first	second
1	$P = 10 \text{ kPa}$	$x = 0$
2S	$P = 5 \text{ MPa}$	$S_{2S} = S$
2	$P = 5 \text{ MPa}$	$\eta_p = 80\%$
3	$P = 5 \text{ MPa}$	$T = 500^\circ\text{C}$
4S	$P = 10 \text{ kPa}$	$S_{4S} = S_3$
4	$P = 10 \text{ kPa}$	$\eta_t = 80\%$

How to design a simple Rankine power cycle

- Next step is to determine the enthalpy, h-values for every point

Point 1: $x_1=0, P_1=10\text{ kPa}$: table A5, $h_1=191.8 \frac{\text{kJ}}{\text{kg}}$

Point 2s: $s \& v$ constant $\rightarrow dh = Tds + vdP$, $h_{2s} - h_1 = v(P_{2s} - P_1) = 191.8 + 0.001(5000 - 10)$

$$h_{2s} = 196.8 \frac{\text{kJ}}{\text{kg}}$$

Point 2: $\eta_{s,p} = \frac{h_{2s} - h_1}{h_2 - h_1} \rightarrow h_2 = h_1 + \frac{h_{2s} - h_1}{\eta_{s,p}}$
 $h_2 = 198.0 \frac{\text{kJ}}{\text{kg}}$

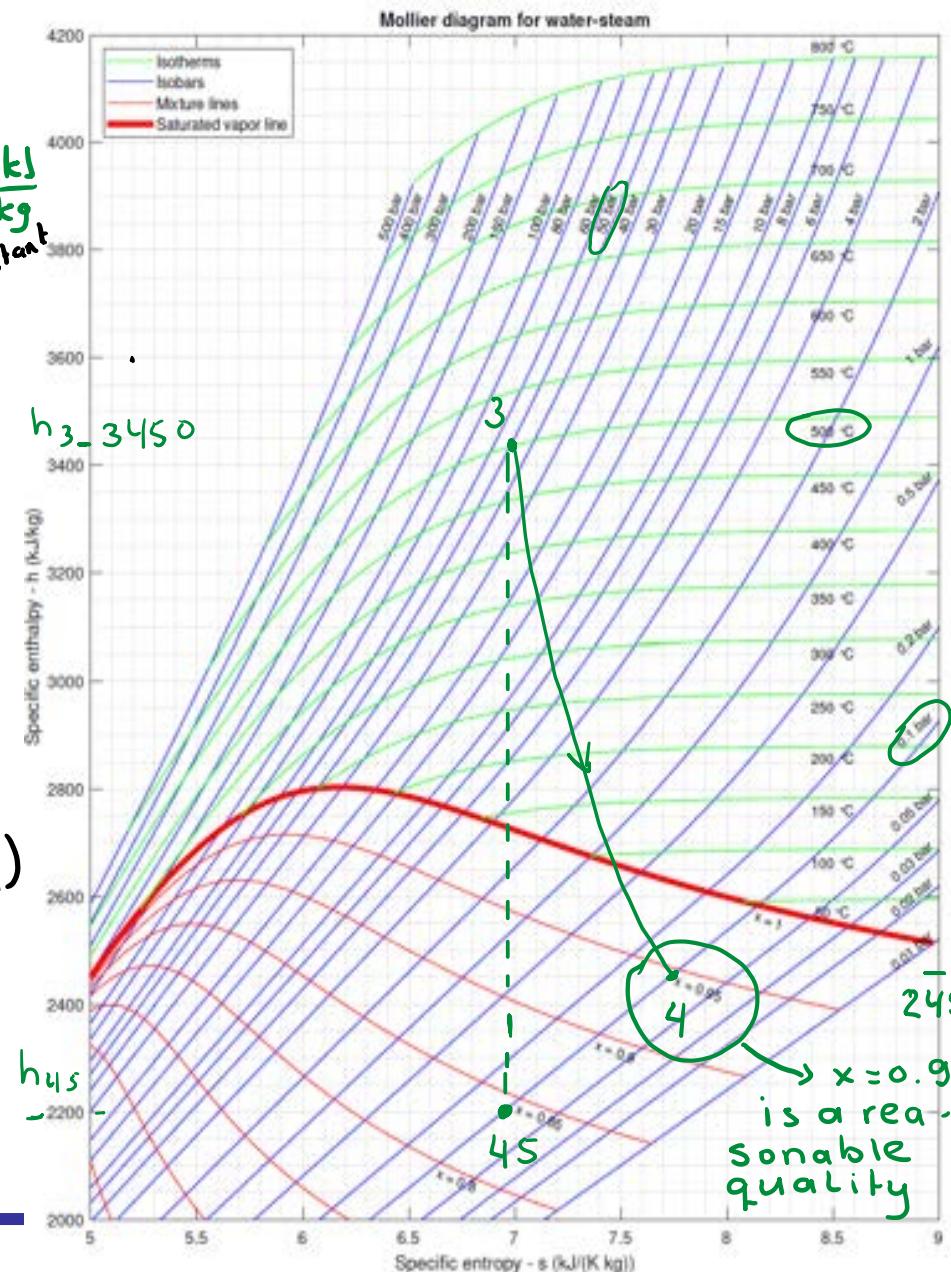
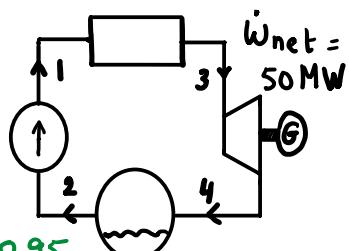
Point 3: Mollier diagram $\rightarrow h_3 = 3450 \frac{\text{kJ}}{\text{kg}}$

Point 4s: Same entropy as 3, vertical below 3 on Mollier diagram on the 10 kPa isobar $h_{4s} = 2200 \frac{\text{kJ}}{\text{kg}}$

Point 4: $\eta_{s,t} = \frac{h_3 - h_4}{h_3 - h_{4s}} \rightarrow h_4 = h_3 - \eta_{s,t}(h_3 - h_{4s})$

$$h_4 = 2450 \frac{\text{kJ}}{\text{kg}}$$

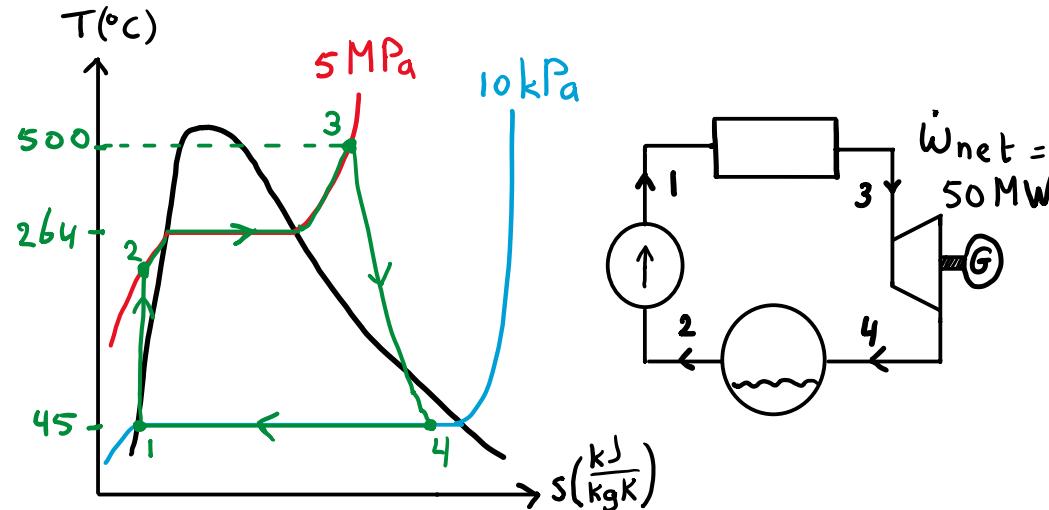
Add point 4 to the Mollier diagram, check if the entropy increases and check the quality at the turbine exit $\rightarrow 0.95$



How to design a simple Rankine power cycle

- Add the h-values to the table and complete the Ts-diagram

	First property	Second property	$h(\frac{kJ}{kg})$
1	$P_1 = 10kPa$	$x_1 = 0$	191.8
2s	$P_{2s} = 5MPa$	$s_{2s} = s_1$	196.8
2	$P_2 = 5MPa$	$\eta_{s,p} = 80\%$	198.0
3	$P_3 = 5MPa$	$T_3 = 500^\circ C$	3450
4s	$P_{4s} = 10kPa$	$s_{4s} = s_3$	2200
4	$P_4 = 10kPa$	$\eta_{s,t} = 80\%$	2450



- Analyse the cycle

Specific work/heat in/outputs

$$w_{in} = h_2 - h_1 = 6 \frac{kJ}{kg}$$

$$w_{out} = h_4 - h_3 = 1000 \frac{kJ}{kg}$$

$$q_{in} = h_3 - h_2 = 3250 \frac{kJ}{kg}$$

$$q_{out} = h_4 - h_1 = 2258 \frac{kJ}{kg}$$

$$w_{net} = w_{out} - w_{in}$$

$$w_{net} = 994 \frac{kJ}{kg}$$

Net power output should be 50 MW

$$\dot{W}_{net} = \dot{m} w_{net} \rightarrow \dot{m} = \frac{\dot{W}_{net}}{w_{net}} = \frac{50000}{994}$$

$$\dot{m} = 50.3 \frac{kg}{s}$$

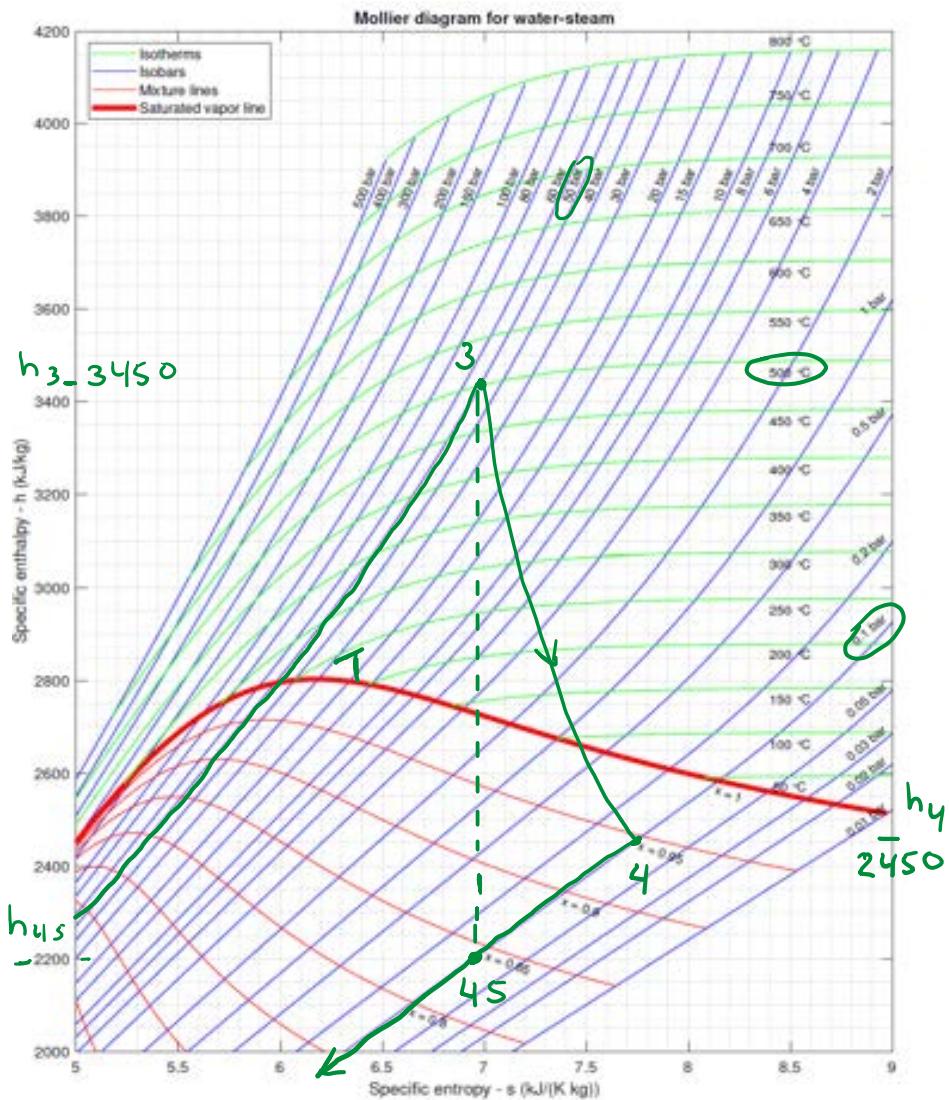
$$\text{Thermal efficiency : } \eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{m} w_{net}}{\dot{m} q_{in}}$$

$$\eta_{th} = 0.306 \rightarrow 31\%$$

$$\text{Total heat input} \rightarrow \dot{Q}_{in} = \dot{m} \cdot q_{in} = 163.5 \text{ MW}$$

How to design a simple Rankine power cycle

- Discussion of the results
- Net power output is 50 MW
- Mass flow is 50.3 kg/s
- Total power input is 163.5 MW
- Thermal efficiency is 31%
- The cycle meets the requirements
- 31% efficiency is good for a simple Rankine cycle so this seems to be a good design
- If you program the cycle in Matlab you can try different combinations of pressures and temperatures to optimize the cycle
- Realize that the power output can easily be changed by adjusting the mass flow, 100 kg/s gives 99.4 MW



- We designed the cycle!

Increasing the Rankine Cycle Performance

- The efficiency of a simple Rankine cycle is not very high
- It can be optimized by playing with the turbine inlet temperature and the pressures
- However the efficiency can be improved further by adding extra devices
- Means to **improve the efficiency of the simple Rankine cycle** are the use of
 - Extra heaters → reheating
 - Open & closed feedwater heaters → regenerative feed water heating



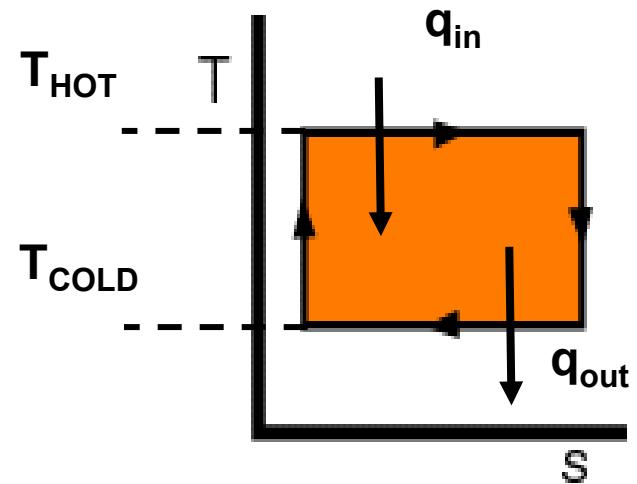
- The idea behind these improvements is to higher the average temperature at which heat is added, why ?

Increasing the Rankine Cycle Performance

- Why do we want a higher average temperature for adding heat?
- Recapitulate Carnot engine, ideal engine with the highest possible efficiency
- This is achieved by adding the heat isothermal and isentropic pressure increase and decrease
- The efficiency is determined by the highest and lowest temperature
- The larger the temperature difference the higher the efficiency

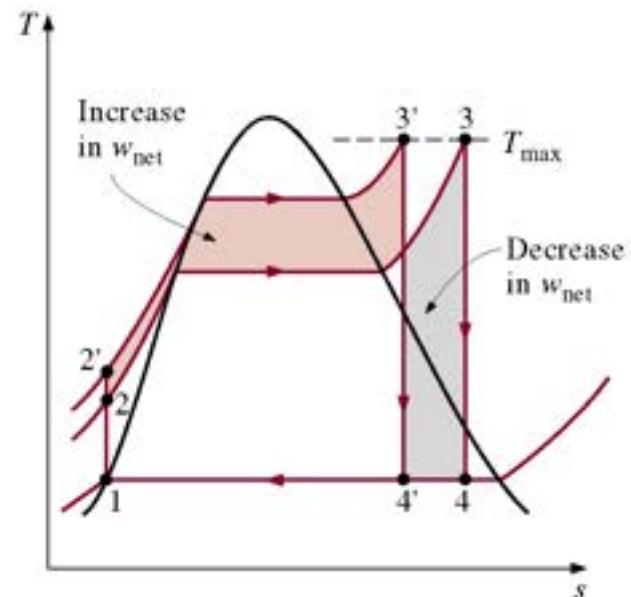
$$\rightarrow \text{Carnot efficiency} = 1 - \frac{T_{COLD}}{T_{HOT}}$$

- Therefore the higher the average temperature at which the heat is added the higher the efficiency



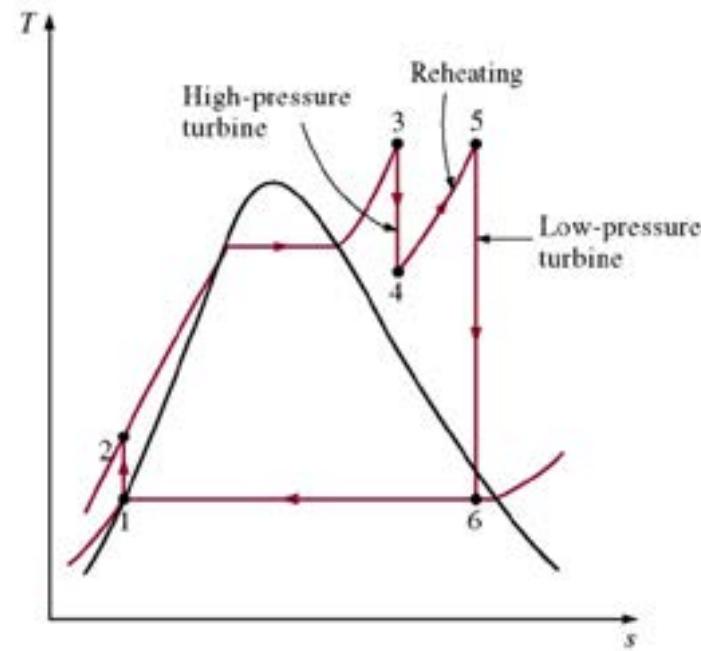
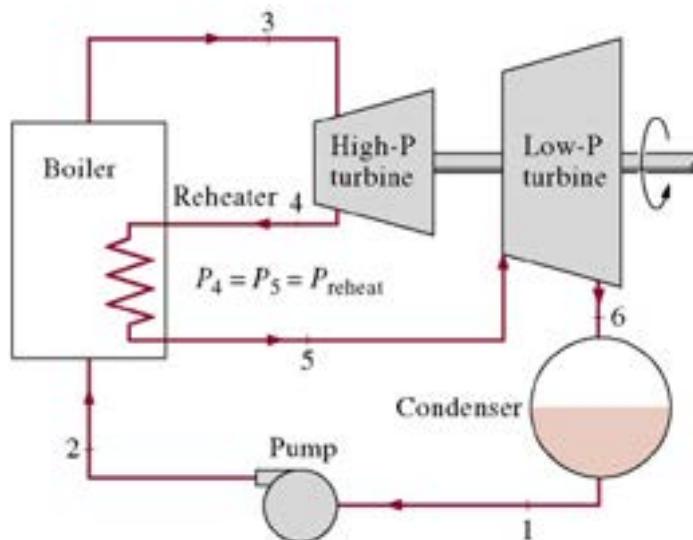
Improvement Rankine Cycle: Reheating

- A higher boiler pressure increases the efficiency of a Rankine cycle as the heat on average is added at a higher temperature ($3 \rightarrow 3'$)
- However the moisture content in the turbine outlet increases to unacceptable levels ($4 \rightarrow 4'$)
- How can we take advantage of the increased efficiencies at higher boiler pressures without facing the problem of excessive moisture content at the final stage of the turbine?
 - Superheat the steam to higher temperatures, however the temperature is limited by the material properties of the boiler and turbine, T_{\max} around 620°C (important which material to choose)
 - **Reheating**



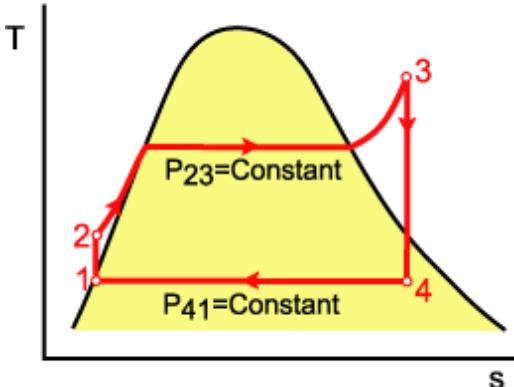
Improvement Rankine Cycle: Reheating

- For reheating a second turbine is added and the expansion process takes place in two steps
 - The steam is expanded to an intermediate pressure and sent back to the boiler (the optimum reheat pressure is about one-fourth of the maximum)
 - It is reheated at constant pressure usually to the inlet temperature of the first turbine
 - Steam expands in the second stage to the condenser pressure

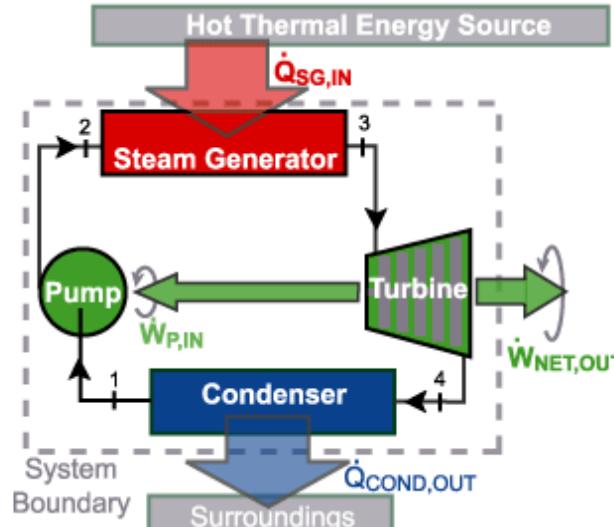


Improvement Rankine Cycle: Reheating

- Without reheat

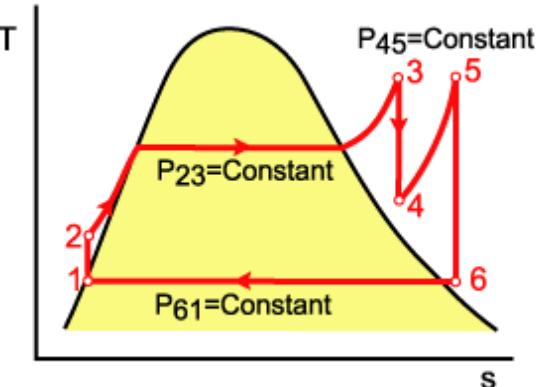


ThermoNet: Wiley

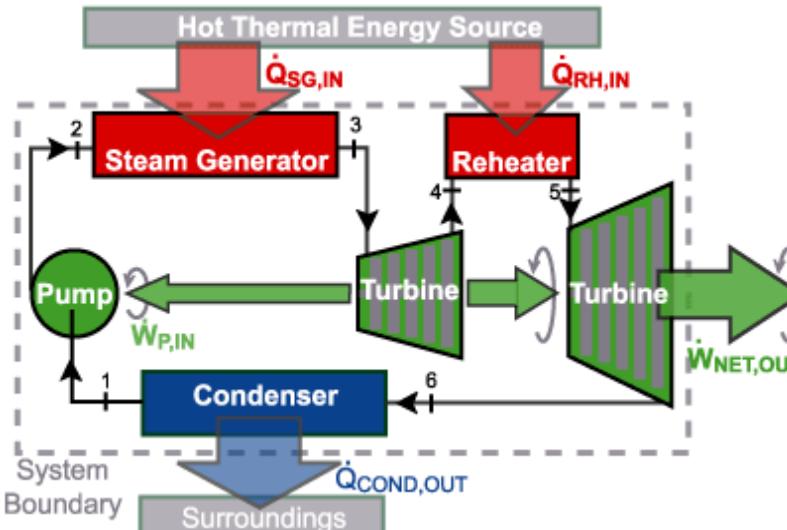


- The efficiency of a Rankine cycle can be improved by reheating as the heat is added to the steam at a higher average temperature

- With reheat



ThermoNet: Wiley



- Reheating decreases the liquid fraction in the turbine → better reliability

Improvement Rankine Cycle: Reheating

- The total heat input is the sum of the heat input in the steam generator and the reheat

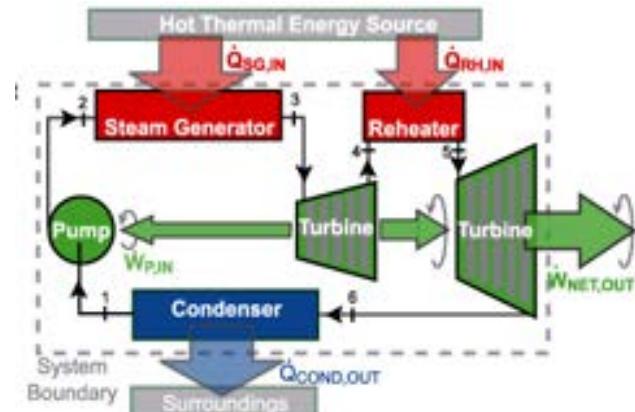
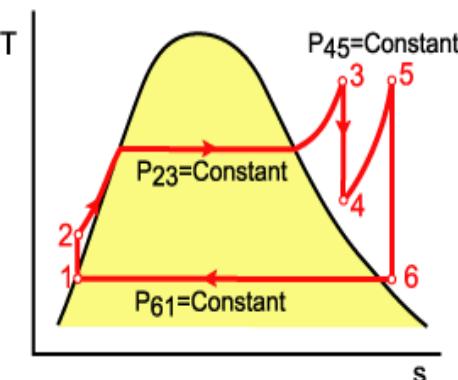
$$\begin{aligned}q_{in,\text{total}} &= q_{in,\text{sg}} + q_{in,\text{rh}} \\&= (h_3 - h_2) + (h_5 - h_4)\end{aligned}$$

- The total work produced is the sum of the work of both turbines

$$W_{out,\text{total}} = W_{out,\text{turb1}} + W_{out,\text{turb2}} = (h_3 - h_4) + (h_5 - h_6)$$

- The net work output of the reheat Rankine cycle is

$$W_{net} = W_{out,\text{total}} - W_{in,\text{pump}} = (h_3 - h_4) + (h_5 - h_6) - (h_2 - h_1)$$



- The efficiency therefore becomes

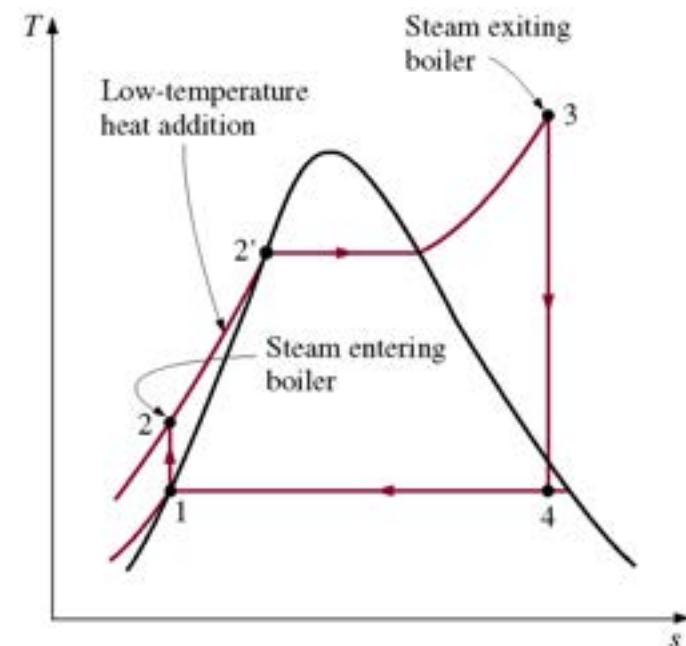
$$\eta_{RANKINE} = \frac{w_{NET,OUT}}{q_{IN}} = \frac{(h_3 - h_4) + (h_5 - h_6) - (h_2 - h_1)}{(h_3 - h_2) + (h_5 - h_4)}$$

Improvement Rankine Cycle: Feed Water Heating

- The first part of the heat-addition process in the boiler takes place at relatively low temperatures
- This lowers the average temperature at which the heat is added to the steam which decreases the efficiency

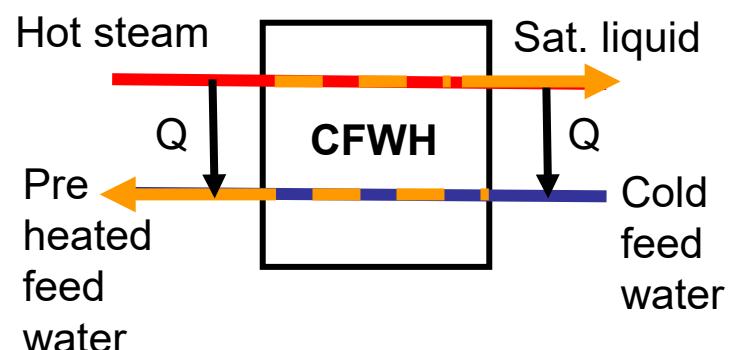
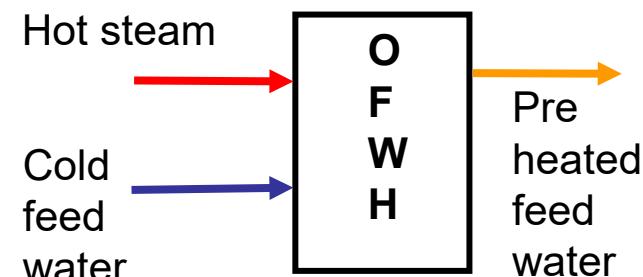
(remember Carnot: $\eta_{\text{Carnot}} = 1 - \frac{T_{\text{COLD}}}{T_{\text{HOT}}}$)

- To avoid this the liquid should leave the pump at a higher temperature
- Use a part of the steam to preheat the feed water
 - regenerative feed water heating
- The device where the feed water is heated is called a feed water heater, basically this is a heat exchanger where heat is transferred from the steam to the feed water, there are
 - open and closed feed water heaters



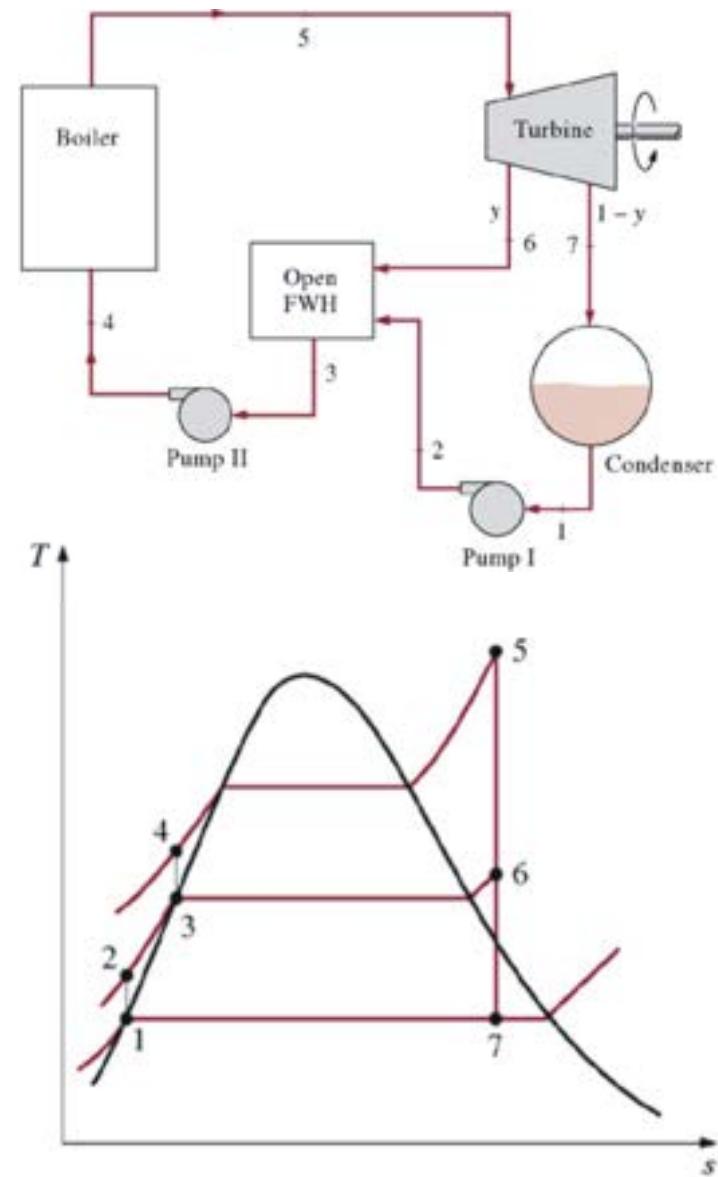
Improvement Rankine Cycle: Feed water Heating

- There are two types of feedwater heaters, open and closed
- In an open feed water heater (OFWH) heat is transferred from the steam to the feed water by mixing the two streams (this is called a mixing chamber)
- In a closed feed water heater (CFWH) heat is transferred from the steam to the feed water without mixing them but by using a closed heat exchanger



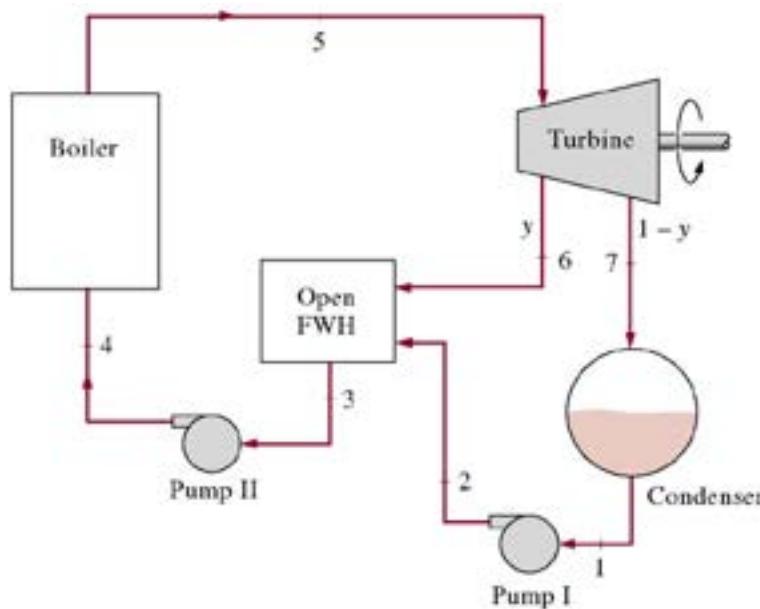
Improvement Rankine Cycle: Feed Water Heating

- Regenerative feed water heating: steam bled from turbine is used to heat feed water entering boiler
- However extracting steam from the turbine reduces the mass flow rate through
 - The lower pressure turbine stages → reduces $w_{NET,OUT}$
 - The condenser → reduces q_{OUT}
- However preheating the feed water → **reduces q_{IN}**
- The **net effect** is
 - An increase in η_{TH}
 - A reduction of $w_{NET,OUT}$

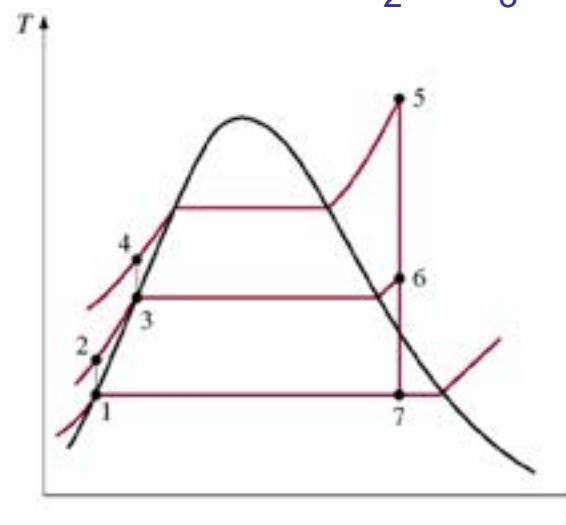


Rankine Cycle with Open Feed Water Heater

- The **open feed water heater** is a mixing chamber in which the steam extracted from the turbine mixes with the feed water exiting the first pump
- Ideally the mixture leaves the heater as a saturated liquid
 $\rightarrow h_3 = h_{\text{sat-liquid}@P3}$ (to find in table 5)
- The fraction of the steam extracted is such that the mixture leaves the open feed water heater as a saturated liquid (in the ideal situation)

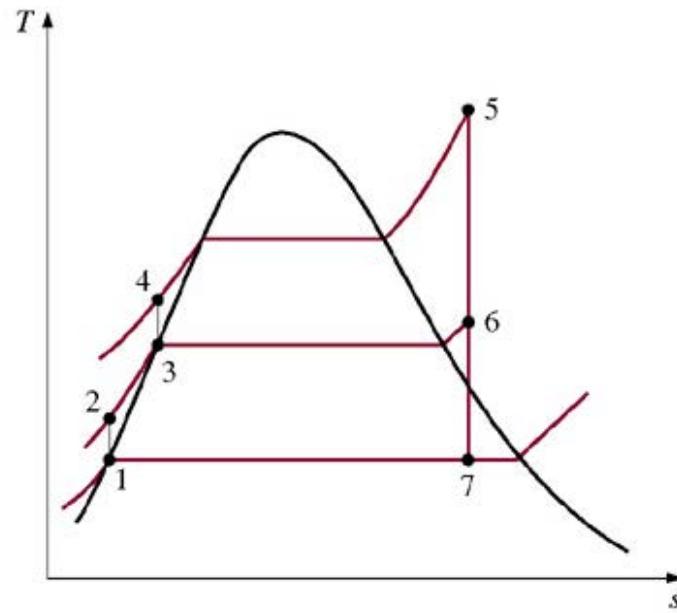
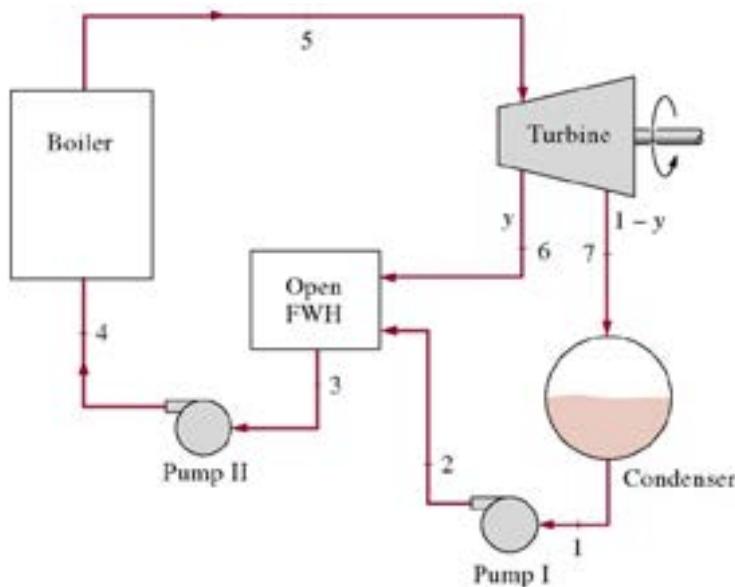


- Note $P_2 = P_3 = P_6$



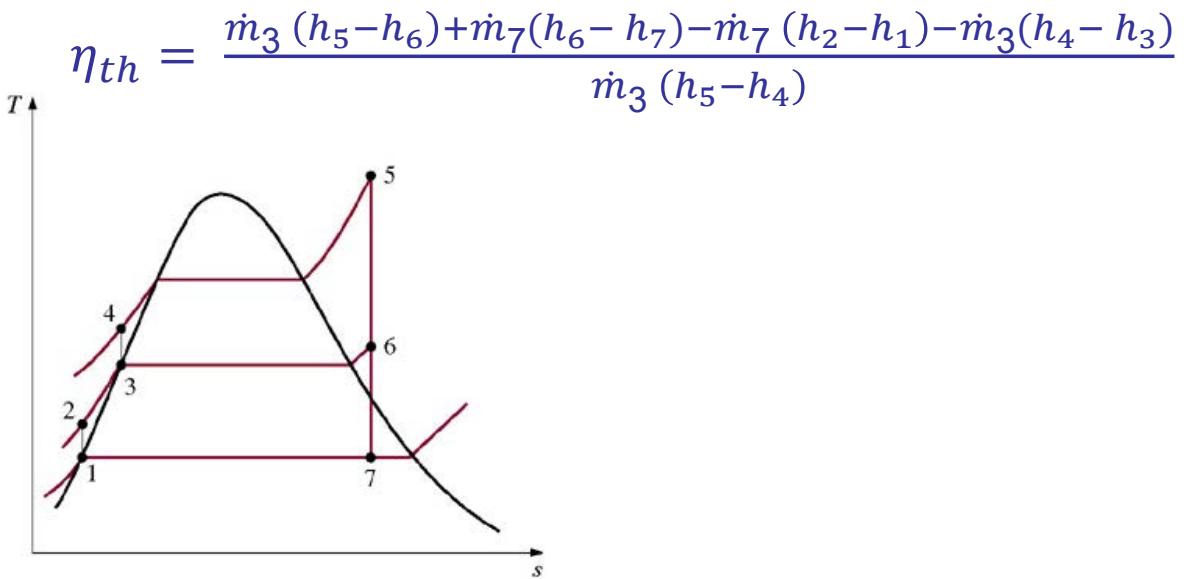
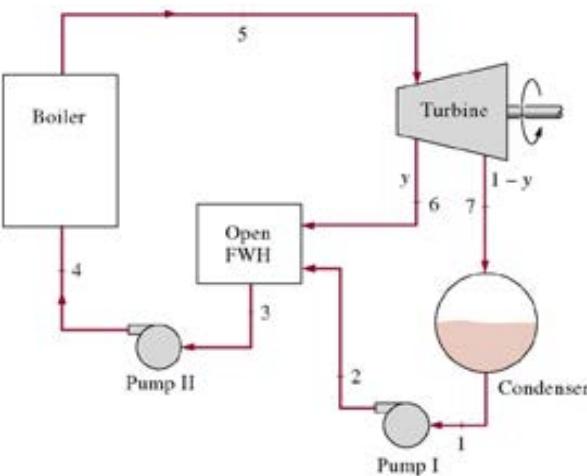
Rankine Cycle with Open Feed Water Heater

- Analyzing the Rankine cycle with an **open feed water heater**
- The mass flow changes throughout the cycle
- Three different mass flows: $\dot{m}_7 = \dot{m}_1 = \dot{m}_2$ & $\dot{m}_3 = \dot{m}_4 = \dot{m}_5 = \dot{m}_6$
- Extra relations are required
 - Mass balance mixing chamber: $\dot{m}_6 + \dot{m}_2 = \dot{m}_3$
 - Energy balance mixing chamber: $\dot{m}_6 h_6 + \dot{m}_2 h_2 = \dot{m}_3 h_3$



Rankine Cycle with Open Feed Water Heater

- Three different mass flows: $\dot{m}_7 = \dot{m}_1 = \dot{m}_2$ and $\dot{m}_3 = \dot{m}_4 = \dot{m}_5$ and \dot{m}_6
- Mass balance mixing chamber: $\dot{m}_6 + \dot{m}_2 = \dot{m}_3$
- Energy balance mixing chamber: $\dot{m}_6 h_6 + \dot{m}_2 h_2 = \dot{m}_3 h_3$
 - Power heat in- and output: $\dot{Q}_{in} = \dot{m}_3 (h_5 - h_4)$ and $\dot{Q}_{out} = \dot{m}_7 (h_7 - h_1)$
 - Power work output: $\dot{W}_{out} = \dot{m}_3 (h_5 - h_6) + \dot{m}_7 (h_6 - h_7)$
 - Power work input: $\dot{W}_{in} = \dot{m}_7 (h_2 - h_1) + \dot{m}_3 (h_4 - h_3)$
- Thermal efficiency: $\eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_{out} - \dot{W}_{in}}{\dot{Q}_{in}} =$



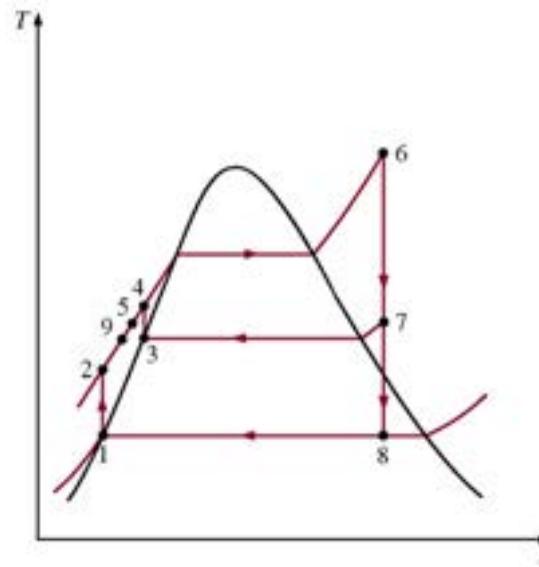
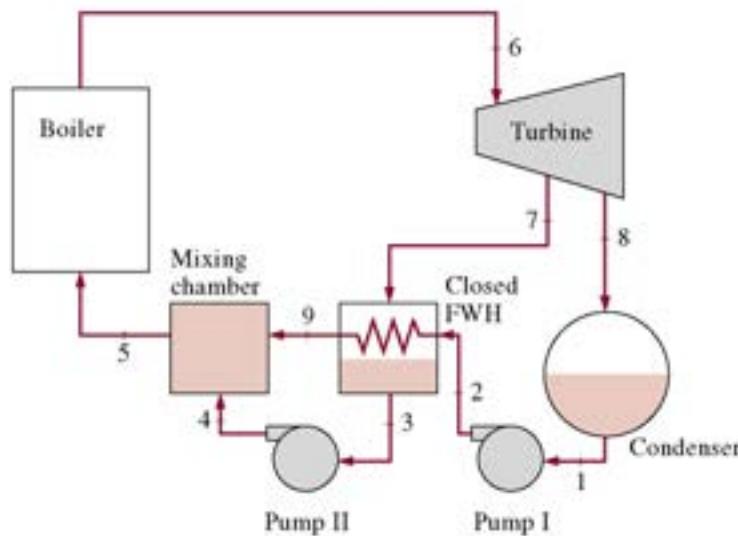
BREAK



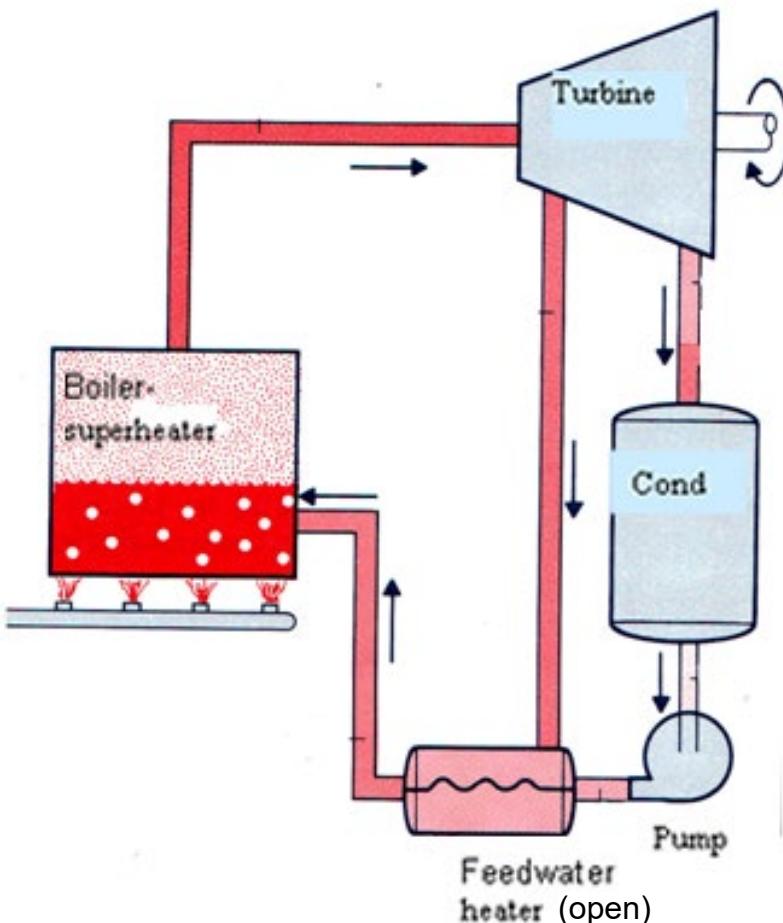
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Rankine Cycle with Closed Feed Water Heater

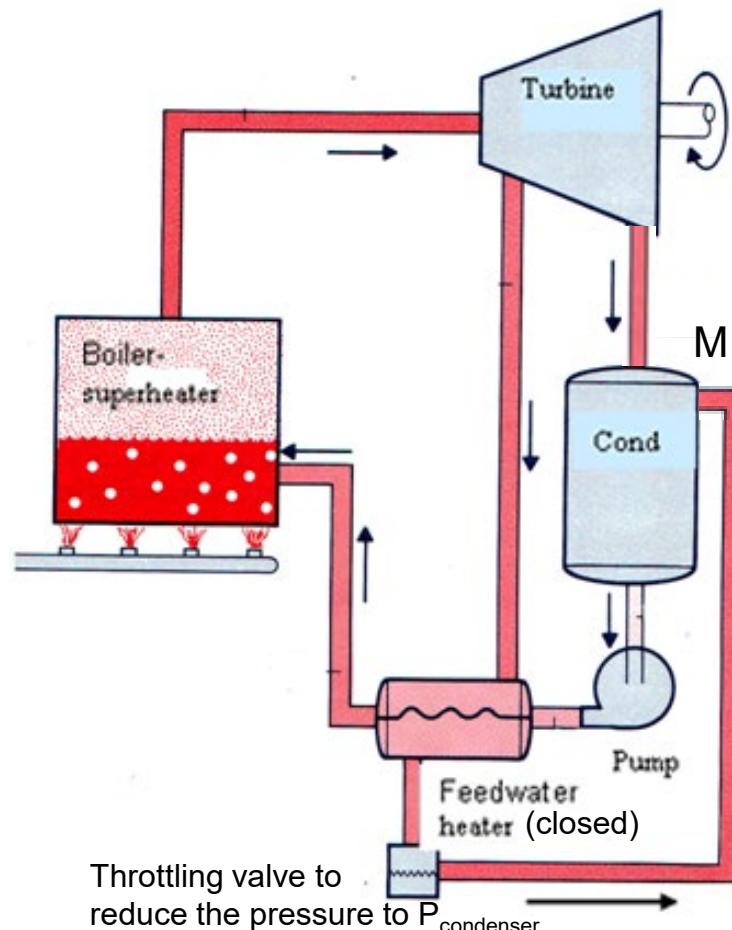
- The **closed feed water heater** is a heat exchanger in which the heat of the steam extracted from the turbine is transferred to the feed water exiting the first pump
- In an **ideal** closed feed water heater the feed water is heated to the exit temperature of the extracted steam ($T_9 = T_3$) and the steam leaves the heater as a saturated liquid at the extraction pressure $\rightarrow h_3 = h_{\text{sat-liquid}@P7}$ (table 5)
- Both streams are mixed in a mixing chamber (in this figure) or the saturated steam is rerouted to the condenser via a throttling valve (see next slide)



Improvement Rankine Cycle: feed water heater



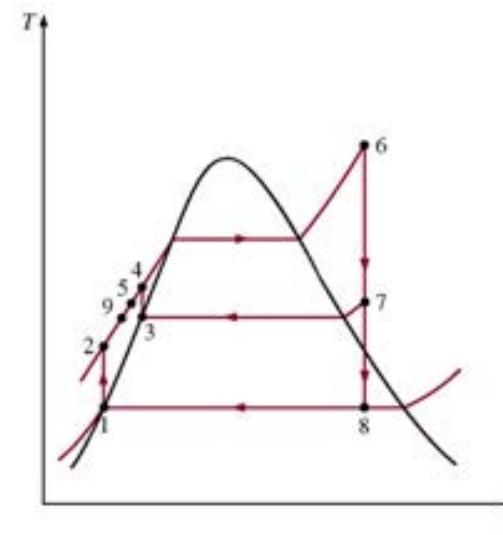
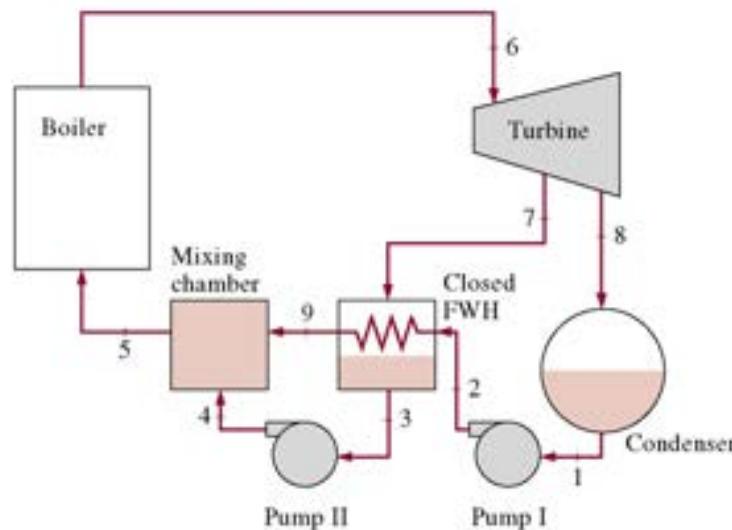
Open feed water heater, mixing is performed in the open feed water heater.



Closed feedwater heater with the steam rerouted to the condenser. Mixing is performed at point M. Note the pressures for mixing should be equal.

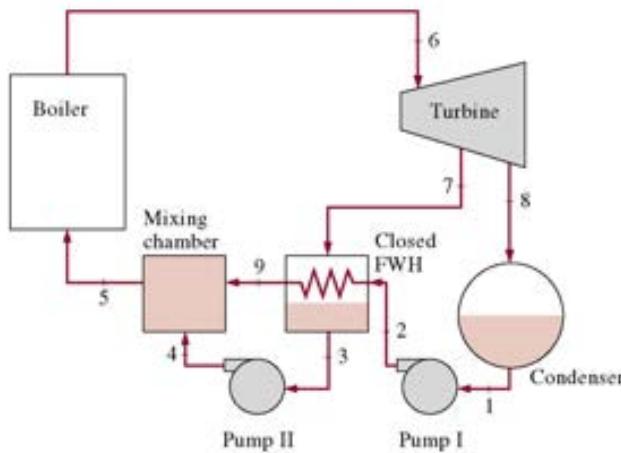
Rankine Cycle with Closed Feed Water Heater

- Analyzing the Rankine cycle with a **closed feed water heater**
- The mass flow changes throughout the cycle
- Three different mass flows: $\dot{m}_7 = \dot{m}_3 = \dot{m}_4$ & $\dot{m}_8 = \dot{m}_1 = \dot{m}_2 = \dot{m}_9$ & $\dot{m}_5 = \dot{m}_6$
- Extra relations are required
 - Energy balance closed feed water heater: $\dot{m}_7(h_7 - h_3) = \dot{m}_2(h_9 - h_2)$
 - Mixing chamber relations
 - Mass balance mixing chamber: $\dot{m}_5 = \dot{m}_4 + \dot{m}_9$
 - Energy balance mixing chamber: $\dot{m}_5 h_5 = \dot{m}_4 h_4 + \dot{m}_9 h_9$

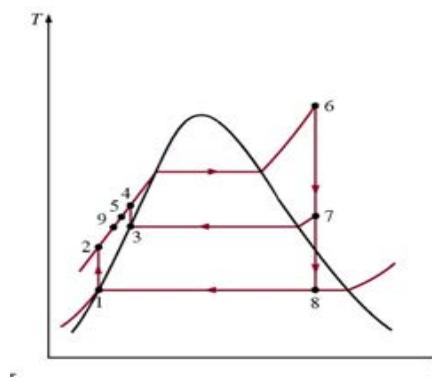


Rankine Cycle with Closed Feed Water Heater

- Energy balance closed feed water heater: $\dot{m}_7(h_7 - h_3) = \dot{m}_2(h_9 - h_2)$
- Energy balance mixing chamber: $\dot{m}_5 h_5 = \dot{m}_4 h_4 + \dot{m}_9 h_9$
- Mass balance mixing chamber: $\dot{m}_5 = \dot{m}_4 + \dot{m}_9$
 - Power heat in- and output: $\dot{Q}_{in} = \dot{m}_5(h_6 - h_5)$ and $\dot{Q}_{out} = \dot{m}_8(h_8 - h_1)$
 - Power work output: $\dot{W}_{out} = \dot{m}_5(h_6 - h_7) + \dot{m}_8(h_7 - h_8)$
 - Power work input: $\dot{W}_{in} = \dot{m}_8(h_2 - h_1) + \dot{m}_3(h_4 - h_3)$
- Three different mass flows: $\dot{m}_7 = \dot{m}_3 = \dot{m}_4$ & $\dot{m}_8 = \dot{m}_1 = \dot{m}_2 = \dot{m}_9$ & $\dot{m}_5 = \dot{m}_6$
- Thermal efficiency: $\eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_{out} - \dot{W}_{in}}{\dot{Q}_{in}} =$

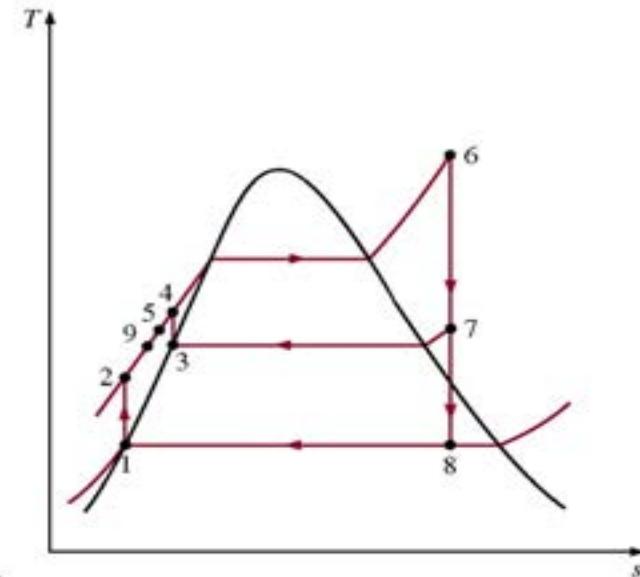
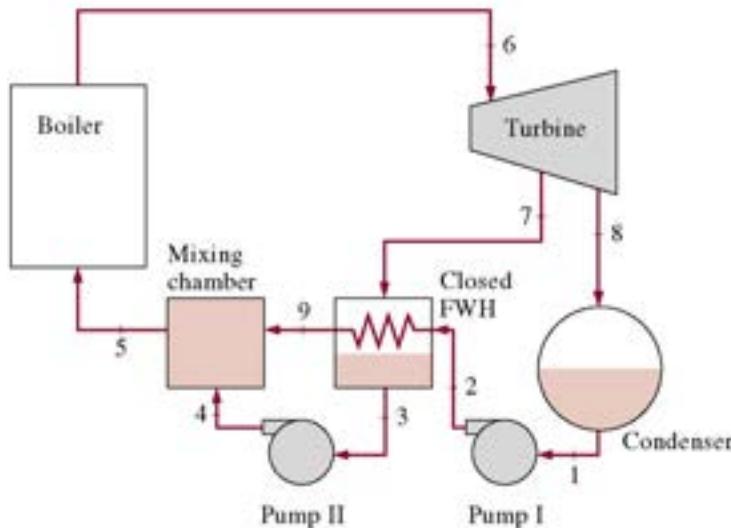


$$\eta_{th} = \frac{\dot{m}_5(h_6 - h_7) + \dot{m}_8(h_7 - h_8) - \dot{m}_8(h_2 - h_1) - \dot{m}_3(h_4 - h_3)}{\dot{m}_5(h_6 - h_5)}$$

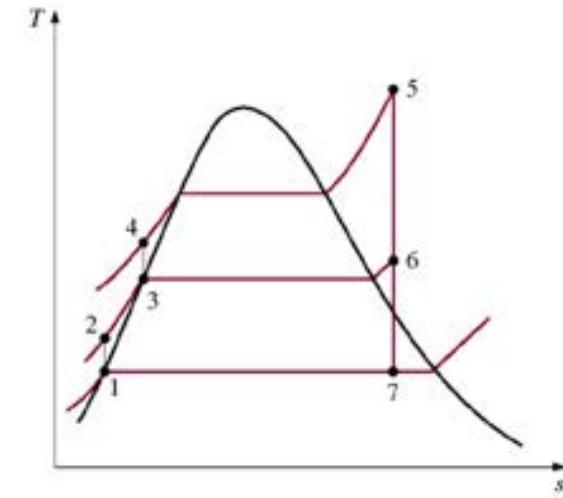
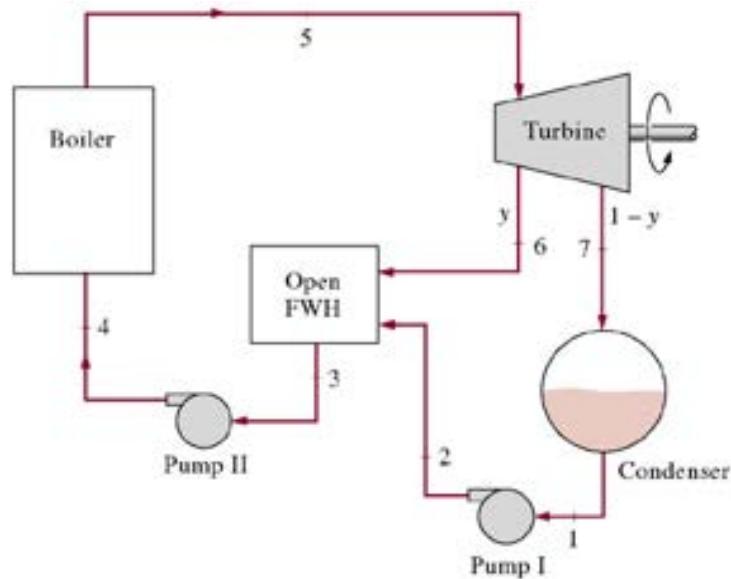


Open and closed feed water heaters

Closed feed water heater

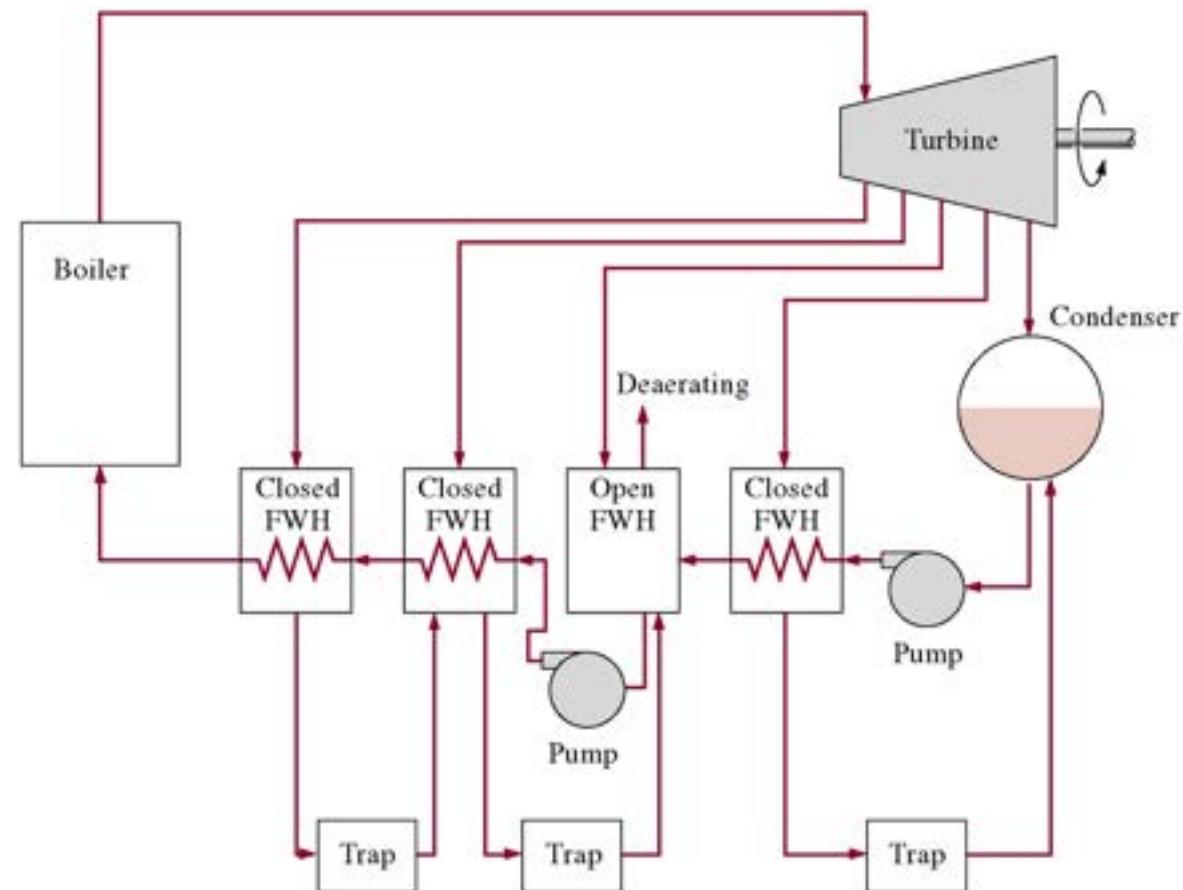


Open feed water heater



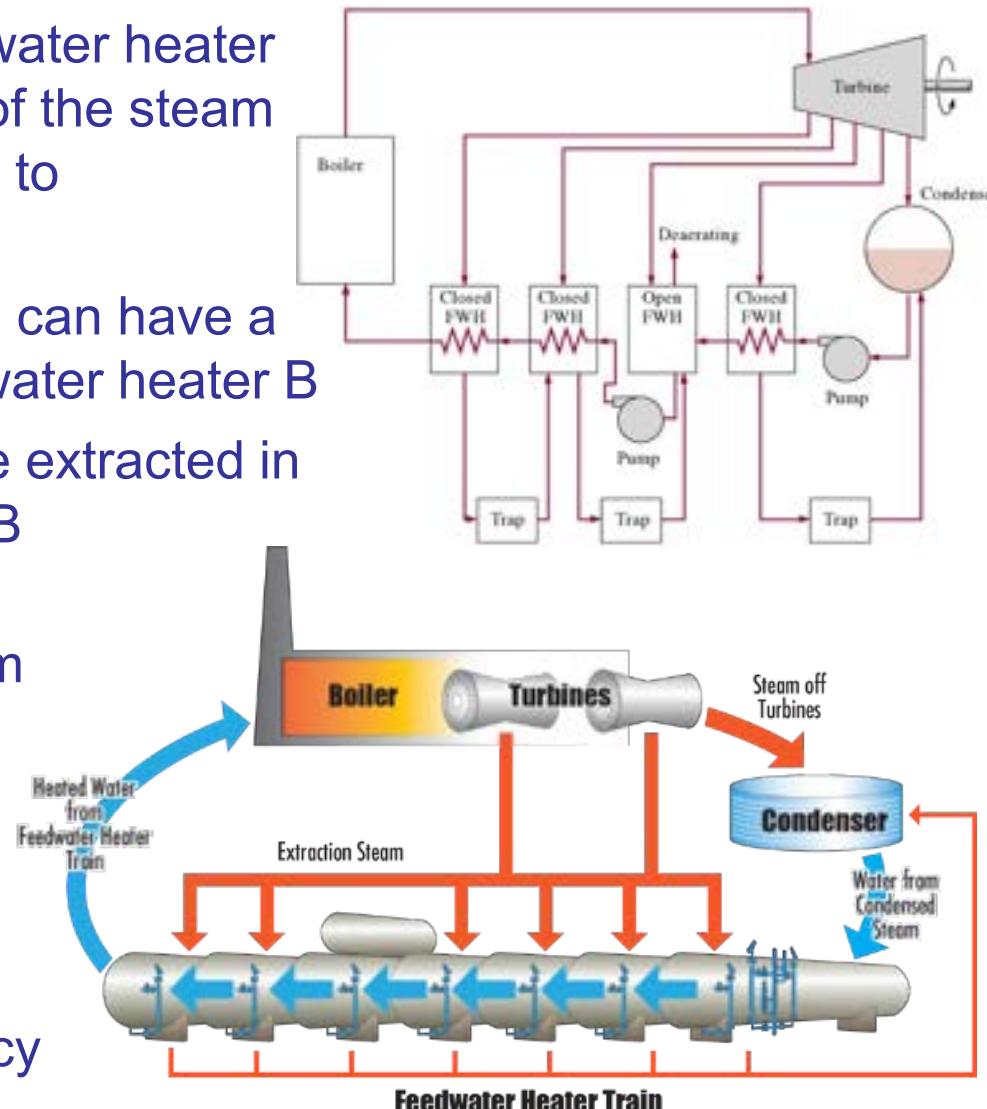
Combination of Open and Closed Feed Water Heaters

- Most steam power plants use a combination of open and closed feed water heaters (often up to 8 feed water heaters are used)
- **Open feed water heater:** simple, inexpensive, good heat transfer, however each heater requires a separate pump
- **Closed feed water heater:** more complex, more expensive, heat transfer is less, however not all of them need a pump



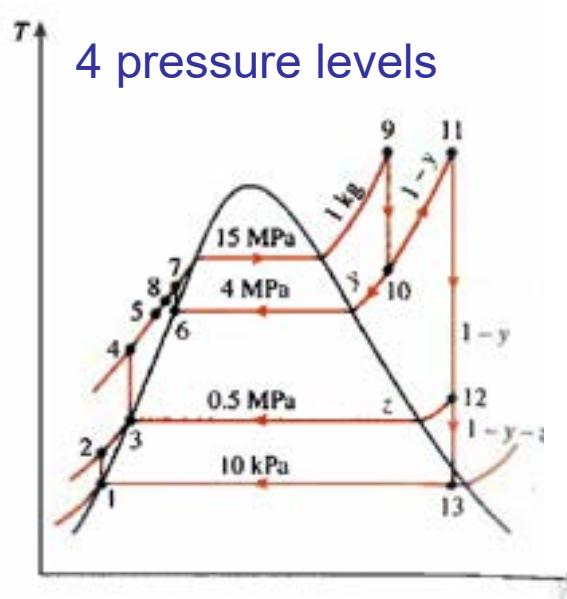
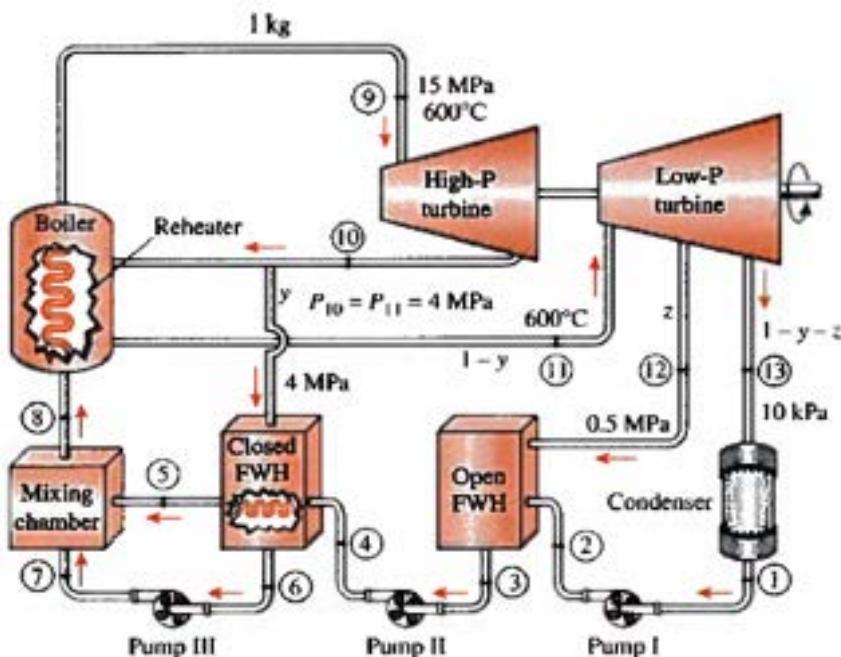
Combination of Open and Closed Feed Water Heaters

- Why so many feed water heaters are used?
- The use of more than one feed water heater increases the efficiency as part of the steam is longer in the turbine, available to produce work
- In feed water heater A the steam can have a lower temperature than in feed water heater B
- Therefore the steam for A can be extracted in a later stage than the steam for B
- Feed water heater B needs relatively high temperature steam which is extracted in an early stage
- A train of feedwater heaters is common in power plants, they significantly improve the efficiency



Combination of Reheater, Open and Closed FWH

- Most systems used for power generation are complicated systems combining two or more turbines with reheating and several open and closed feed water heaters
- To derive the thermal efficiency all power in- and outputs should be considered
- Thermal efficiency: $\eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_{out-HPT} + \dot{W}_{out-LPT} - \dot{W}_{in-p1} - \dot{W}_{in-p2} - \dot{W}_{in-p3}}{\dot{Q}_{in-boiler} + \dot{Q}_{in-reheater}}$

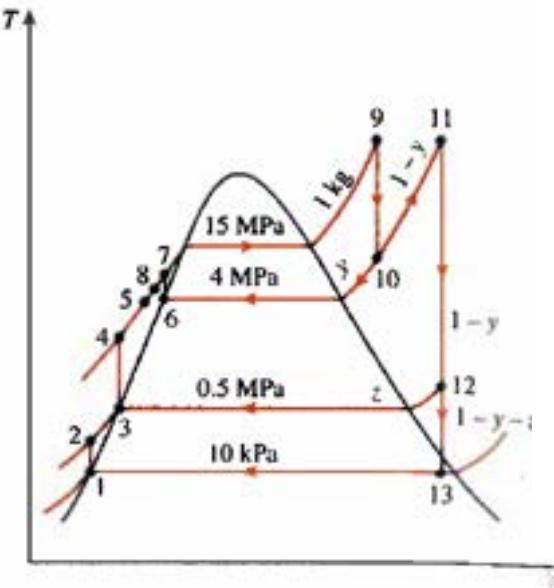
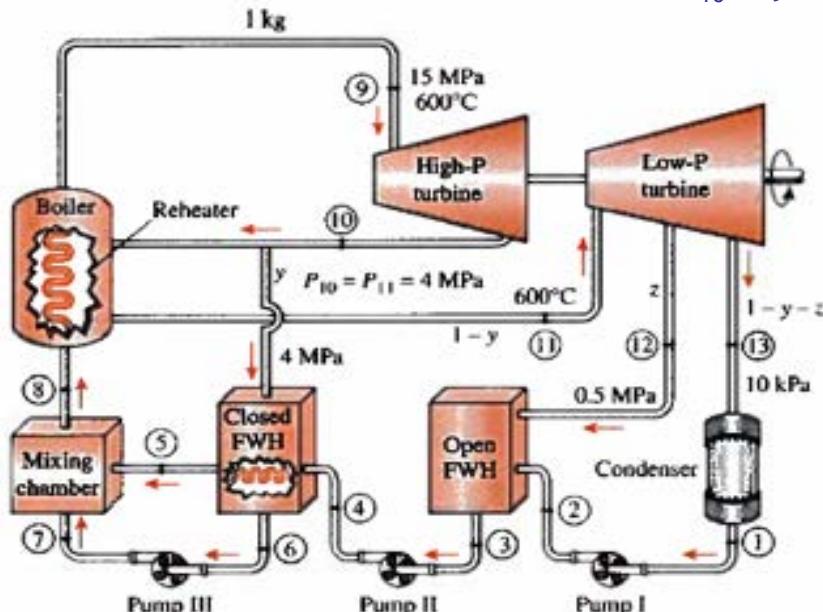


6 mass flows:
 $\dot{m}_8 = \dot{m}_9 = \dot{m}_{10}$
 $\dot{m}_{13} = \dot{m}_1 = \dot{m}_2$
 $\dot{m}_3 = \dot{m}_4 = \dot{m}_5$
 $\dot{m}_6 = \dot{m}_7$
 $\dot{m}_{12} & \dot{m}_{11}$

Mass flows can be related using the mass balances and energy balances over the feedwater heaters

Combination of Reheater, Open and Closed FWH

$$\eta_{th} = \frac{\dot{m}_{10}(h_9 - h_{10}) + \dot{m}_{11}(h_{11} - h_{12}) + \dot{m}_{13}(h_{12} - h_{13}) - \dot{m}_{13}(h_2 - h_1) - \dot{m}_3(h_4 - h_3) - \dot{m}_6(h_7 - h_6)}{\dot{m}_{10}(h_9 - h_8) + \dot{m}_{11}(h_{11} - h_{10})}$$



6 mass flows:

$$\begin{aligned}\dot{m}_8 &= \dot{m}_9 = \dot{m}_{10} \\ \dot{m}_{13} &= \dot{m}_1 = \dot{m}_2 \\ \dot{m}_3 &= \dot{m}_4 = \dot{m}_5 \\ \dot{m}_6 &= \dot{m}_7 \\ \dot{m}_{12} &\text{ & } \dot{m}_{11}\end{aligned}$$

Mass flows can be related using the mass balances and energy balances over the feedwater heaters

- 6 equations needed to find 6 mass flows
 1. Energy balances closed feed water heater: $\dot{m}_6(h_{10} - h_6) = \dot{m}_4(h_5 - h_4)$
 2. Energy balance open feed water heater: $\dot{m}_{12}h_{12} = \dot{m}_2h_2 + \dot{m}_3h_3$
 3. Mass balances open feed water heater: $\dot{m}_3 = \dot{m}_2 + \dot{m}_{12}$
 4. Energy balance mixing chamber: $\dot{m}_8h_8 = \dot{m}_5h_5 + \dot{m}_7h_7$
 5. Mass balances mixing chamber: $\dot{m}_8 = \dot{m}_5 + \dot{m}_7$
 6. Finally a power input or output should be given to determine the main mass flow
- All h values can be found from the tables and / or diagrams

Co-generation / Combined heat and power

- So far, we have seen the simple Rankine cycle and we improved its efficiency by adding extra devices to build an as efficient as possible Rankine cycle
- These Rankine cycles are among the most commonly used vapor power cycles to generate electricity
- So far in all heat cycles discussed the **goal was to convert** an as large as possible portion of **the heat** transferred to the working fluid **into work** (the most valuable form of energy)
- However, some of the energy of the heat input, q_{in} can not be converted to work due to the restrictions of the second law, therefore heat, q_{out} from all heat cycles is “lost” to the surroundings (this represents significant energy losses)
- The loss of a heat cycle can be further reduced by using this rejected heat in a useful way

Co-generation / Combined heat and power

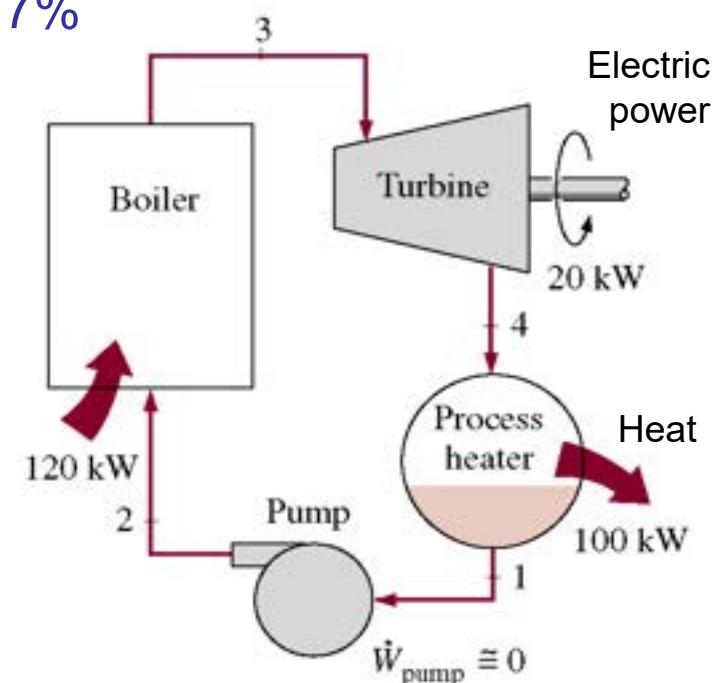
- To reduce the loss of a heat cycle the rejected heat should be used
- Sometimes a lot of heat (150 - 200°C) is needed for:
 - Process heating → E.g. desalination of seawater
 - Feedstock for chemical process
 - Local heating (city heating) → E.g. our university (need about 85°C)
 - Driving absorption air-conditioning cycle
- Bleed steam from the turbine and use it for heating, doing so more or even all energy from the input heat can be used
- **Co-generation** or **combined heat and power** (CHP) is the production of more than one useful form of energy (such as process heat and electric power) from the same energy source
- This way a power plant can produce electricity while meeting the process-heat requirements of certain industrial processes or heat for heating houses

Ideal co-generation Rankine Cycle Plant

- Consider a simple ideal co-generation power plant
- The thermal efficiency of this plant is only 17%

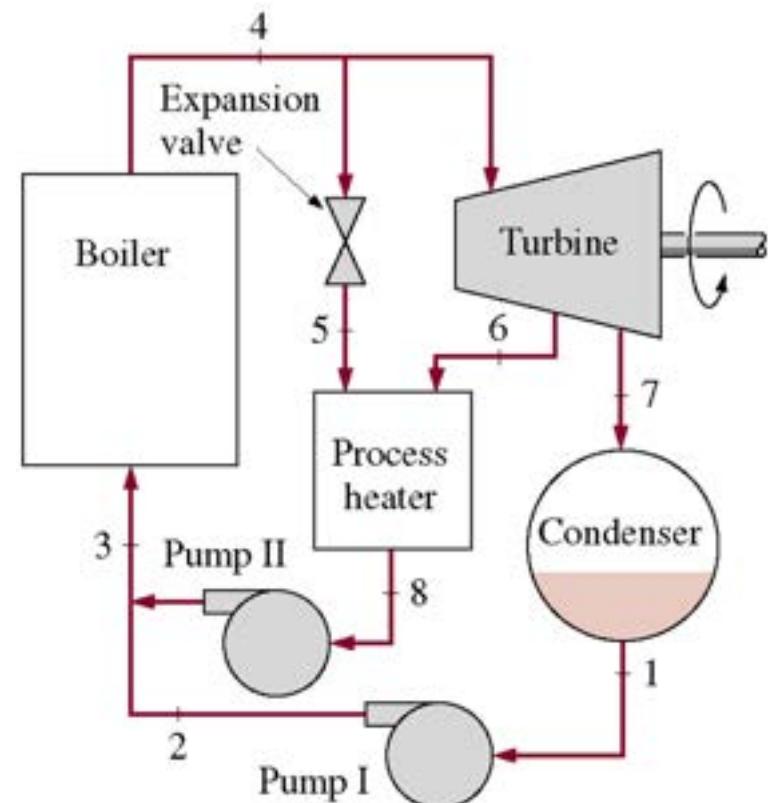
$$\eta_{HE} = \frac{w_{OUT} - w_{IN}}{q_{IN}} = \frac{20}{120} = 0.17$$

- However, in addition to the work delivered the heat rejected in, what is called, the process heater (100 kW) is also useful
- This reduces the energy loss
- As this is a different form of energy it is not considered in the thermal efficiency, but it is considered in a different number
- The **utilization factor**, ε_u is defined as: $\varepsilon_u = \frac{\text{Network-output} + \text{Process-heat}}{\text{Total-heat-input}}$
- For this ideal co-generation cycle: $\varepsilon_u = \frac{W_{NET} + Q_{PROCESS}}{Q_{IN}} = 1$



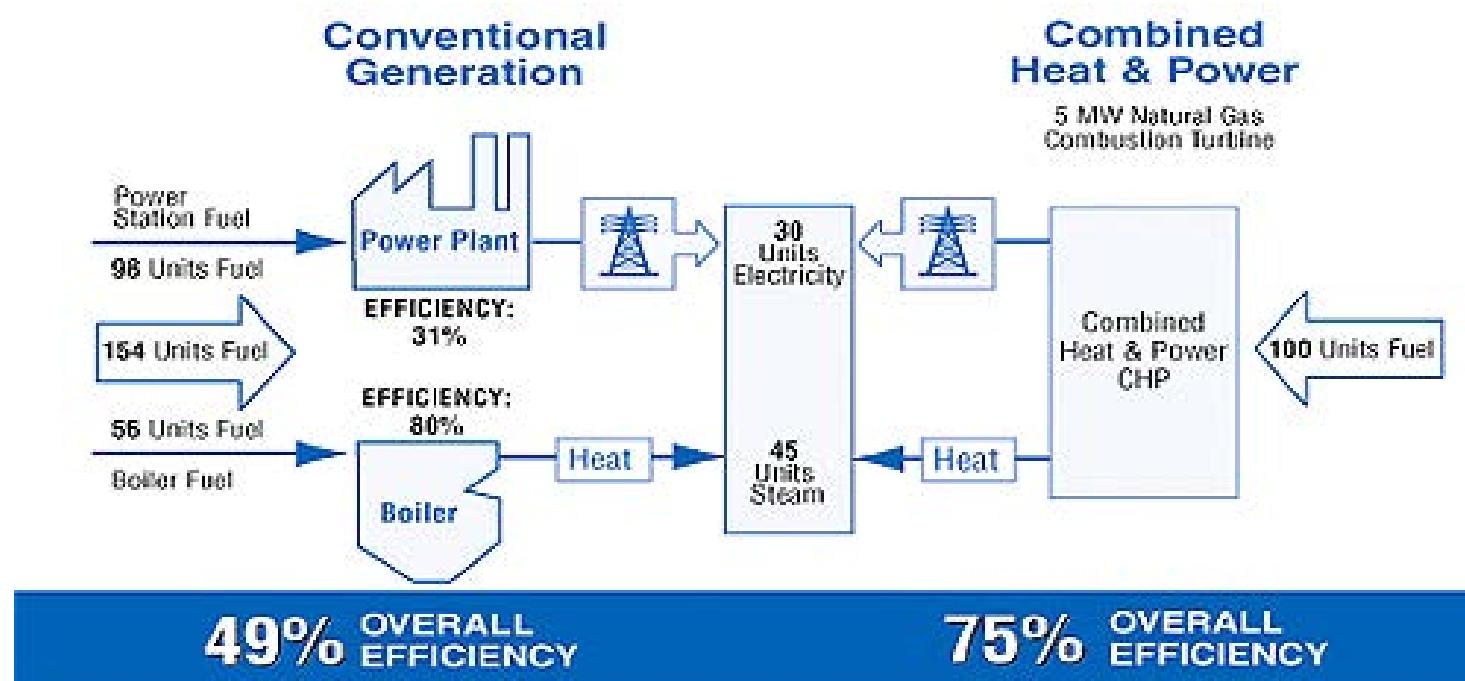
Co-generation plant with adjustable loads

- The ideal co-generation or CHP plant of the previous slide is not practical because it cannot adjust to variations in power and process-heat loads
- A more practical but more complex plant has the ability to adjust the heat and power by adjusting the mass flows through point 5, 6 and 7
- No power and maximum heat is produced when $m_4 = m_5$ ($m_6 = m_7 = 0$)
- Maximum power and no heat is produced when $m_4 = m_7$ ($m_6 = m_5 = 0$)
- Under optimal conditions the plant simulates the ideal plant and all fluid goes via point 6 ($m_7 = m_5 = 0$)



Combined Heat and Power System

- The overall efficiency or utilization factor of conventional generation versus combined heat and power (CHP)

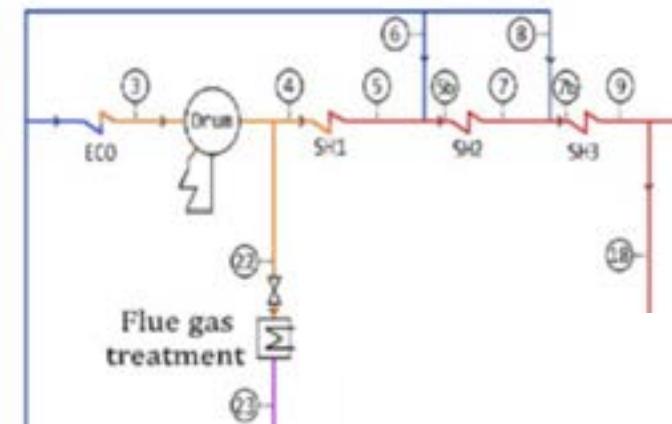


Example of a typical CHP system, to produce 75 units of useful energy (30 in the form of electricity and 45 in the form of steam), the conventional generation or separate heat and power systems use 154 units of energy—98 for electricity production and 56 to produce heat—resulting in an overall efficiency of 49 percent. However, the CHP system needs only 100 units of energy to produce the 75 units of useful energy from a single fuel source, resulting in a total system efficiency of 75 percent (<http://epa.gov/chp/basic/efficiency.html>)

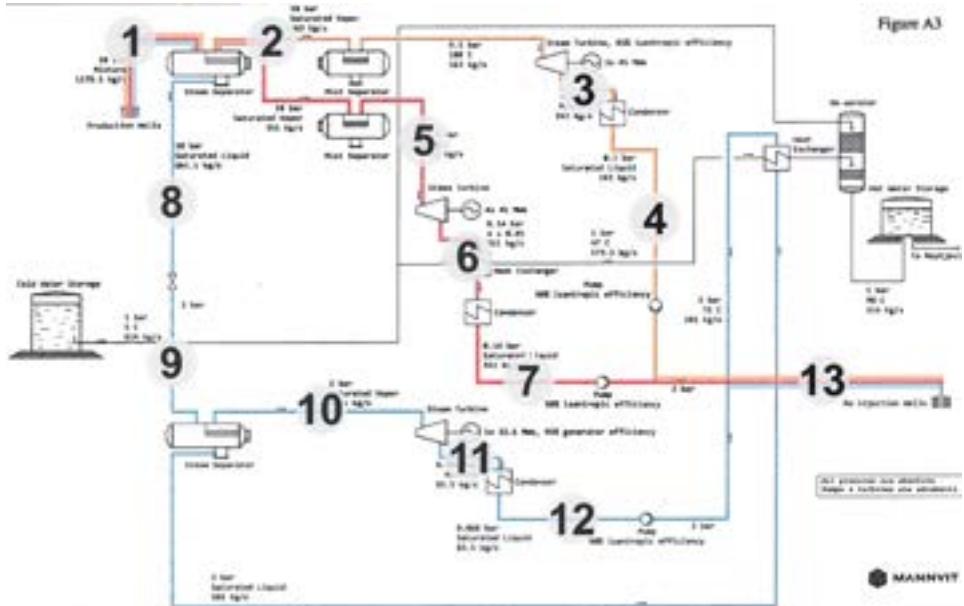
Example of real power systems

- The cycles we have seen so far are all simplified
- Real cycles are way more complicated
- They have a lot of additional devices, tubes and valves to control the flows
- Small additional flows and valves for regulation of the flow are present
- Heat losses in the pipes and tubes occur
- Pressure drops occur over the pipes and devices like boilers, condensers, heat exchangers
- Steam separators and deaerators are present to get rid of unwanted droplets or air in the working medium
- Additional devices to clean flue gasses can be present

Boiler of a biomass power plant. Due to variations in the composition of biomass the temperature in the boiler can vary. The cold blue flows are used to control the temperature of the red hot flow going to the turbine. A little bit of the saturated steam is tapped and used to clean the flue gases.



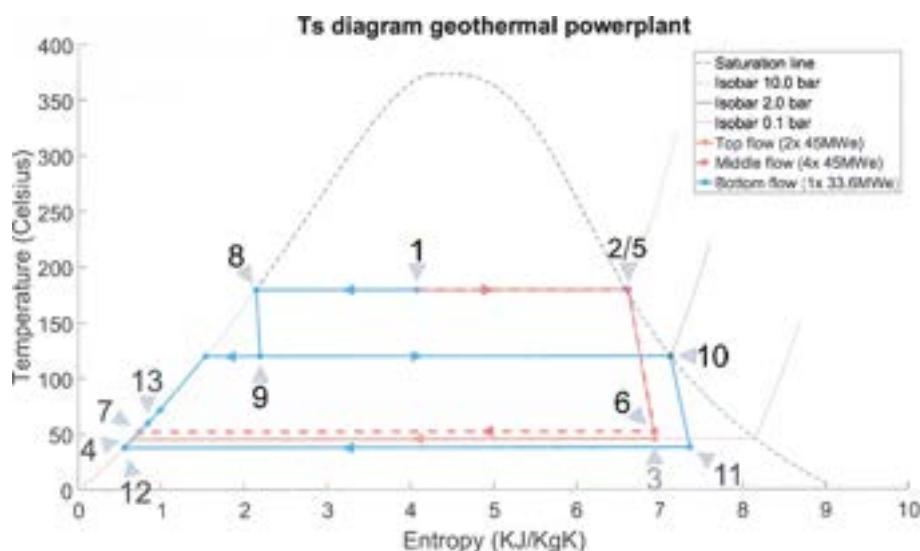
Geothermal Power Plant, Hellisheiði, Iceland



This power plant uses geothermal heat that has absorbed inside the thick layer of melted hot rock beneath the earth's crust, called magma. The power plant generates electricity as well as heat for district heating.

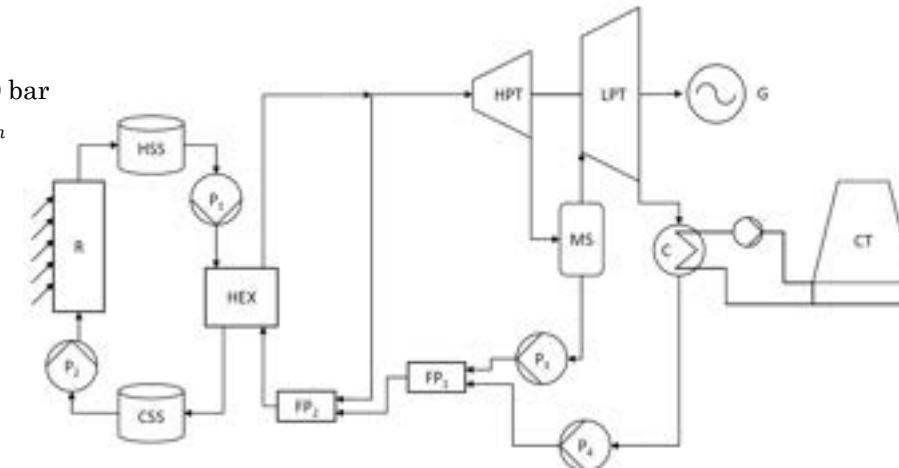
The net power output is around 300 MW and the heat supplied to the city is in the order of 230 MW.

The thermal efficiency of the cycle is around 19% while the utilization factor is around 32%. The main mass flow in the cycle is 1180 kg/s.

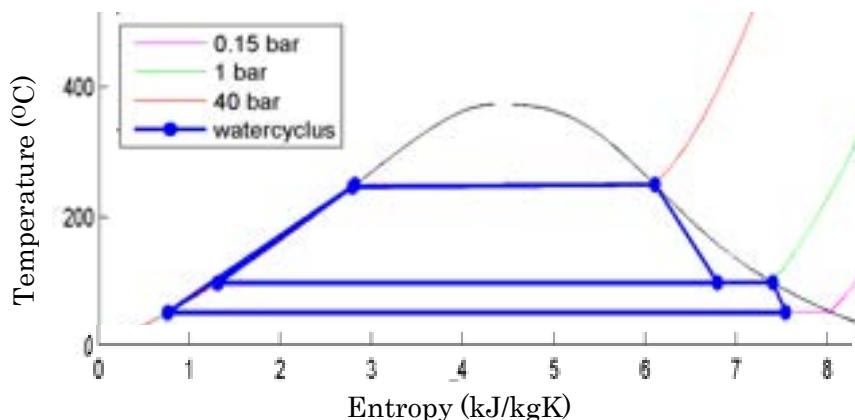


PS 10 Solar Power Plant, Seville, Spain

Temperature cold salt	247°C
Temperature hot salt	565°C
HEX steam outlet	$x = 1 @ 40 \text{ bar}$
Net solar power absorption	50.8 MW _{th}
Efficiency salt system	94%
Efficiciency heat exchanger	100%
HPT exhaust pressure	1.0 bar
HPT exhaust moisture content	10 wt%
LPT exhaust pressure	0.15 bar
LPT exhaust moisture content	7 wt%
Generator nominal efficiency	95%
Pump 3 isentropic efficiency	91%
Pump 4 isentropic efficiency	88%
Feedwater preheater pressure	40 bar

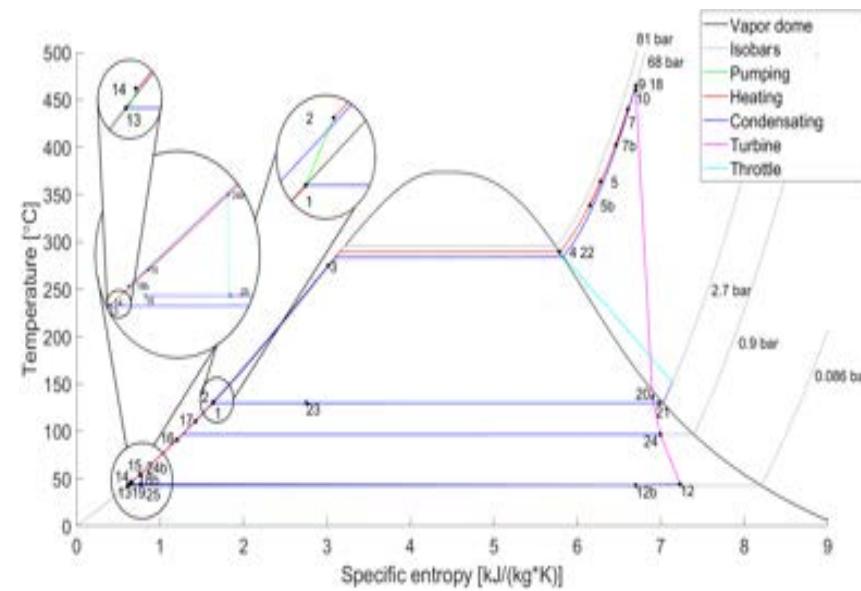
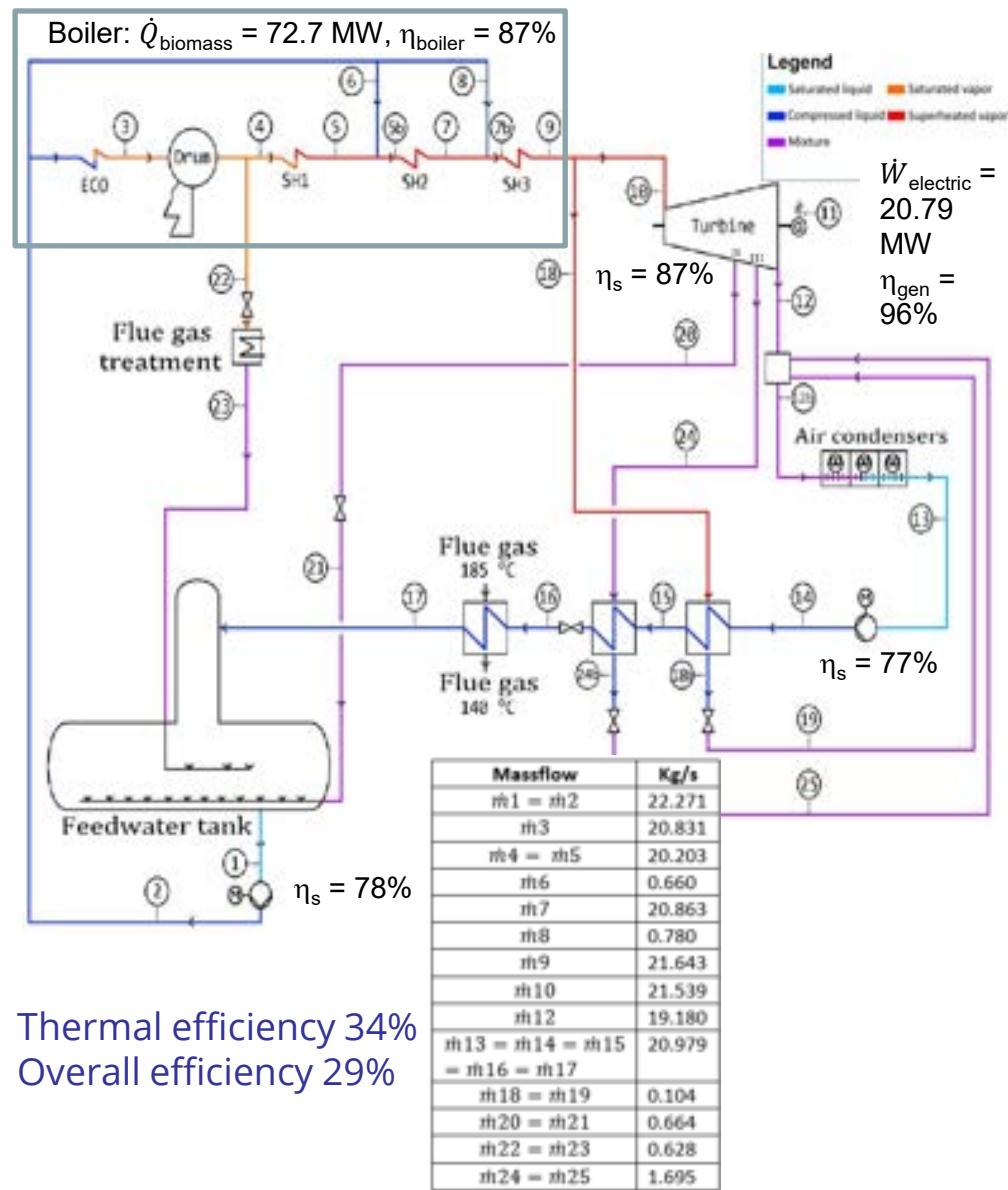


HPT	High pressure turbine
LPT	Low pressure turbine
HEX	Heat exchanger
CSS	Cold salt storage
HS	Hot salt storage
P1	Pump 1
P2	Pump 2
P3	Pump 3
P4	Pump 4
SS	Steam separator
FP1	Feedwater preheater 1
FP2	Feedwater preheater 2
R	Solar radiation receiver
C	Condenser
G	Generator
CT	Cooling tower

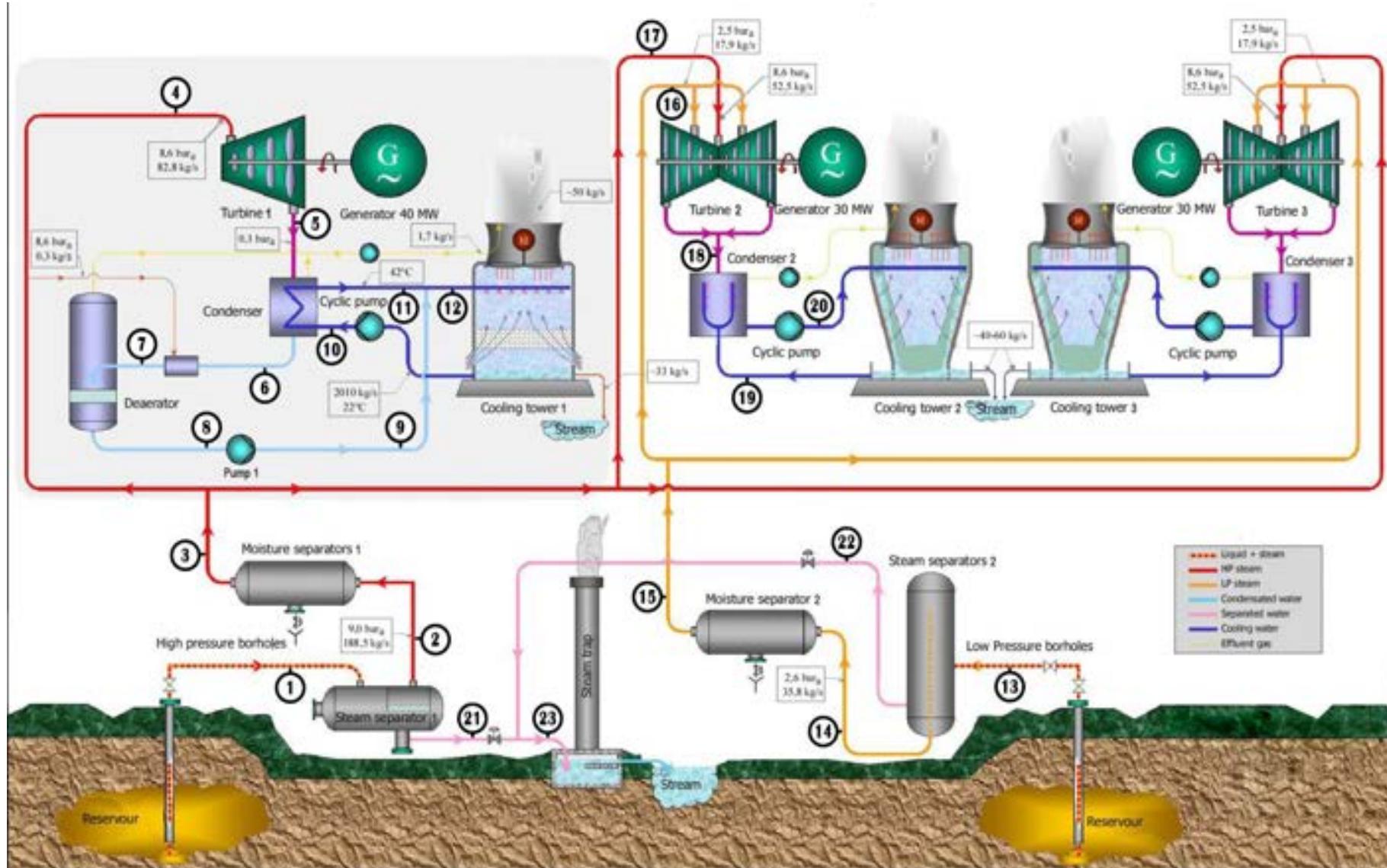


Simplified flow scheme with added salt storage and data of the PS10 solar power plant in Seville, Spain.
Analysing the cycle results in a thermal efficiency of only 21%. The net power output is around 10 MW. The main mass flow of the water is 28 kg/s and of the salt 97 kg/s.

Twence Biomass Power Plant, Hengelo, NL



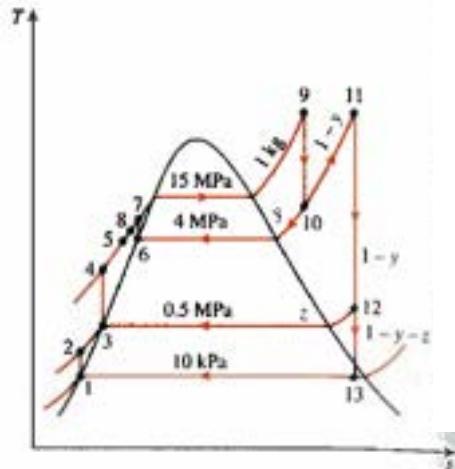
Landsvirkjun geothermal power plant, Iceland



Geothermal power plant to be analysed in this years project for first year BSc ME students

Recapitulate Class 8

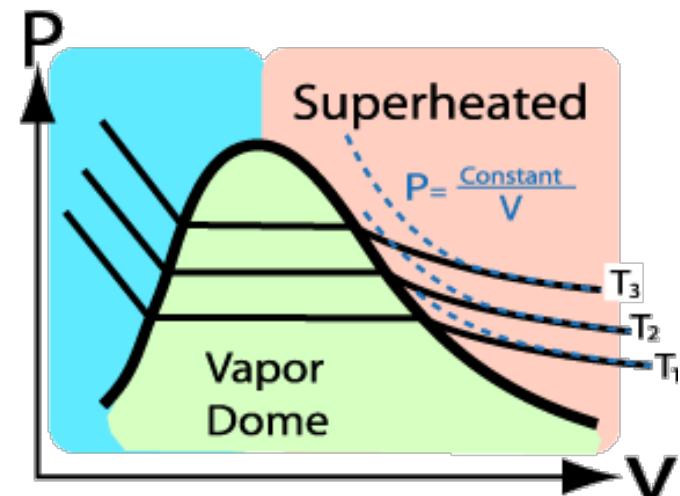
- Designing a simple Rankine cycle
 - Design parameters: turbine inlet P & T, condenser P & T
- Improve the efficiency of the Rankine cycle by adding extra devices
 - Extra heater → reheating
 - Open & closed feedwater heater → regenerative feedwater heating
- Thermal efficiency: $\eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_{out-HPT} + \dot{W}_{out-LPT} - \dot{W}_{in-p1} - \dot{W}_{in-p2} - \dot{W}_{in-p3}}{\dot{Q}_{in-boiler} + \dot{Q}_{in-reheater}}$
- Take the mass flows into account and relate the mass flows using:
 - Energy balances closed feed water heater
 - Energy balances mixing chambers / OFWH'ers
 - Mass balances mixing chambers / OFWH'ers
- The energy loss can be reduced by combining heat & power generation (Co-generation)
- Examples of real power plants



Ts-diagram Rankine cycle with reheating and feed water heating

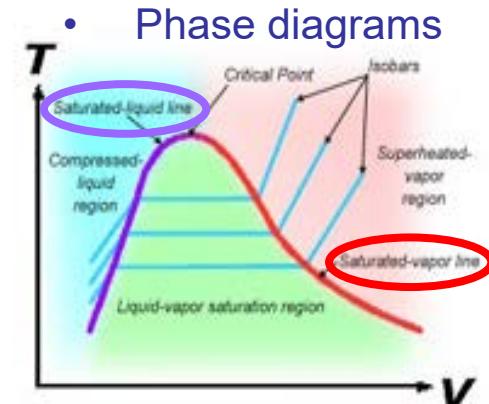
Next Class 9: Properties of gases

- In class 7 & 8 we met the **vapor power cycle**, a cycle using a **working fluid that undergoes a phase transition** through the cycle (Rankine cycle)
- The subject of class 10 & 11 is the **gas power cycle**, a cycle using **gas as working fluid** through the whole cycle (Brayton cycle)
- In class 9 we will see how we can get energy values for air or other gases, like we learned in class 3 for water
 - Diagrams and tables
 - Ideal gas law, $Pv = RT$
- Internal energy for ideal gas
- Enthalpy for ideal gas
- Entropy changes for ideal gas
- Specific heat capacities for gases
 - C_p : for constant pressure
 - C_v for constant volume



Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal efficiency $\eta_{thermal} = \frac{Net\ electrical\ power\ output}{Rate\ of\ fuel\ energy\ input} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- 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 $du = \delta q - \delta w \rightarrow \Delta u = q - w$
 - Open system $q_{in} + w_{in} + (h + ke + pe)_{in} = q_{out} + w_{out} + (h + ke + pe)_{out}$
- S increases, second law $ds_{total} = ds_{system} + ds_{surroundings} = \delta s_{gen} > 0$
- Inequality of Clausius $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)
- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdP$
- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$
- Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$
- Coefficient of performance $(COP)_{HP} = \frac{q_{HOT,OUT}}{w_{IN}}$ and $(COP)_{REF} = \frac{q_{COLD,IN}}{w_{IN}}$



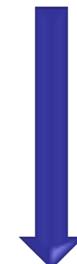
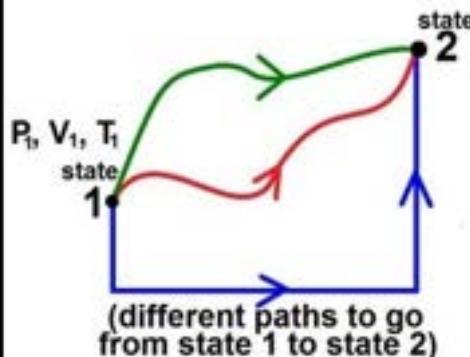
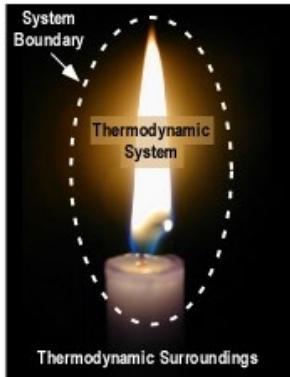
Class 9: Thermodynamic Properties of Pure Substances: Gases

A hot air balloon rises as the hot air inside the balloon is less dense and therefore lighter than the air outside the balloon.

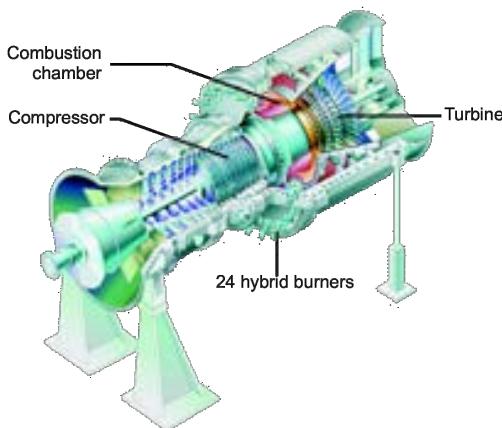


Roadmap Engineering Thermodynamics

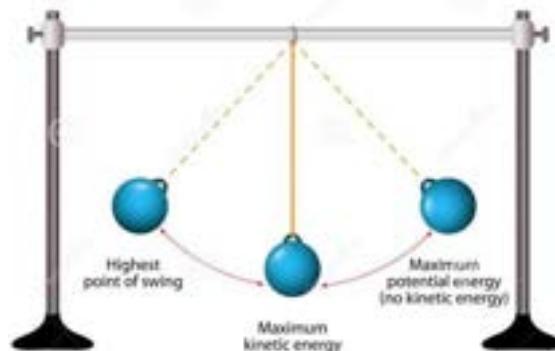
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



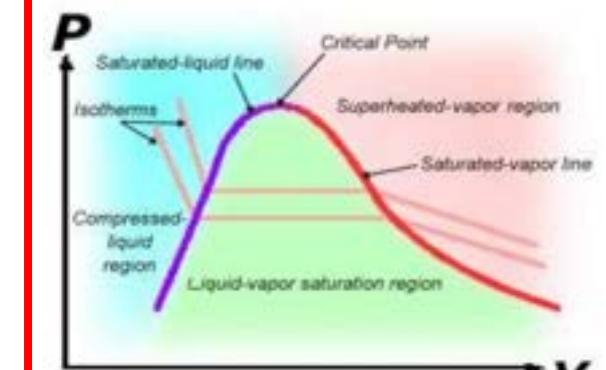
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

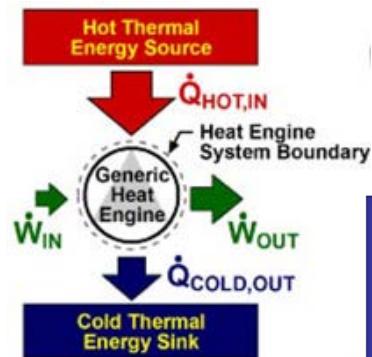


- Properties of Substances (Class 3, 9)

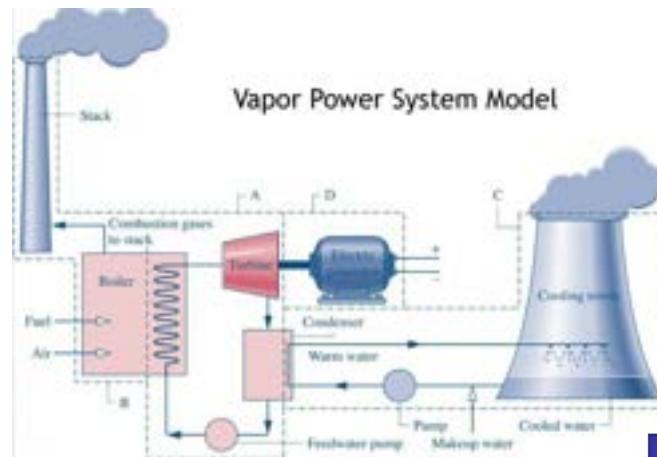


Roadmap Engineering Thermodynamics

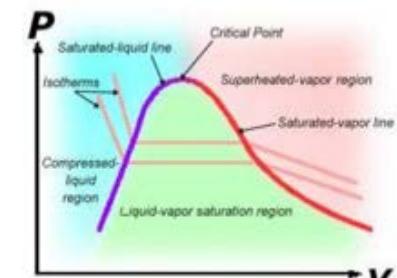
Thermodynamic cycles (Class 6)



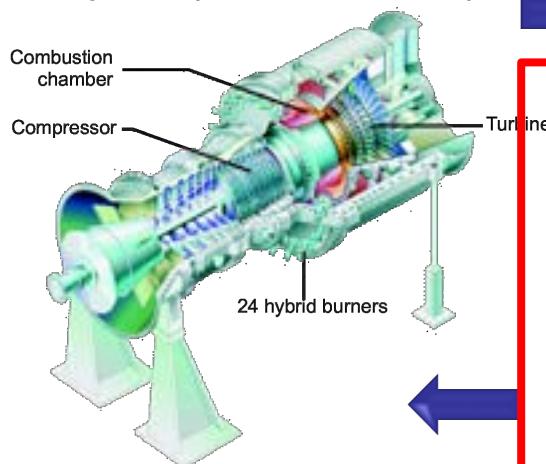
Vapor power cycles – Rankine cycle (Class 7, 8)



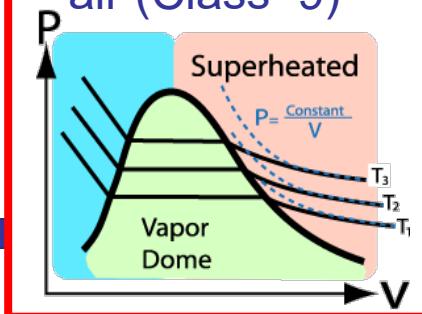
Properties of water (Class 3)



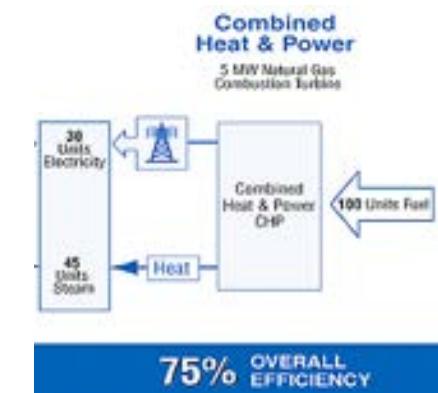
Gas power cycles – Brayton cycle (Class 10, 11)



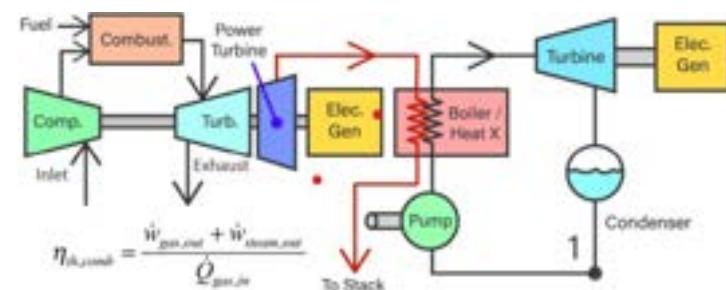
Properties of air (Class 9)



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



75% OVERALL EFFICIENCY



Classes 9-10-11: Thermodynamic Power Cycles

- In class 1 to 6 we introduced all the (basic) tools we need to study thermodynamic systems that generate power or heat / cold
- Done, class 7 & 8: **vapor power cycles**, cycles using a **working fluid** that **undergoes a phase transition** (mostly water) through the cycle (Rankine cycle)
- To do, class 10 & 11: **gas power cycles**, cycles using **gas as working fluid** through the whole cycle (Brayton cycle)
- **First class 9: properties for gases** (Like we did properties for water in class 3)
- **Refrigeration and heat pump cycles**, cycles moving heat opposite to the natural direction using power are treated in module 3



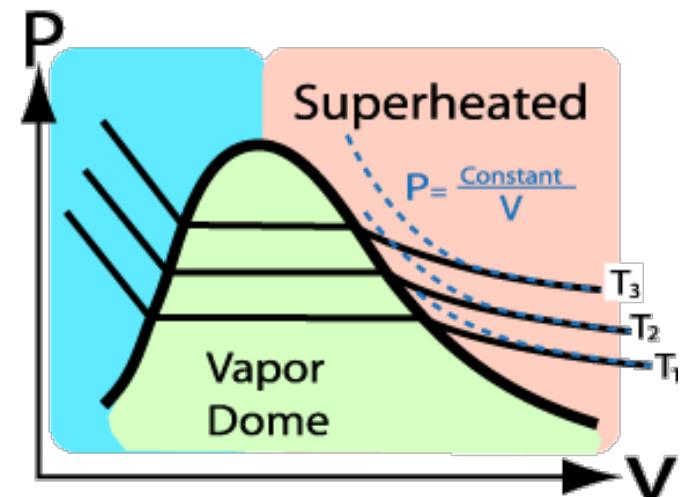
Jet engines are an example of gas power cycles



Power plants typically use vapor power cycles to generate electricity, e.g., the power plant in Geertruidenberg (NL)

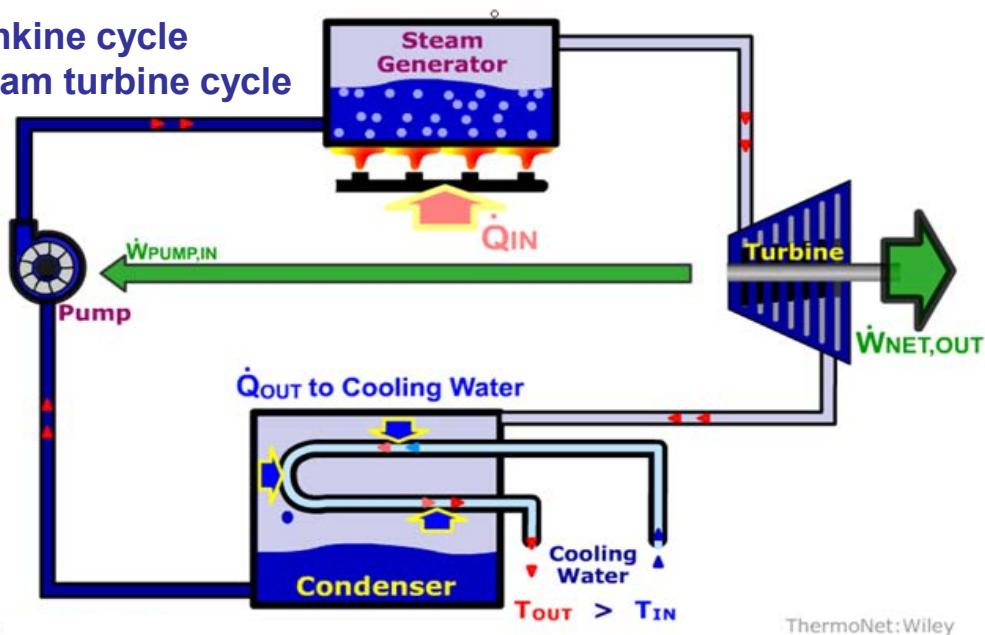
Content Class 9

- Properties of gases
- How can we get energy values for air or other gases, like we learned in class 3 for water
 - Diagrams and tables
 - Ideal gas law, $Pv = RT$
- Internal energy for ideal gas
- Enthalpy for ideal gas
- Entropy changes for ideal gas
- Specific heat capacities for gases
 - C_p : for constant pressure
 - C_v for constant volume
- **Learning goal:** declare and explain the behavior of gases at different temperatures and pressures

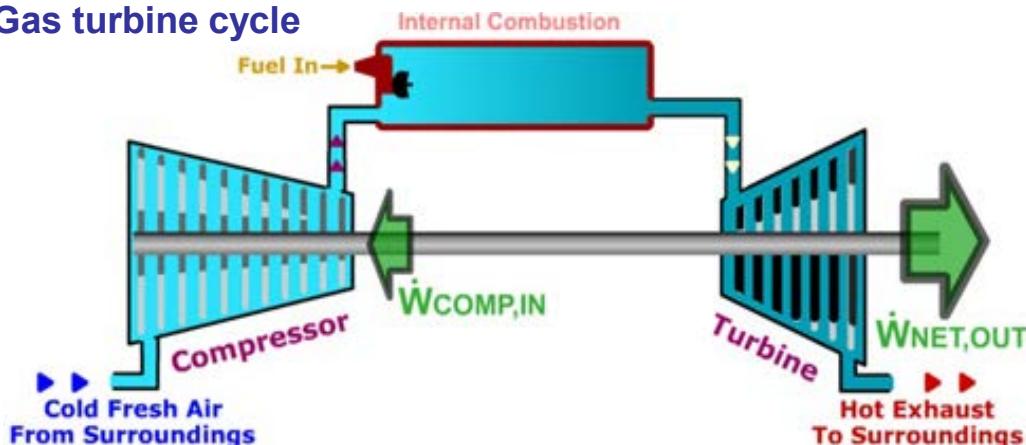


Steam turbine cycle versus gas turbine cycle

Rankine cycle
Steam turbine cycle



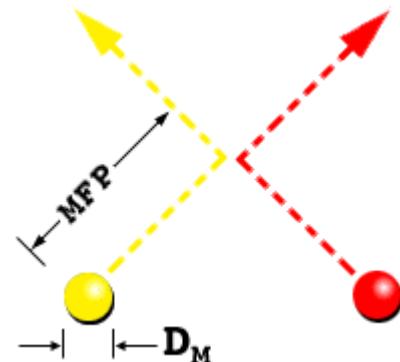
Open Brayton cycle
Gas turbine cycle



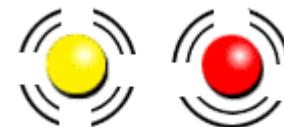
- The **Rankine cycle** (also steam turbine or vapor power cycle) uses water as working fluid
- Water undergoes a phase transition during the cycle
- We know how they work and how to analyse them
- The **Brayton cycle** (also gas turbine or gas power cycle) is a similar power cycle using air as working fluid
- The air is always in the gas phase, no phase transition
- Before we can analyze them, we need to know how we can find data for gas

Gases

- How is a **gas** different from a solid or a liquid ?
- In gases molecules are relatively far apart compared to liquids and solids
- The molecules do not feel one another's presence except during collisions
- This has a few implications
 - Gases have a low density
 - Gases are highly compressible
- They behave different than liquids and solid and therefore the way to find their properties and how to handle the formulas is different



Molecules are far apart if the mean distance they travel before hitting another one is much larger than their diameter



Molecules do not feel their presence as their molecular fields are localized close around their centers

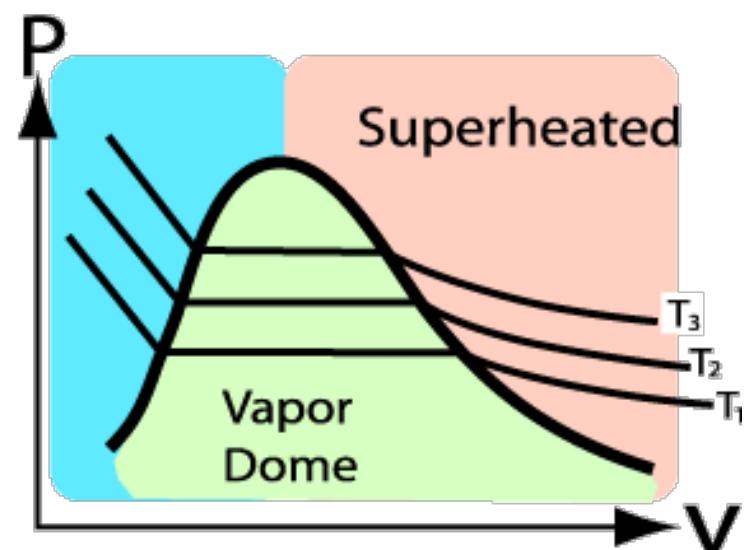
Tables, Diagrams and Equations of State

- Two properties known?
 - All other properties can be found using a table, diagram or formula
(This is stated in the State principle)
- For water properties, like v , T and P can be looked up in tables or diagrams

Table of Steam Properties

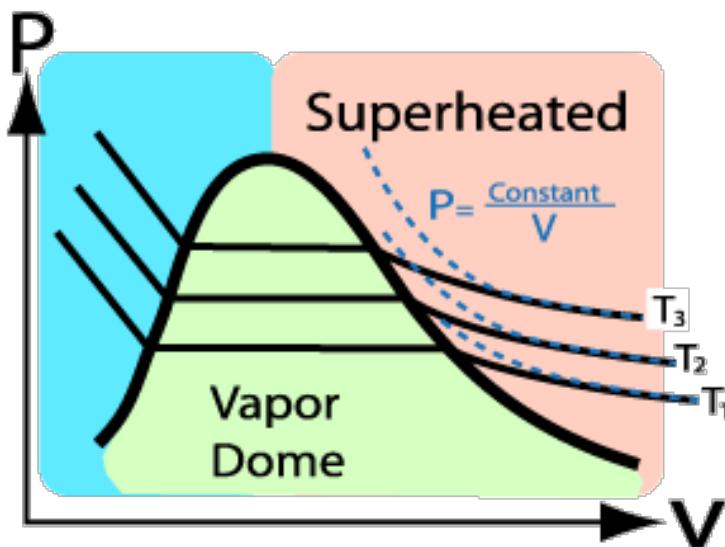
P (kPa)	T ($^{\circ}\text{C}$)	v (m^3/kg)
100	100	1.696
100	120	1.793
100	160	1.984

ThermoNet: John Wiley Publishers



Tables, Diagrams and Equations of State

- A relation describing the curves would be handy in e.g., computer programs (Matlab)
- Curves in the diagrams are not continuous and this makes a mathematical description difficult for the whole region
- However, in the superheated region the isotherms can be represented by a mathematical relation: $P = \frac{\text{Constant}}{V}$



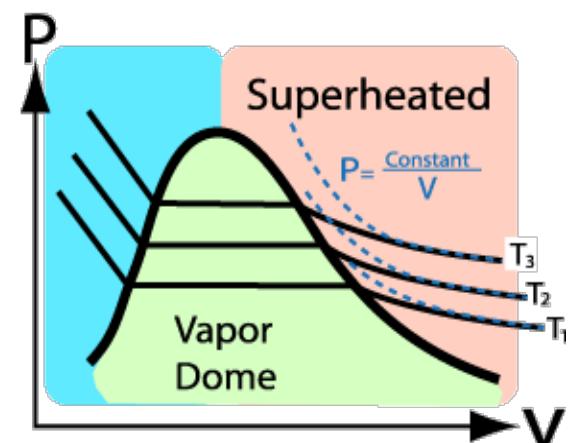
- Note: Xsteam.m can be used in Matlab to program a vapor power cycle. XSteam is based on data from a table, it returns the value you want based on the data implemented. Data in between are calculated based upon interpolation.

Ideal gas equation

- Unlike liquids for gases the relation between P, T and v of an ideal gas can be specified in an **equation of state for an ideal gas**
- An **equation of state** is any equation that relates the pressure, temperature, and specific volume of a substance
- The simplest and best-known equation of state for substances in the gas phase is **the ideal-gas equation of state**
- This equation predicts the P-v-T behavior of a gas quite accurately within some properly selected region
- In the superheated region the isotherms in a PV-diagram can be represented by the mathematical relation, $P = \frac{\text{Constant}}{v}$, which leads to the **Ideal gas equation of state**:

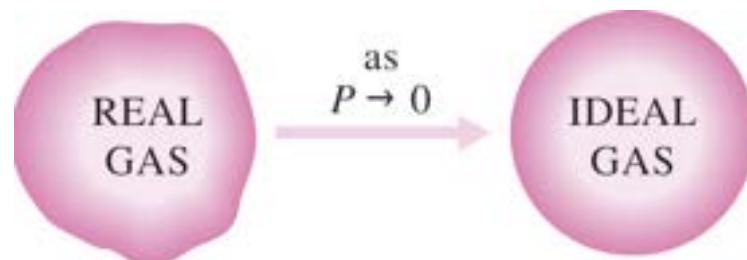
$$Pv = RT$$

T in Kelvin and P absolute pressure in Pascal (or kPa)



Ideal gas equation

- The ideal gas equation is only valid under specific conditions
- Validity
 - Real gases only behave as an ideal gas at low densities (i.e., low pressure, high temperature)
 - At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature)



Ideal gas equation

- Ideal gas equation of state: $Pv = RT$
- There are various versions of the ideal gas equation, but they all describe the same phenomena

$$PV = nR_u T \quad \leftarrow \quad n=m/M$$

$$PV = (m/M)R_u T \quad \leftarrow \quad R_u = RM$$

$$PV = mRT \quad \leftarrow \quad v = V/m$$

$$Pv = RT \quad \leftarrow \quad v= 1/\rho$$

$$P = \rho RT$$

- R_u = universal gas constant (J/molK)
- R = specific gas constant (kJ/kgK)
- n = number of particles (mol)
- m = total mass (kg)
- M = molar mass (kg/mol)
- V = total volume (m^3)
- v = specific volume (m^3/kg)
- ρ = density (kg/m^3)

- Last two versions mostly used in mechanical engineering
- The first one is mostly known from high school

Universal and Specific Gas Constant

- The ideal gas equation
 - In chemistry mostly $PV = nR_uT$ is used
 - In thermodynamics mostly $Pv = RT$ (fluid dynamics $P/\rho = RT$)
 - R_u is the **universal gas constant**, same for every gas
 - R is the **specific gas constant**, unique for every gas
- Both are related by: $R_u = RM$
where M is the molar mass

<u>Substance</u>	<u>R, kJ/kg·K</u>
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

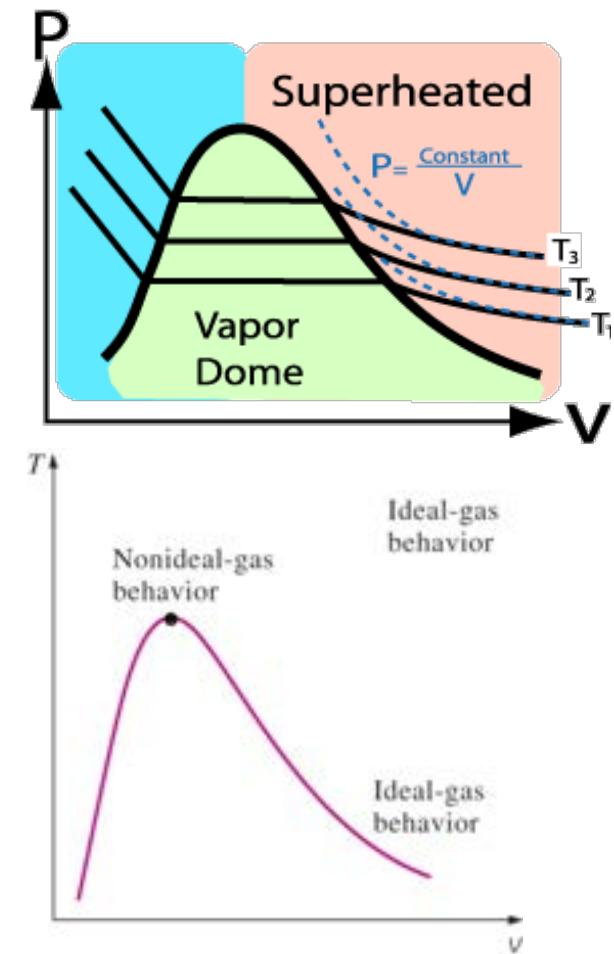
Different substances have different specific gas constants.

Universal and Specific Gas Constant

- The universal gas constant (R_u) and the specific gas constant (R), are related by $R_u = RM$, where M is the molar mass
- Example**
- Universal Gas Constant (R_u):** All gases have same value
 - $R_u = 8.314 \text{ kJ/(kmol.K)}$
- Specific Gas Constant (R):** Each gas has a unique value, e.g., air:
 - $R_{\text{air}} = 0.287 \text{ kJ/(kg.K)}$ (Table 1 or 2)
 - $M_{\text{air}} = 28.97 \text{ kmol/kg}$
 - $R_{\text{air}} \cdot M_{\text{air}} = 0.287 \times 28.97 = 8.314 \text{ kJ/(kmol.K)}$

Ideal Gas and Compressibility Factor

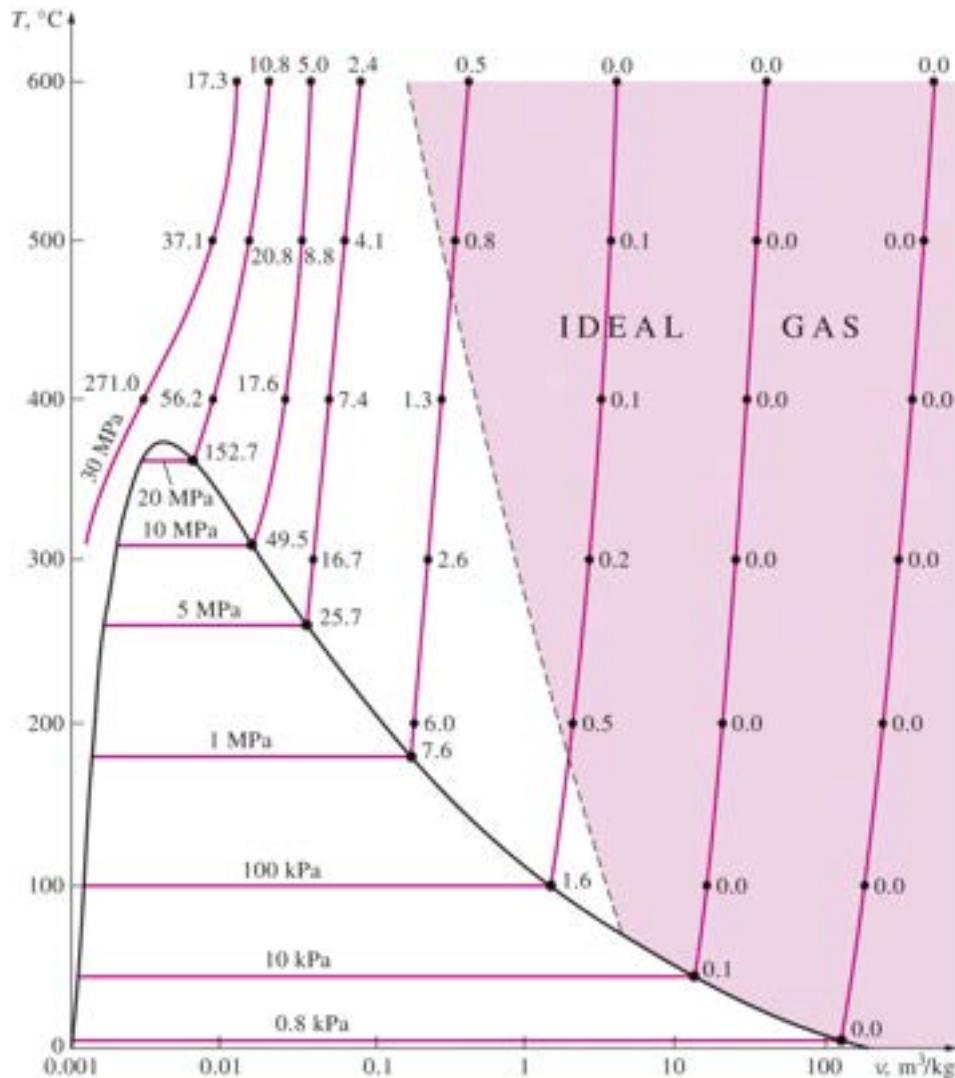
- When is it reasonable to assume that a substance behaves as an ideal gas?
- An ideal gas is one that follows the ideal gas law, $Pv = RT$
- All real gases deviate significantly from the ideal gas law near their saturation region (see graph), but they behave more and more like an ideal gas farther into the superheated region
- The generalized compressibility factor, Z , is used to quantify how closely a substance behaves to an ideal gas
- Z is dimensionless and defined as: $Z = \frac{Pv}{RT}$
- The closer Z approaches 1 the better the gas approximates an ideal gas



Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.

Is Water Vapor an Ideal Gas?

- At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent)
- At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line
- In air-conditioning applications, the water vapor in the air can be treated as an ideal gas
- In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations cannot be used



Percentage of error ($\left[\frac{|v_{\text{table}} - v_{\text{ideal}}|}{v_{\text{table}}} \right] \times 100$) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.

Other Equations of State

- Besides the ideal gas equation of state there are other equations of state for specific situations to relate P, T and v for gases
- The **Van der Waals' equation** (1873), is an attempt to remove restrictions of the ideal gas law, if $a = 0$ and $b = 0$ this reduces to the ideal gas equation

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

- The **Redlich-Kwong Equation** is accurate at temperatures above T_{CR}

$$P = \frac{RT}{v-b_{RK}} - \frac{a_{RK}}{v(v+b_{RK})T^{1/2}}$$

- The **Benedict-Webb-Rubin Equation of State** (1940), describes the PvT-behavior of hydro-carbons, constants are given in table 3-4

$$P = \frac{RT}{v} + \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) \left(\frac{1}{v^2} \right) + \frac{(bRT-a)}{v^3} + \frac{\alpha a}{v^6} + c \frac{1+\gamma/v^2}{v^3 T^2} \exp\left(\frac{-\gamma}{v^2}\right)$$

- The **Virial Equation of State**, where B, C, ... are functions of temperature)

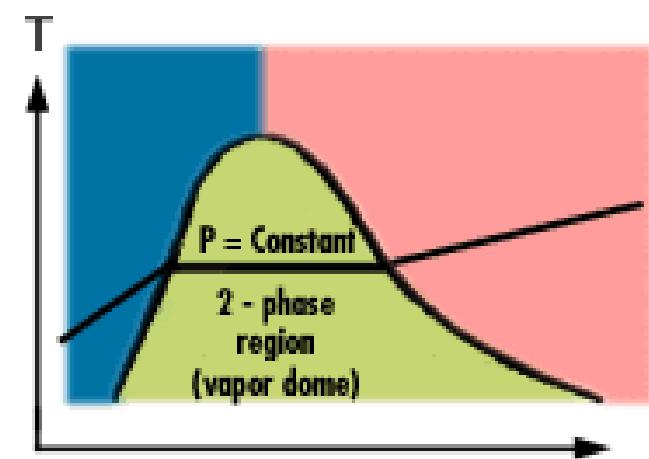
$$P = \frac{RT}{v} \left(1 + \frac{B}{v} + \frac{C}{v^2} + \dots \right)$$

Case Math B2: Van der Waals en Virial Equation of State.

Not for the exam

Internal Energy

- The **internal energy** is the energy associated with intermolecular motion, electronic and translational kinetic energy
- Internal energy (like other energies) is measured relative to a reference state (in contrast to e.g., temperature measured relative to the lowest possible temperature and pressure measured relative to vacuum)
- Internal energy is a property and therefore it can be described by two other independent properties e.g., T and P
 - For a real (not ideal) gas, $u = u(T, P)$
 - For an **ideal gas**, $u = u(T) \neq u(P)$
(prove in module 3)
- Outside the two-phase region there is a relation between u and T
- Inside the two-phase region u is independent of T , but depends on the quality of the mixture, x



Enthalpy

- Enthalpy is like internal energy
- Enthalpy is also measured relative to a reference state also
- Enthalpy is also a property and therefore it can be described by two other independent properties, e.g., T and P
- **Enthalpy**
 - Recall $h = u + Pv$
 - For a real (not ideal) gas, $h = h(T, P)$
 - For an ideal gas, $Pv = RT \rightarrow h = u(T) + RT$
 - Therefore, for an **ideal gas**, $h = h(T) \neq h(P)$ (prove in module 3)
- T, u and h are **dependent** properties for ideal gases
- Changes of u & h with respect to T are very important as thermodynamics deals with energy changes and differences
- For an isothermal process u and h are constant for ideal gases

Specific heat

- **Specific heat, c [kJ/kgK]**: the amount of energy required to raise the temperature of a unit mass of a substance by one degree in a specified way
- Approximately specific heat is defined as: $c = \frac{de}{dT}$
- The specific heat depends on:
 - the substance (water, oil, air, helium, steel, wood,...)
 - the temperature
 - the process (constant pressure or constant volume)
- Values for the specific heat of solid, liquids and various gases can be found in tables 2 and 3

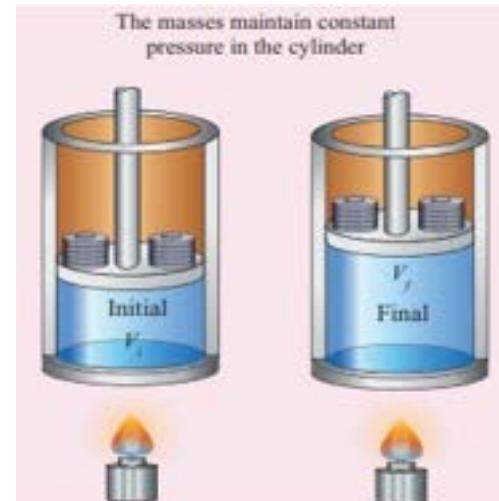
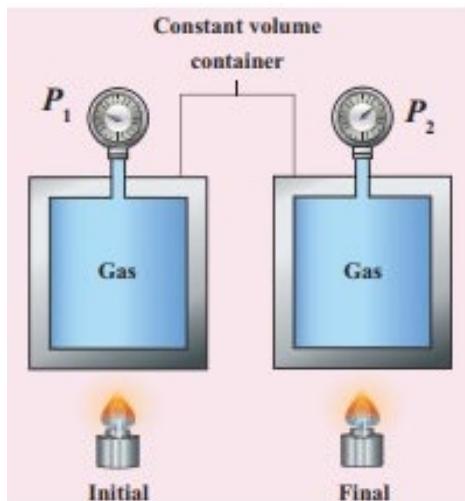


Specific heat – different process

- Depending on the **process** different forms of heat capacity are defined:
 1. **Specific heat at constant volume, c_v :** The energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant
 2. **Specific heat at constant pressure, c_p :** The energy required to raise the temperature of the unit mass of a substance by one degree as the pressure is maintained constant
- Specific heat capacity (c_v) for **constant volume** process: $c_v = \left(\frac{\partial u}{\partial T}\right)_v$
- Specific heat capacity (c_p) for **constant pressure** process: $c_p = \left(\frac{\partial h}{\partial T}\right)_p$
- In general $c_p > c_v$ as extra energy is needed to expand the volume in order to keep the pressure constant ($\delta w = Pdv$)

Specific heat – different process

- The **specific heat** depends on the **substance** and the **process** involved, imagine a volume with gas, which process costs more energy?
 1. Heating at constant volume (isochoric) → P as well as T will increase
 2. Heating at constant pressure (isobaric) → v as well as T will increase



Adding heat in an isochoric process results in an increase in temperature, also the pressure increases but no work is performed.

Adding heat in an isobaric process results in an increase in temperature as well as in an expansion of the volume. Volume work is performed on the environment, $\delta w = Pdv$.

- To achieve the same rise in temperature for the isobaric process more energy is needed as part of it is converted into work done on the environment, therefore $c_p > c_v$

Specific Heats for Ideal Gases

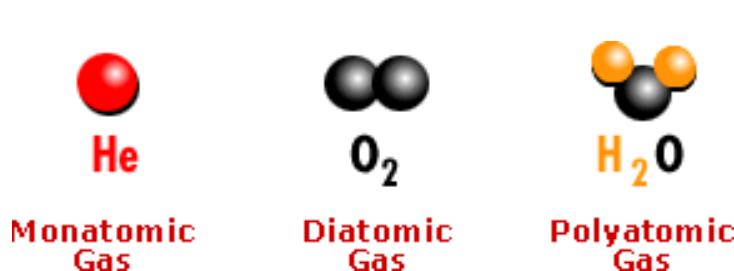
- In general, internal energy and enthalpy are functions of T and P, however, for an ideal gas, these properties are functions of temperature only (prove in module 3), therefore specific heats are functions of temperature only
- Enthalpy for an **ideal gas**, $h = h(T) \neq h(P)$ and

$$c_P = \left(\frac{\partial h}{\partial T} \right)_P = \frac{dh}{dT} \rightarrow \boxed{dh = c_P dT} \rightarrow \Delta h = \int_{T_1}^{T_2} c_P dT$$

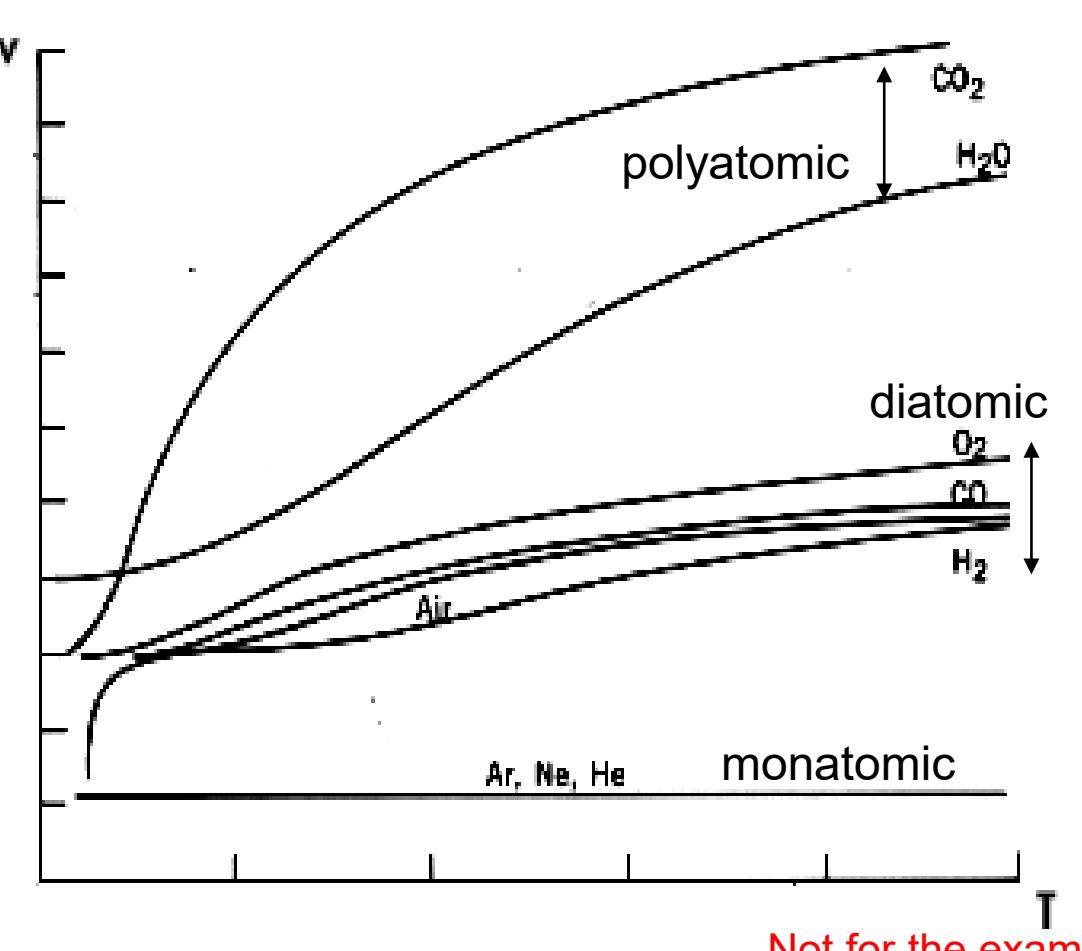
- Similarly, **internal energy** for **ideal gas**, $u = u(T) \neq u(P)$ and
- $c_v = \left(\frac{\partial u}{\partial T} \right)_v = \frac{du}{dT} \rightarrow \boxed{du = c_v dT} \rightarrow \Delta u = \int_{T_1}^{T_2} c_v dT$
- In general, the specific heat depends on temperature ($c_i = c_i(T)$) which makes the integral touch to evaluate

Specific Heats for Ideal Gases

- Specific heat at constant volume versus temperature for three types of gases



- For a non monatomic gas (e.g. O₂, H₂O) the specific heat depends on the temperature
- For a monatomic gas (e.g. He) the specific heat is constant



Not for the exam

Specific Heats for Ideal Gases

- For ideal gases always: $\Delta u = \int_{T_1}^{T_2} c_v dT$ & $\Delta h = \int_{T_1}^{T_2} c_p dT$ as the specific heat does not depend on temperature
- For ideal gases, the specific heat at constant pressure and constant volume are related (use $h = u + Pv$)
 - $dh = du + d(Pv) = du + d(RT) = du + RdT$ (as $Pv = RT$)
 - $c_p dT = c_v dT + RdT$ (as $dh = c_p dT$ and $du = c_v dT$)
 - $(c_p - c_v)dT = RdT$
 - and therefore: $R = c_p - c_v$ ($c_p > c_v$)

Specific Heats for Solids and Liquids

- Unlike gases, **solids and liquids** are **incompressible**, and therefore there is no difference in the specific heat for constant volume or pressure
- The volume does not change $\rightarrow v = \text{constant} \rightarrow dv = 0$
- No difference between specific heat for constant pressure and constant volume
$$\left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\partial(u + Pv)}{\partial T}\right)_P = \left(\frac{\partial u}{\partial T}\right)_P + \left(v \frac{\partial P}{\partial T}\right)_P + \left(P \frac{\partial v}{\partial T}\right)_P \approx \frac{\partial u}{\partial T}$$
 - $c_p = c_v$ (often denoted as c) and therefore: $\Delta u = \Delta h = \int_{T_1}^{T_2} cdT$
 - Values of c_p and c_v can be found in tables 2 and 3
- **Example:** water enters a cooling tower at 10 degree C and leaves it at 15 degree C. How much energy is transferred to the water per kg?

Energy balance: $e_{in} = e_{out} \rightarrow (h + ke + pe + q + w)_{in} = (h + ke + pe + q + w)_{out}$
neglecting ke , pe energie and realizing that w_{out-in} and q_{out} are zero this reduces to:

$$q_{in} = h_{out} - h_{in} = \Delta h = \int_{T_{in}}^{T_{out}} cdT = c(T_{out} - T_{in}) = 4.2(15 - 10) = 21 \text{ kJ/kg}$$

BREAK



<https://www.cafepress.com/+thermodynamics+mugs>

Entropy Change for Ideal Gases

- An expression for the entropy change of an ideal gas can be derived from the Gibbs equations
- First, we use the Gibbs equation with the internal energy
- For **internal energy**, the Gibbs equations is: $du = Tds - Pdv$
- This can be rewritten to: $ds = \frac{du}{T} + \frac{P}{T} dv$ (*)
- For an ideal gas it holds: $du = c_v dT$ and $Pv = RT$
- Substituting these relations in * results in: $ds = \frac{c_v dT}{T} + \frac{R}{v} dv$
- Integrating: $\int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} \frac{c_v dT}{T} + \int_{v_1}^{v_2} \frac{R}{v} dv$
- The left-hand side and the second part at the right-hand side can be evaluated to: $s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v dT}{T} + R \ln \frac{v_2}{v_1}$ (this is allowed as R is constant)
- As c_v , in general, is a function of T ($c_v(T)$) the integral that is left cannot be evaluated very easily

Entropy Change for Ideal Gases

- A similar derivation can be done for the Gibbs equations with the enthalpy
- For **enthalpy**, the Gibbs equations is: $dh = Tds + \nu dP$
- This can be rewritten to: $ds = \frac{dh}{T} - \frac{\nu}{T} dp$ (*)
- For an ideal gas it holds: $dh = c_p dT$ and $P\nu = RT$
- Substituting these relations in * results in: $ds = \frac{c_p dT}{T} - \frac{R}{P} dP$
- Integrating: $\int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} \frac{c_p dT}{T} - \int_{P_1}^{P_2} \frac{R}{P} dP$
- The left-hand side and the second part at the right-hand side can be evaluated to: $s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p dT}{T} - R \ln \frac{P_2}{P_1}$ (this is allowed as R is constant)
- As c_p in general is a function of T ($c_p(T)$) the integral that is left can not be evaluated very easily
- Is this one different from the one resulting from $du = Tds - Pd\nu$?

Entropy Change for Ideal Gases

- Gibbs for u , $du = Tds - Pdv$ gives: $s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v dT}{T} + R \ln \frac{v_2}{v_1}$
- Gibbs for h , $dh = Tds + vdp$ gives: $s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_P dT}{T} - R \ln \frac{P_2}{P_1}$
- Using $c_p - c_v = R$ it can be shown that both equations for $\Delta s = s_2 - s_1$ are equal:

$$\begin{aligned}s_2 - s_1 &= \int_{T_1}^{T_2} \frac{c_v dT}{T} + R \ln \frac{v_2}{v_1} = \int_{T_1}^{T_2} \frac{[c_p - R]dT}{T} + R \ln \frac{v_2}{v_1} \\&= \int_{T_1}^{T_2} \frac{c_p dT}{T} - R \int_{T_1}^{T_2} \frac{dT}{T} + R \ln \frac{v_2}{v_1} = \int_{T_1}^{T_2} \frac{c_p dT}{T} - R \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \\&= \int_{T_1}^{T_2} \frac{c_p dT}{T} - R(\ln \frac{T_2}{T_1} - \ln \frac{v_2}{v_1}) = \int_{T_1}^{T_2} \frac{c_p dT}{T} - R \ln \frac{T_2 v_1}{T_1 v_2} = \int_{T_1}^{T_2} \frac{c_p dT}{T} - R \ln \frac{P_2}{P_1} = s_2 - s_1\end{aligned}$$

- Both relations give the same results
- Which one to use depends on the situation, process and given properties

Entropy Change for Ideal Gases

- Gibbs for u , $du = Tds - Pdv$ gives: $s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v dT}{T} + R \ln \frac{v_2}{v_1}$
- Gibbs for h , $dh = Tds + vdp$ gives: $s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p dT}{T} - R \ln \frac{P_2}{P_1}$
- If c_V or c_P can be assumed **independent** of the temperature, e.g., in a restricted / small temperature range, the integrals are easy to evaluate to give two expressions for the entropy difference

$$s_2 - s_1 = c_V \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad (\text{from } du)$$

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (\text{from } dh)$$

- Both can be used and will give similar results
- Which one is the best to use depends on the given properties of the process e.g., if P is constant, $P_1 = P_2$, then $\rightarrow \ln \frac{P_2}{P_1} = 0$, this can be a reason to choose the second one

Isentropic Process for Ideal Gases

- For an isentropic process, $\Delta s = 0$ and c_p and c_v independent of T the two equations for $s_2 - s_1$ reduce to $0 = \ln \frac{T_2}{T_1} + \frac{R}{c_v} \ln \frac{v_2}{v_1}$ and $0 = \ln \frac{T_2}{T_1} - \frac{R}{c_p} \ln \frac{P_2}{P_1}$

Rewriting the first one $0 = \ln \frac{T_2}{T_1} + \frac{R}{c_v} \ln \frac{v_2}{v_1}$  $\ln \left(\frac{T_2}{T_1} \right)_s = -\frac{R}{c_v} \ln \left(\frac{v_2}{v_1} \right)_s$

and using:

- Define $k = c_p/c_v$
- $R = c_p - c_v$
- $R/c_v = (c_p - c_v)/c_v = k-1$
- Values for k table 2a, 2b
- Air at 300 K, $k = 1.4$

$$\ln \left(\frac{T_2}{T_1} \right)_s = \ln \left(\left(\frac{v_1}{v_2} \right)_s \frac{R}{c_v} \right)$$

$$\exp \left(\ln \left(\frac{T_2}{T_1} \right)_s \right) = \exp \left(\ln \left(\left(\frac{v_1}{v_2} \right)_s \frac{R}{c_v} \right) \right)$$

$$\left(\frac{T_2}{T_1} \right)_s = \left(\frac{v_1}{v_2} \right)_s^{\frac{R}{c_v}}$$

Results in: $\left(\frac{T_2}{T_1} \right)_s = \left(\frac{v_1}{v_2} \right)_s^{k-1} \Rightarrow T v^{k-1} = \text{constant}$

ISENTROPIC PROCESS FOR IDEAL GASES

- From $0 = \ln \frac{T_2}{T_1} + \frac{R}{c_V} \ln \frac{v_2}{v_1}$ we derived $\left(\frac{T_2}{T_1}\right)_S = \left(\frac{v_1}{v_2}\right)_S^{k-1} \Rightarrow T v^{k-1} = \text{constant}$

- Similarly, the second one $0 = \ln \frac{T_2}{T_1} - \frac{R}{c_p} \ln \frac{P_2}{P_1}$ can be rewritten in

$$\left(\frac{T_2}{T_1}\right)_S = \left(\frac{P_2}{P_1}\right)_S^{\frac{k-1}{k}} \Rightarrow \frac{P^{\frac{k-1}{k}}}{T} = \text{constant}$$



- The right-hand side of the first equation equals the right-hand side of the second one and combining both equations results in

$$\left(\frac{P_2}{P_1}\right)_S = \left(\frac{v_1}{v_2}\right)_S^k \Rightarrow P v^k = \text{constant}$$

$$\begin{aligned}\frac{R}{c_p} \ln \left(\frac{P_2}{P_1} \right) &= -\frac{R}{c_V} \ln \left(\frac{v_2}{v_1} \right)_S \\ \left(\frac{P_2}{P_1} \right)_S^{\frac{R}{c_p}} &= -\left(\frac{v_2}{v_1} \right)_S^{\frac{R}{c_V}} \\ \left(\frac{P_2}{P_1} \right)_S &= -\left(\frac{v_2}{v_1} \right)_S^{\frac{c_p R}{R c_V}} \\ \left(\frac{P_2}{P_1} \right)_S &= \left(\frac{v_1}{v_2} \right)_S^{\frac{c_p}{c_V}}\end{aligned}$$

Isentropic Process for Ideal Gases

- For isentropic processes ($\Delta s = 0$) involving an ideal gas and assuming c_p and c_v independent of T the following three relations were derived
- All of them can be used, which one is the most convenient depends on the other known properties of the process

$$\left(\frac{T_2}{T_1}\right)_s = \left(\frac{v_1}{v_2}\right)_s^{k-1} \Rightarrow T v^{k-1} = \text{constant}$$

$$\left(\frac{T_2}{T_1}\right)_s = \left(\frac{P_2}{P_1}\right)_s^{\frac{k-1}{k}} \Rightarrow \frac{P^{k-1}}{T} = \text{constant}$$

$$\left(\frac{P_2}{P_1}\right)_s = \left(\frac{v_1}{v_2}\right)_s^k \Rightarrow P v^k = \text{constant}$$

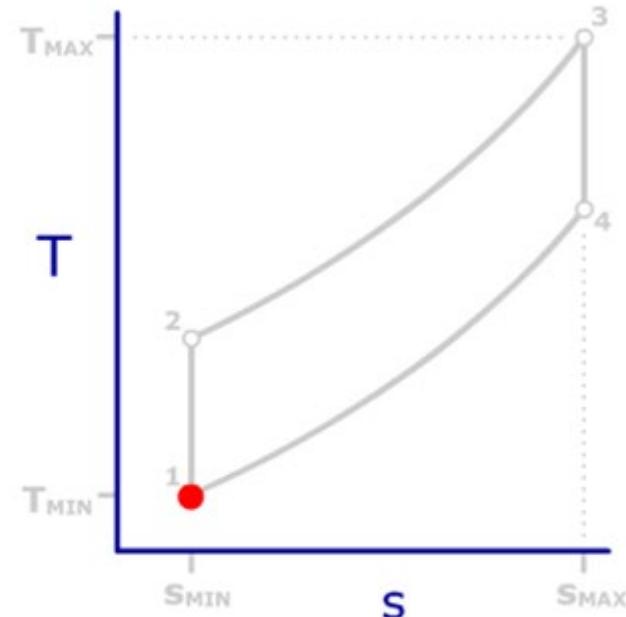
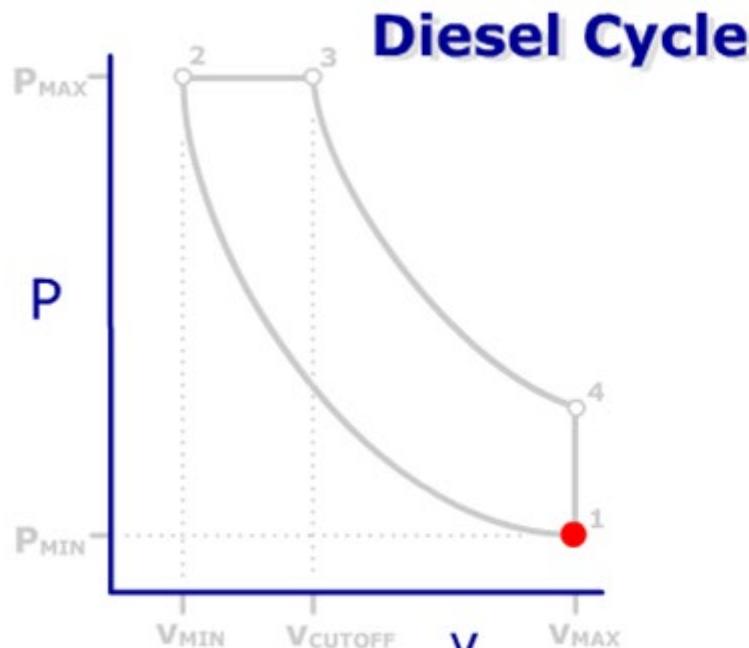
- $k = c_p/c_v$
- $R = c_p - c_v$
- $R/c_v = (c_p - c_v)/c_v = k - 1$

Example: isentropic turbine, $T_{\text{in}} = 800$ degree C, $P_{\text{in}} = 8$ bar, $P_{\text{out}} = 1$ bar. What is T_{out} ?

P and T are given so the second one is the best one to use. For air $k = 1.4$ (table 2):

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)_s^{\frac{k-1}{k}} = 1073 \left(\frac{1}{8}\right)_s^{\frac{1.4-1}{1.4}} = \\ 592 K = 319 C$$

ISENTROPIC PROCESSES IN DIESEL CYCLE

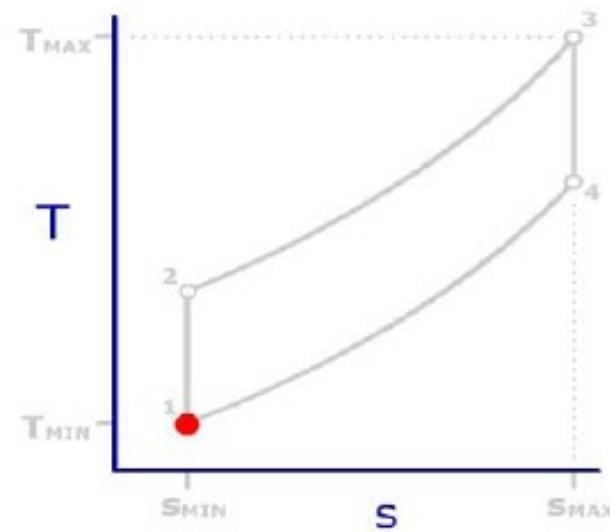


ThermoNet: Wiley

- In a Diesel cycle it is assumed that compression (1-2) and expansion (3-4) are isentropic processes ($\Delta s = 0$). For these processes the relations derived in the previous slides can be used.

Example: Isentropic Process in Diesel Cycle

- Assume a Diesel cycle working on air with the inlet conditions:
 $P_1 = 0.1 \text{ Mpa}$; $T_1 = 27^\circ\text{C}$; $r_v = v_1/v_2 = 20$; $k = 1.4$
- Calculate the pressure and temperature after compression
- Solution:** It is assumed that the compression process is isentropic, $ds = 0$
- Isentropic process $Pv^k = \text{constant}$: $P_2 = P_1 \left(\frac{v_1}{v_2} \right)_s^k = 0.1(20)^{1.4} = 6.6 \text{ MPa}$
- Also, $Tv^{(k-1)} = \text{constant}$: $T_2 = T_1 \left(\frac{v_1}{v_2} \right)_s^{k-1} = 300(20)^{0.4} = 994.3 \text{ K}$
- Also, the ideal gas law is valid for this process but only the ideal gas law is not sufficient to calculate all properties



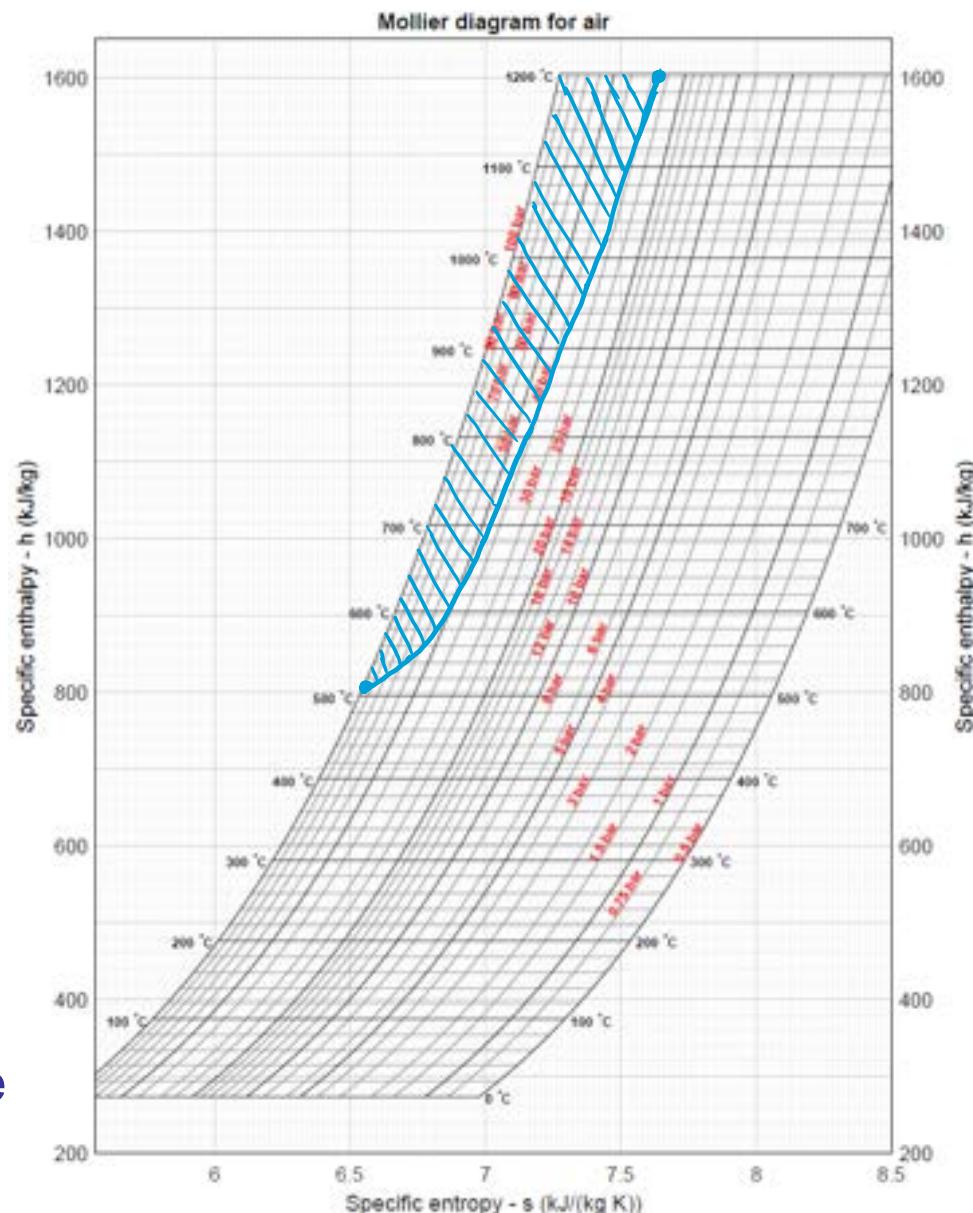
Ideal Gas Tables

- To calculate energy differences for gasses requires knowledge of the values of the specific heats, as a function of temperature
- Correlations exist that provide information on the variation of specific heats with temperature, but evaluating the integrals is tough if c_p and c_v cannot be assumed to be constant (larger temperature range)
- Tabulated data are often used to find changes in internal energy, u and enthalpy, h between states
- Tables relate T , u and h (e.g., table A-17 for air)
- Unlike steam tables, in gas tables the pressure is not tabulated
- Use $Pv = RT$ to relate P , v and T
- Note: energies are measured or given based on a reference state, absolute energies (like absolute pressure and temperature) do not exist
- Different sources can have different reference states
- Lucky, mostly only energy differences are important in thermodynamics



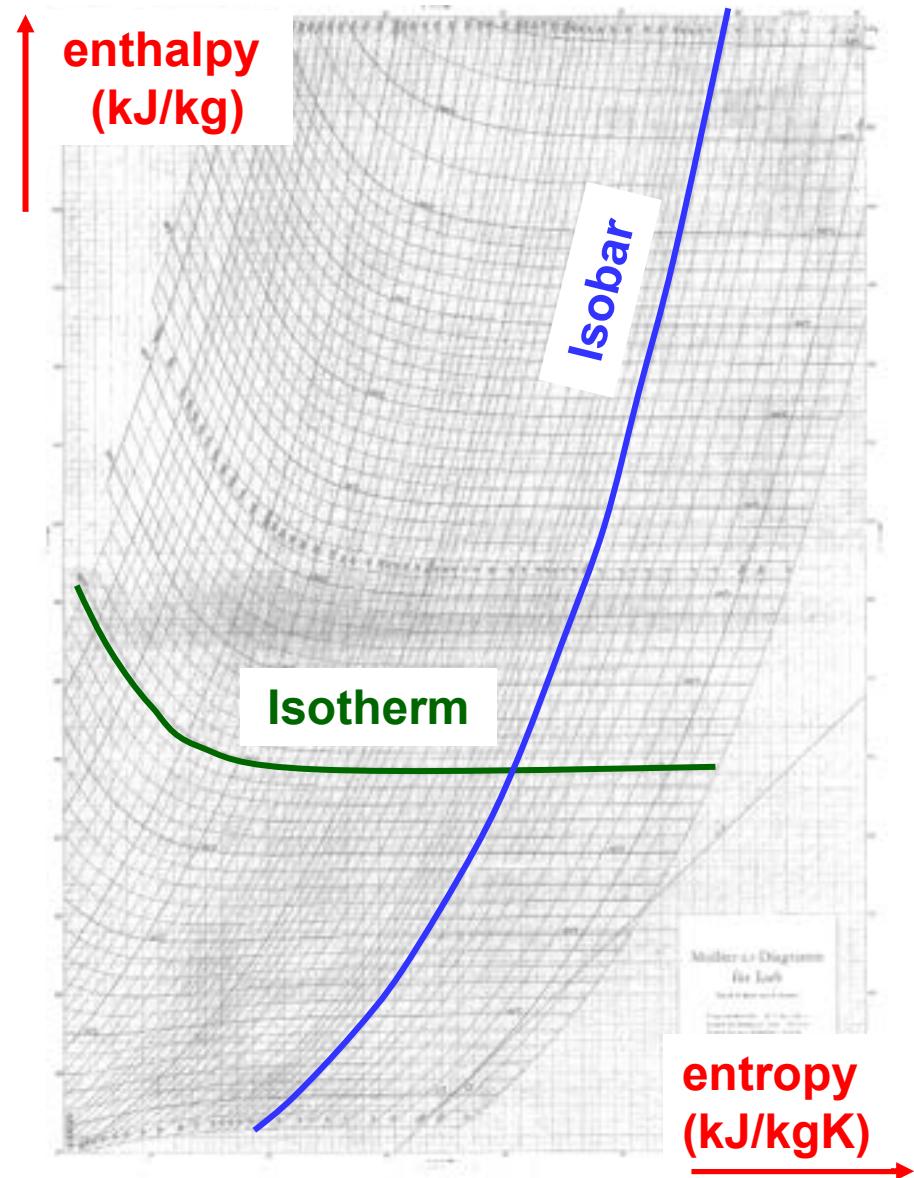
Mollier Diagram Air for Brayton Cycle

- Enthalpy values for air can also be found using the Mollier diagram
- Diagram is less exact, but gives a good overview of the process
- This diagram is made using Matlab
- In the program some assumptions are made, the most important one is that air is assumed to be an ideal gas, however the dependence of the specific heats on temperature is taken into account
- So, the diagram is valid for air assumed to be an ideal gas
- If the air cannot be assumed ideal (high P and high T indicated in blue) the values slightly deviate
- We will use this diagram to analyse the gas power cycles (next class)



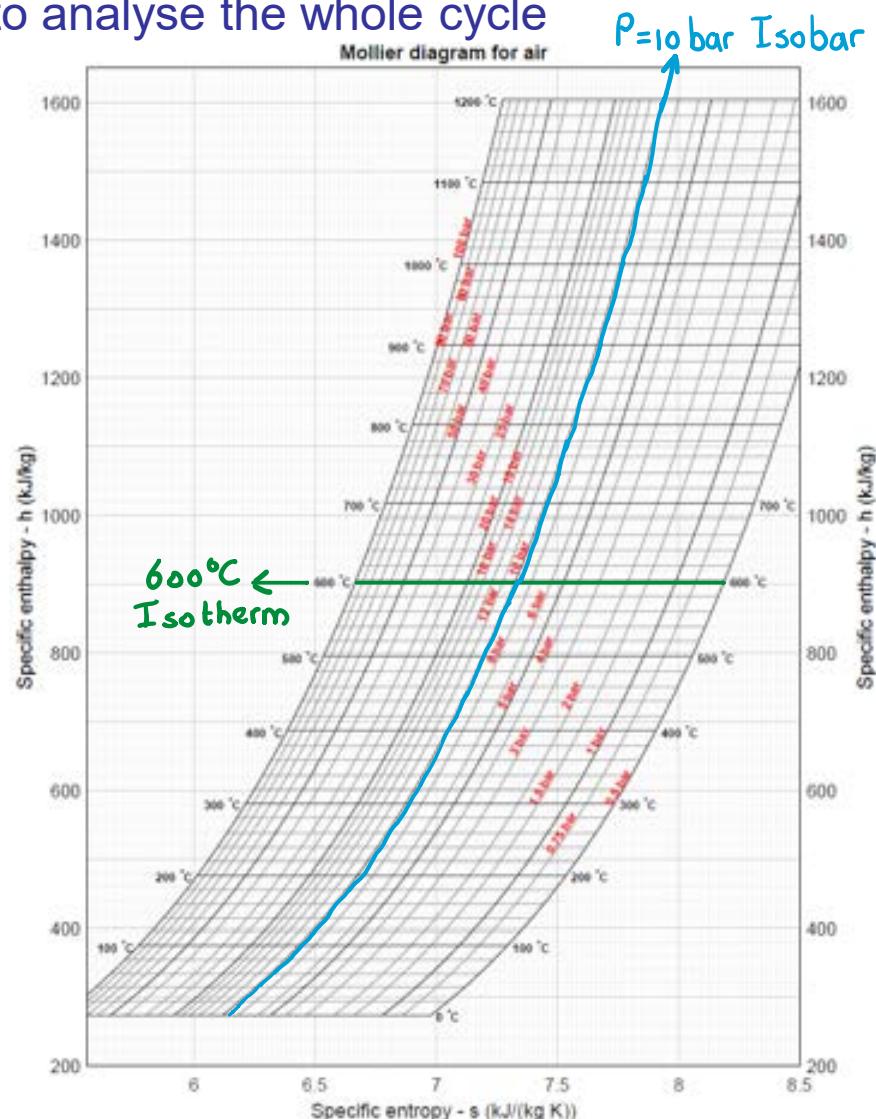
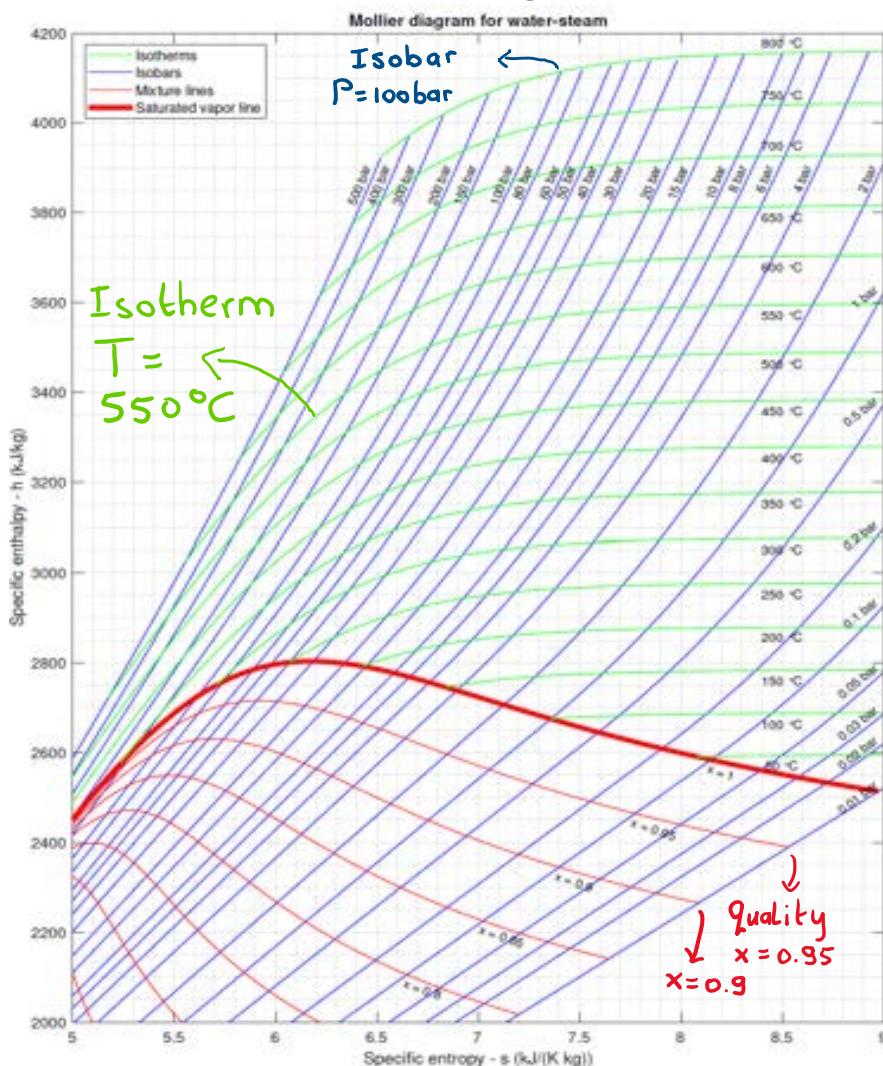
Mollier diagram air

- Scanned version of a Mollier diagram for real air
 - Enthalpy (kJ/kg) on the y-axis, horizontal line → $dh = 0$
 - Entropy (kJ/kgK) on the x-axis, vertical line → $ds = 0$
 - Isobars (in Bar !!)
 - Isotherms (in degree Celsius)
- The main difference with the one in which the air is assumed to be an ideal gas (previous page) is that the isotherms bend upwards in the high T and high P region where the air cannot be approximated as an ideal gas anymore
- This diagram is mostly used in the answers for the assignments

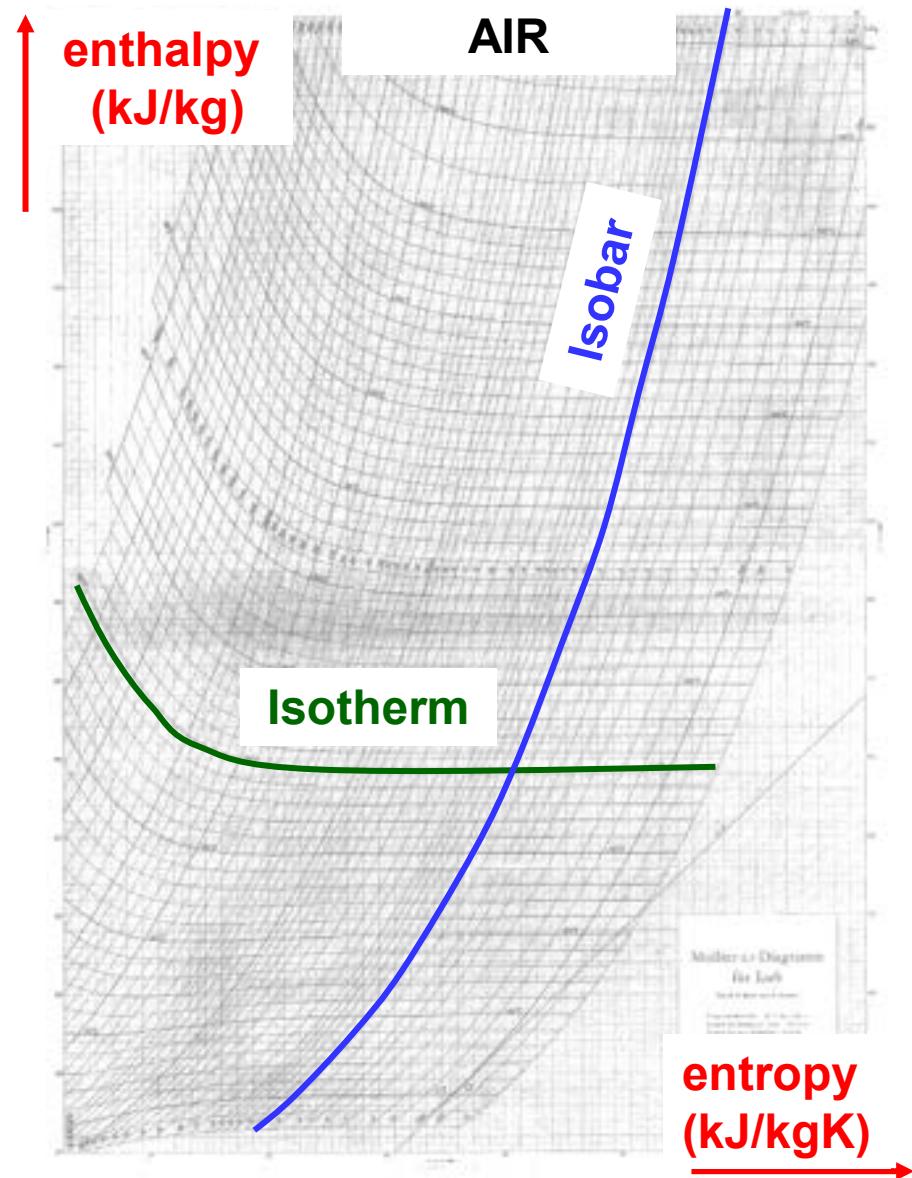
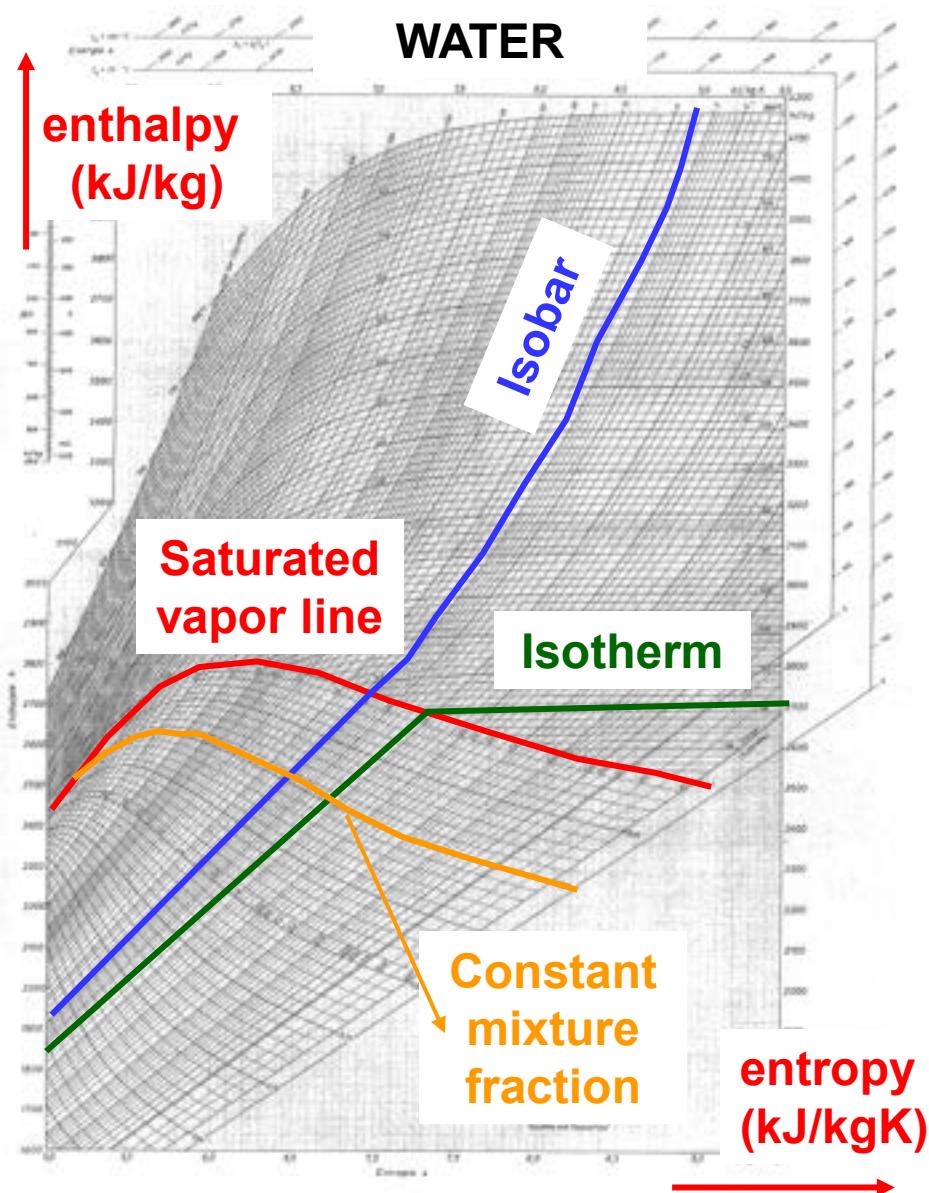


Compare Mollier Diagram Water and Air

- Air: no mixture region and in contrast to the water diagram also data at low T & P are present and the diagram can be used to analyse the whole cycle



Compare Mollier Diagram Water and Air



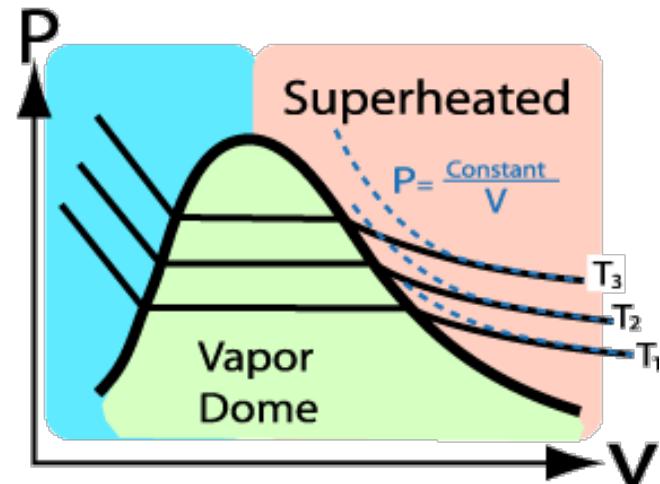
Some Other Thermodynamic Properties

- Besides the specific heat some other thermodynamic properties are needed to describe processes (see module 3)
- **Isothermal compressibility (κ)**: $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$
 - Fractional change in volume for an isothermal change in pressure
- **Coefficient of Thermal Expansion (β)**: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$
 - Fractional change in volume for an isobaric change in temperature
- Together they give for example the change in volume if the pressure and / or temperature are changed: $\frac{dv}{v} = \beta dT - \kappa dP$
- **Joule Thompson Coefficient (μ)**: $\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$
 - Change of temperature for a constant enthalpy (isenthalpic) change of the pressure (throttling)

Not for the exam

Recapitulate class 9

- Ideal gas equation of state: $Pv = RT$
- Tables for ideal gas
- Mollier diagram for air
- Specific heat
 - Constant pressure specific heat, c_p
 - Constant temperature specific heat, c_v
- Relation between them: $c_p - c_v = R$
- Internal energy and enthalpy of ideal gases depends on temperature only, u and h for ideal gas: $du = c_V dT$ and $dh = c_p dT$
- Entropy ideal gas: $s_2 - s_1 = c_V \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$ & $s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$
- Isentropic processes for ideal gas:



$$Pv^k = \text{constant} \quad \& \quad T v^{k-1} = \text{constant} \quad \& \quad \frac{P^{\frac{k-1}{k}}}{T} = \text{constant}$$

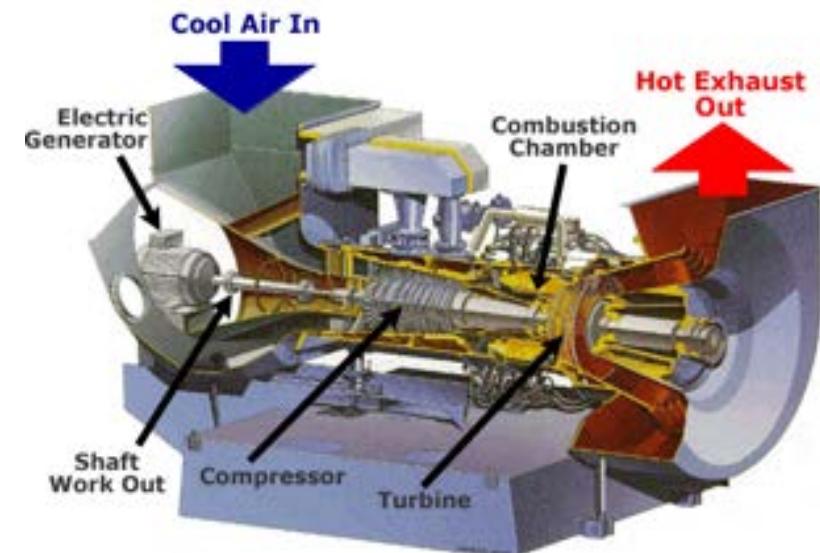
Next Class 10: Gas Power Cycles - Simple

- **Gas power cycles**, cycles using gas as working fluid through the whole cycle to produce power
 - Air-standard cycle
 - Open and closed Brayton cycle
 - Ideal and real Brayton cycle
 - Power in- and output
 - Thermal efficiency
 - Comparison to the Rankine cycle
 - Design parameters
 - Mollier diagram for air



How do jet engines work?

<https://www.youtube.com/watch?v=eA699AKxT7s>



A basic gas turbine engine

Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal efficiency $\eta_{thermal} = \frac{Net\ electrical\ power\ output}{Rate\ of\ fuel\ energy\ input} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Mixture fraction $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$

- Ideal gas law $Pv = RT$, $c_p - c_v = R$
- For an ideal gas $du = c_v dT$ and $dh = c_p dT$

- Conservation of mass $m_{in} = m_{out}$, mass flow rate $\dot{m} = \rho v A$

- Conservation of energy, first law of thermodynamics

- Closed system $du = \delta w - \delta q \rightarrow \Delta u = w - q$
- 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 $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)

- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$

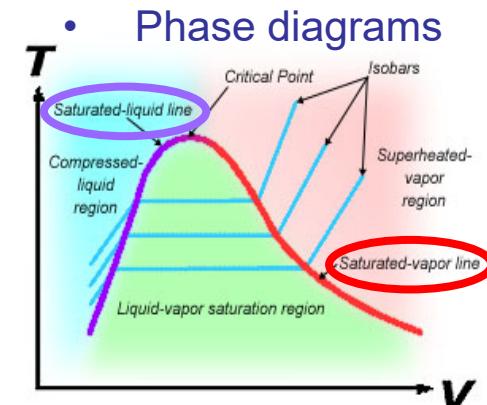
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdp$

- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$

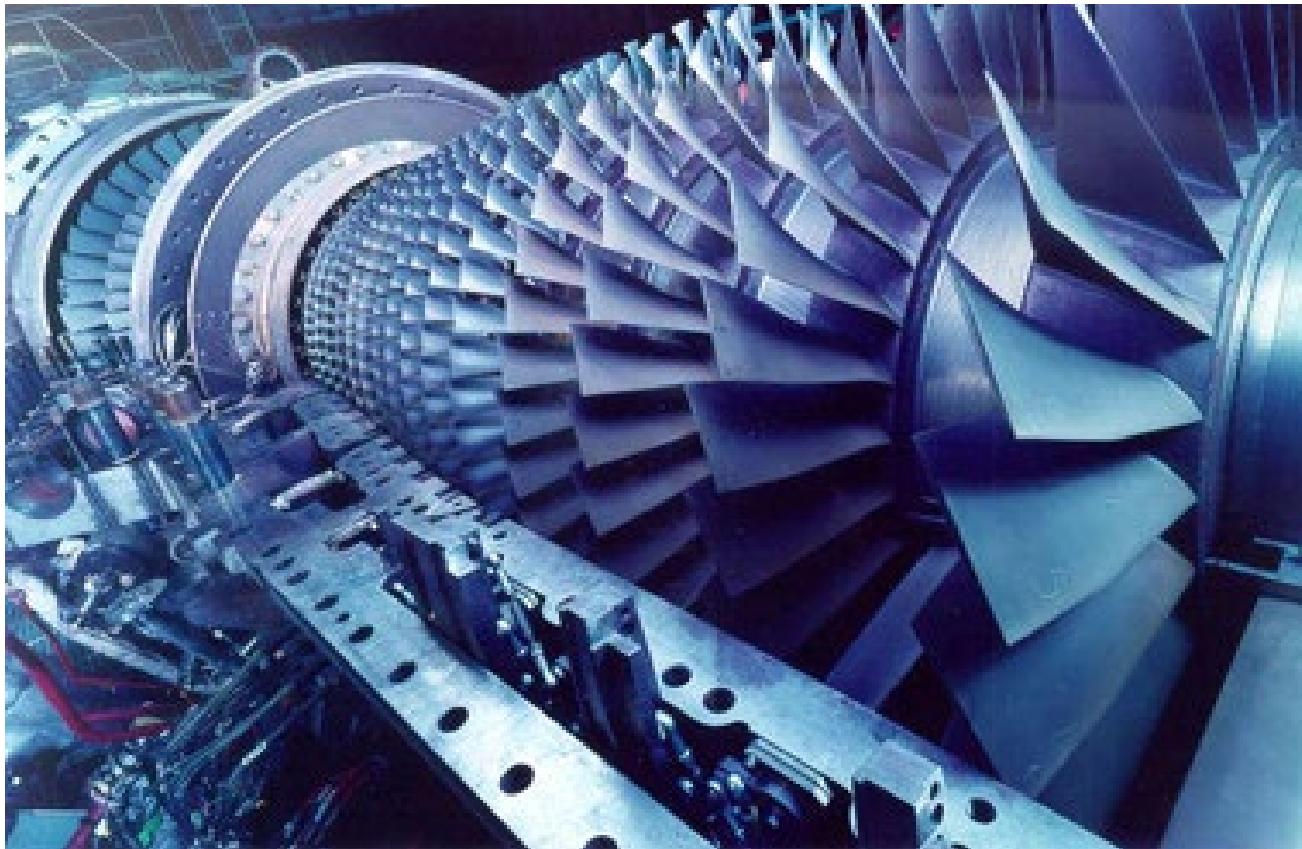
- Isentropic processes ideal gas $Pv^k = \text{constant}$, $Tv^{k-1} = \text{constant}$, $P^{(k-1)/k}/T = \text{constant}$

- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$

Carnot efficiency $\eta_{Carnot} = 1 - \frac{T_{cold}}{T_{hot}}$



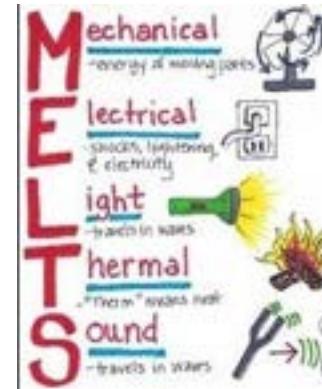
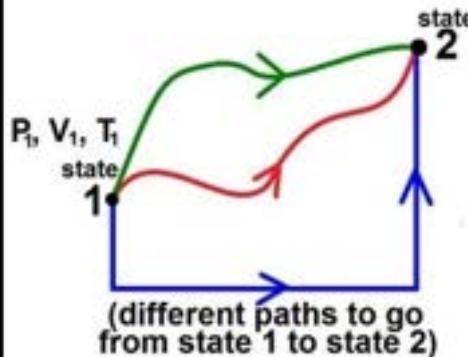
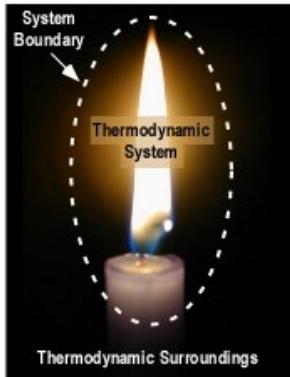
Class 10: Gas power cycles, simple Brayton cycle



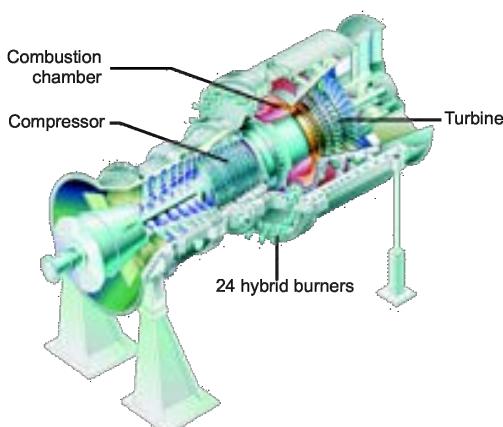
Gas turbine (Beavers Technologies Ltd.)

Roadmap Engineering Thermodynamics

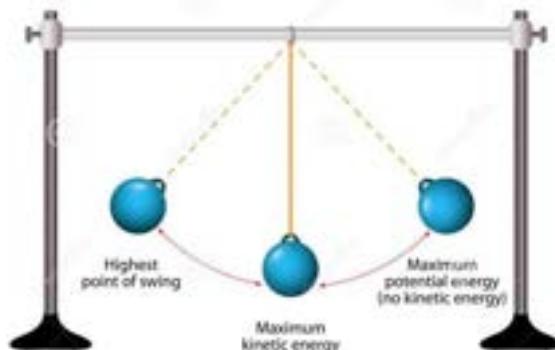
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



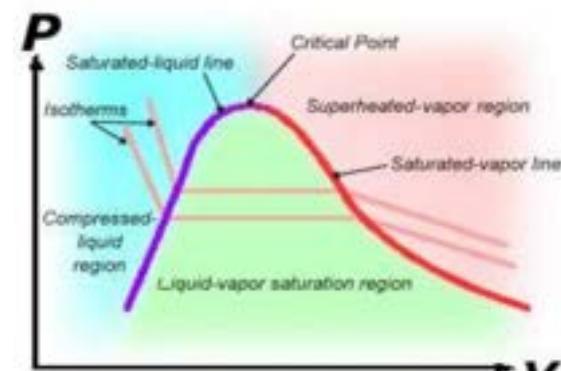
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

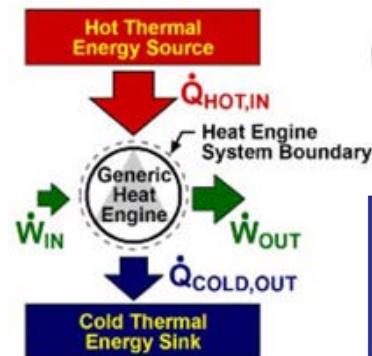


- Properties of Substances (Class 3, 9)

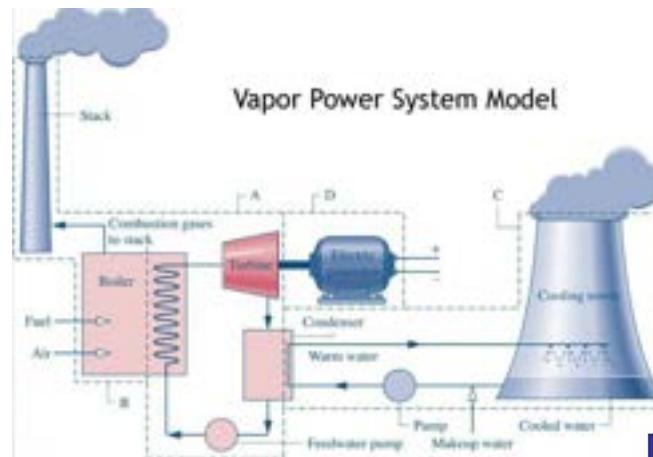


Roadmap Engineering Thermodynamics

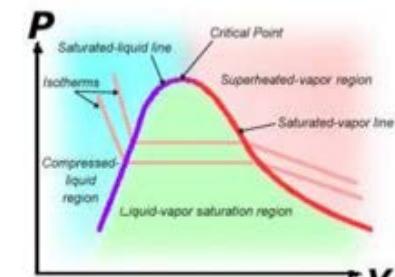
Thermodynamic cycles (Class 6)



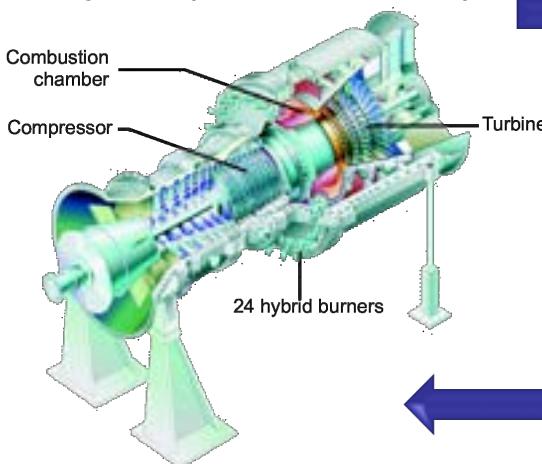
Vapor power cycles – Rankine cycle (Class 7, 8)



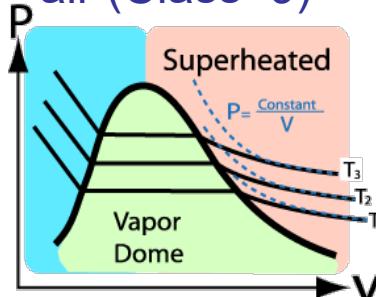
Properties of water (Class 3)



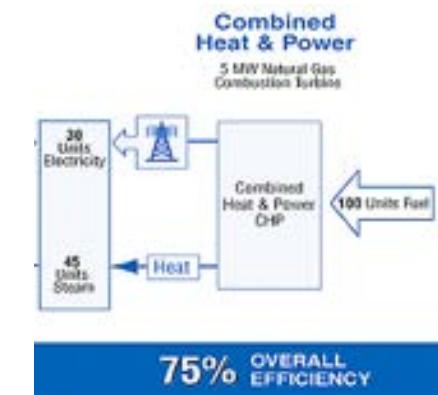
Gas power cycles – Brayton cycle (Class 10, 11)



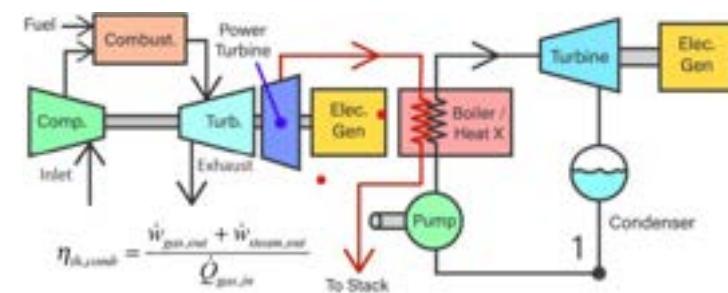
Properties of air (Class 9)



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

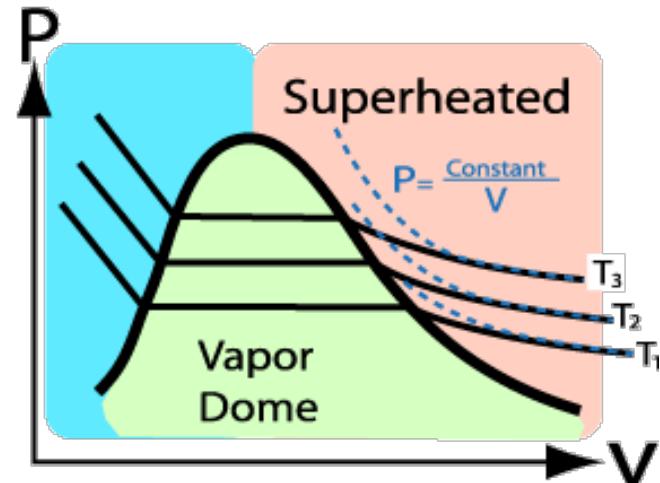


75% OVERALL EFFICIENCY



Recapitulate class 9

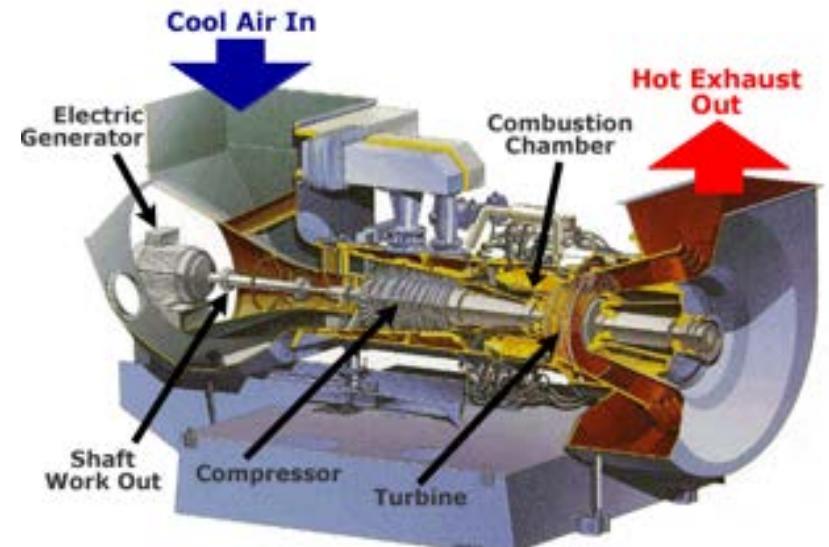
- Ideal gas equation of state: $Pv = RT$
- Tables for ideal gas
- Mollier diagram for air
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 - Constant pressure specific heat, c_p
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- Isentropic processes for ideal gas:



$$Pv^k = \text{constant} \quad \& \quad T v^{k-1} = \text{constant} \quad \& \quad \frac{P^{\frac{k-1}{k}}}{T} = \text{constant}$$

Content Class 10

- **Gas power cycles – Brayton cycle, simple**
- **Gas power cycles**, cycles using gas as working fluid through the whole cycle to produce power
 - Air-standard cycle
 - Open and closed Brayton cycle
 - Ideal and real Brayton cycle
 - Power in- and output
 - Thermal efficiency
 - Comparison to the Rankine cycle
 - Design parameters
 - Mollier diagram for air
- **Learning goal:** recognize a simple thermodynamic system to produce work, explain the configuration, analyse the thermodynamic aspects from the viewpoint of the first law of thermodynamics, interpret and evaluate the results and suggest improvements



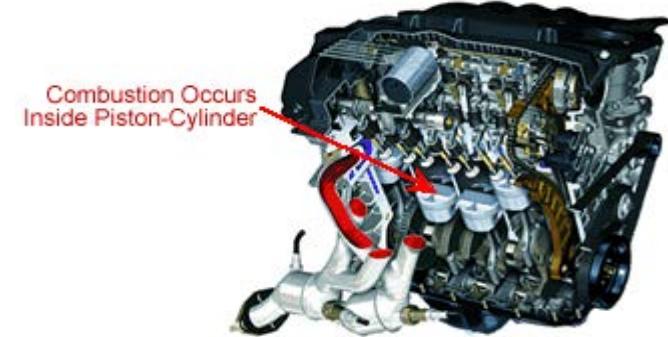
A basic gas turbine engine

Open and Closed Gas Power Cycles

- **Gas power cycles** use gas as working fluid throughout the whole cycle

- **Open cycle**

- Working fluid exchanged with environment (intake & exhaust)
- Internal Combustion (IC)
- Working fluid: $\text{Air} + \text{Fuel} \rightarrow \text{Air} + \text{Combustion Products}$
- Examples: Otto, Diesel, Brayton (Gas Turbine) cycles



Solar Stirling engine

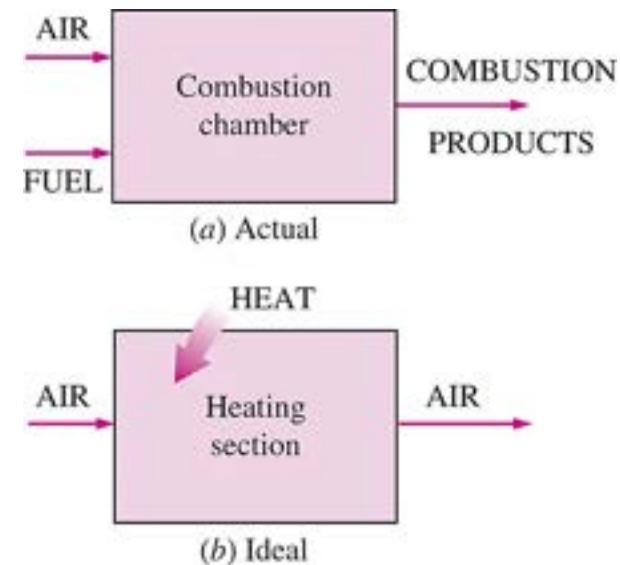
- **Closed cycle**

- Working fluid completely sealed (not exchanged with environment)
- External “Combustion” (EC), nuclear & geothermal, solar energy possible
- Helium common working fluid
- Example: Stirling



The Air Standard Cycle

- The **air-standard cycle** approximates the actual, real gas cycle with some simplifications
 - Good for comparing trends
 - Not good for detailed analyses
- **Air-standard assumptions**
 1. The working fluid is air, which continuously circulates in a closed loop and always behaves as an ideal gas (fuel and combustion products are neglected)
 2. All the processes that make up the cycle are internally reversible
 3. The combustion process is replaced by a heat-addition process from an external source
 4. The exhaust process is replaced by a heat-rejection process that restores the working fluid to its initial state
- **Cold-air-standard assumptions:** the working fluid is considered to be air with constant specific heats at room temperature (25°C)

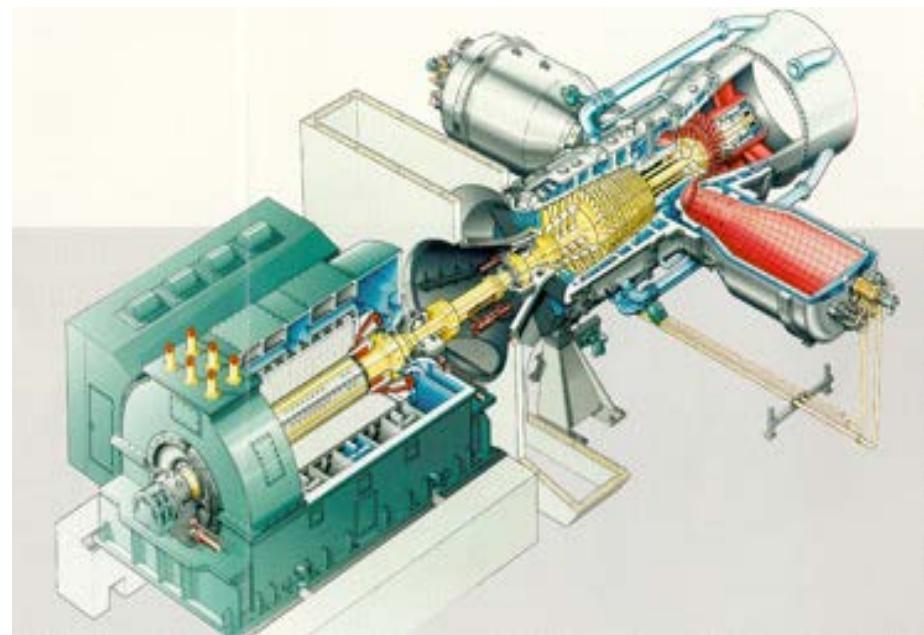


The Brayton Cycle

- The **Brayton cycle** refers to the cycle associated with gas turbine - compressor engines
- They are used in
 - Aircraft
 - Ships
 - Stationary power generation

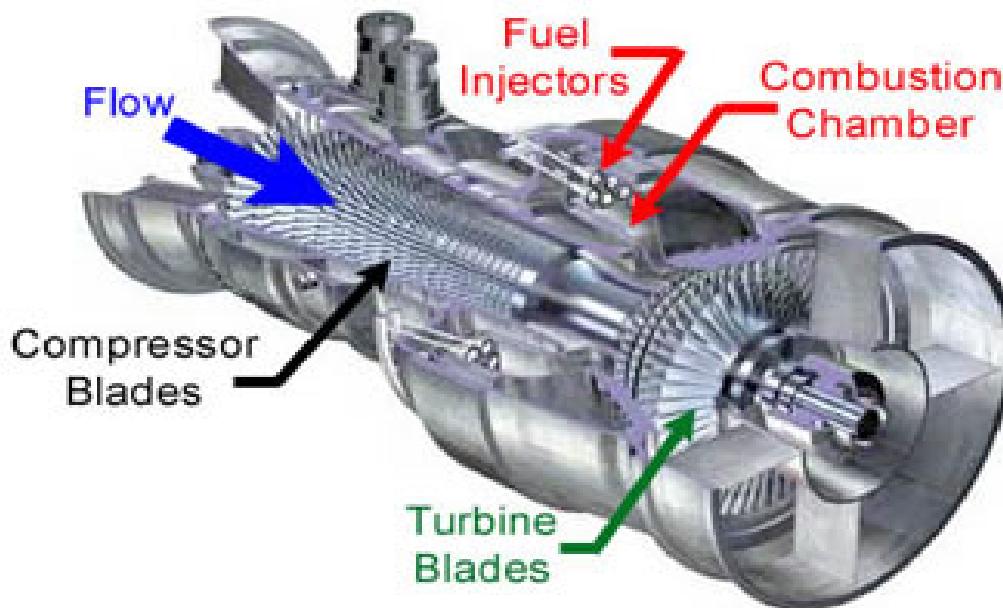


Siemens V94.3 200 MW Gas turbine cycle for electricity production (the green device connected to the axis is the generator)



The Brayton Cycle

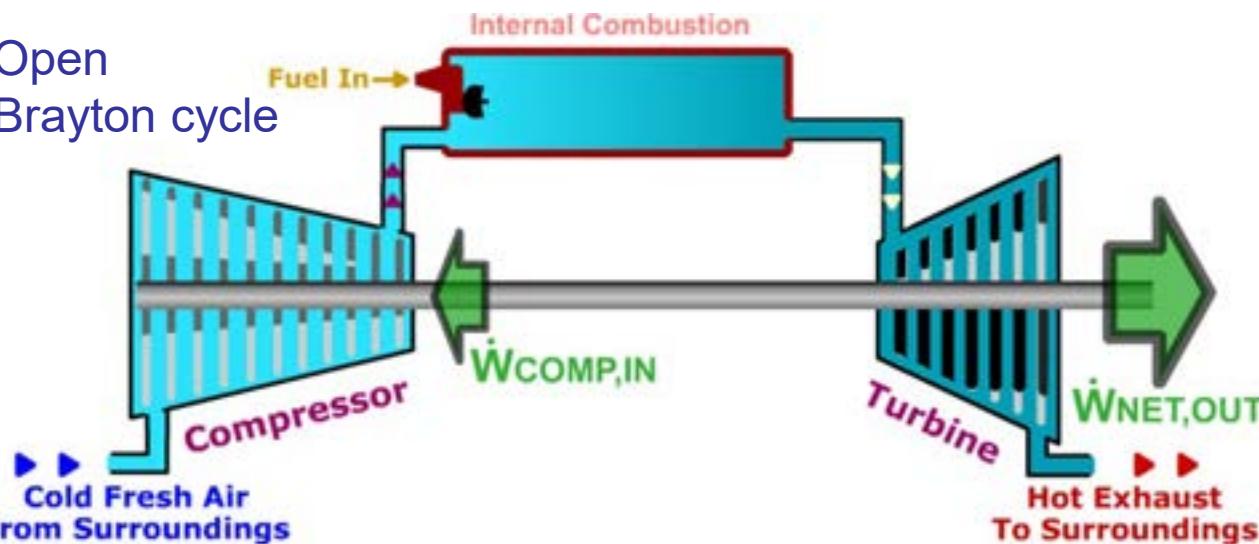
- The cycle is originally developed by **George Bailey Brayton** (1830-1892) for use in piston engines
 - 2 constant pressure and 2 constant entropy processes (ideal)
- **Open** versus **closed** Brayton cycle
 - Commercial gas turbines are open cycles
 - Some research gas turbines are closed cycles



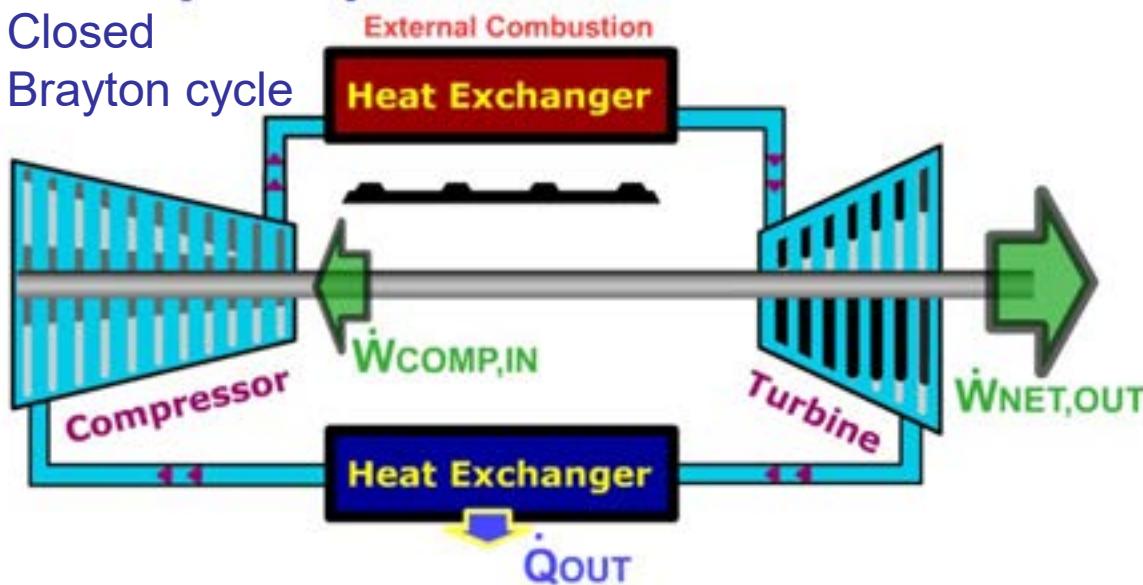
- Why can a gas turbine cycle working with air not be a closed cycle?

Open versus closed Brayton Cycle

Open
Brayton cycle



Closed
Brayton cycle



- Almost all gas turbine cycles commercially used are open cycles
- Why can a gas turbine cycle working with air not be a closed cycle?
- The use air with internal combustion, this consumes the oxygen in the air, after a few rounds there is not enough oxygen left for the combustion process

Gas Turbine Rotor



V94.2, 157 MW, rotor



V64.3A, 67 MW, rotor / annulaire combustor



Principle of the Ideal Brayton Cycle

Principle of the ideal closed Brayton cycle (reversible)

- **1 → 2: Isentropic compression (w_{in})**

Air enters the compressor and is compressed to a higher pressure, the compressor is assumed to be adiabatic and ideal (reversible, isentropic) work is taken from the turbine

- **2 → 3: Isobaric heat addition (q_{in})**

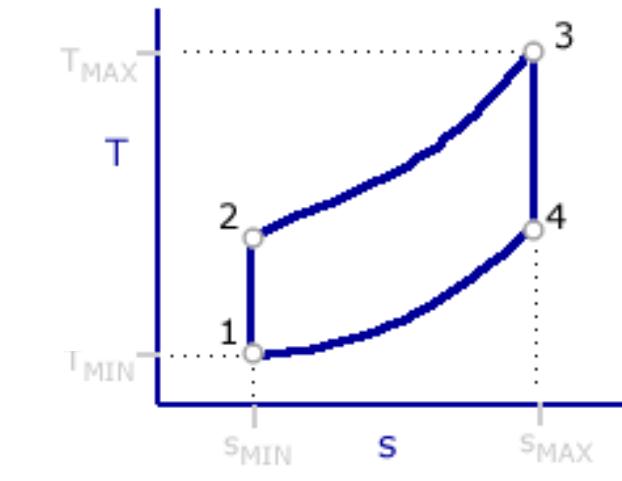
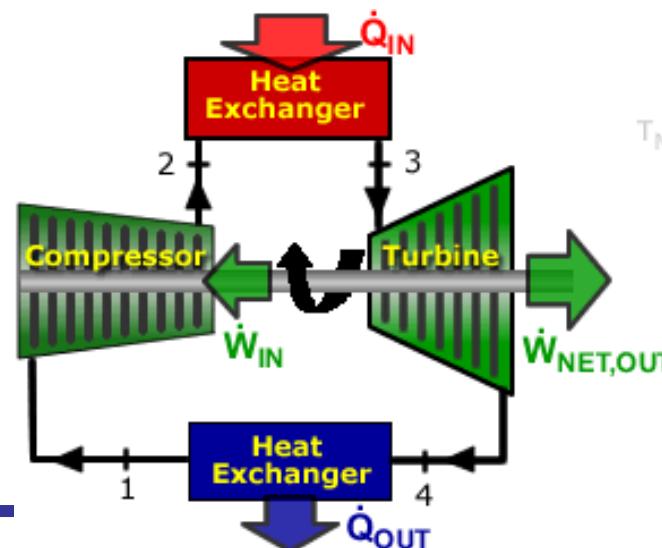
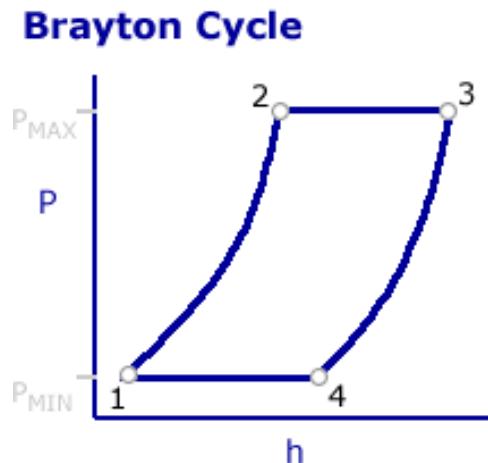
At high pressure, combustion occurs in the combustion chamber, heat is added at constant (high) pressure

- **3 → 4: Isentropic expansion (w_{out})**

The hot gasses are expanded in the turbine producing work, the turbine is assumed to be adiabatic and ideal (reversible, isentropic)

- **4 → 1: Isobaric heat rejection (q_{out})**

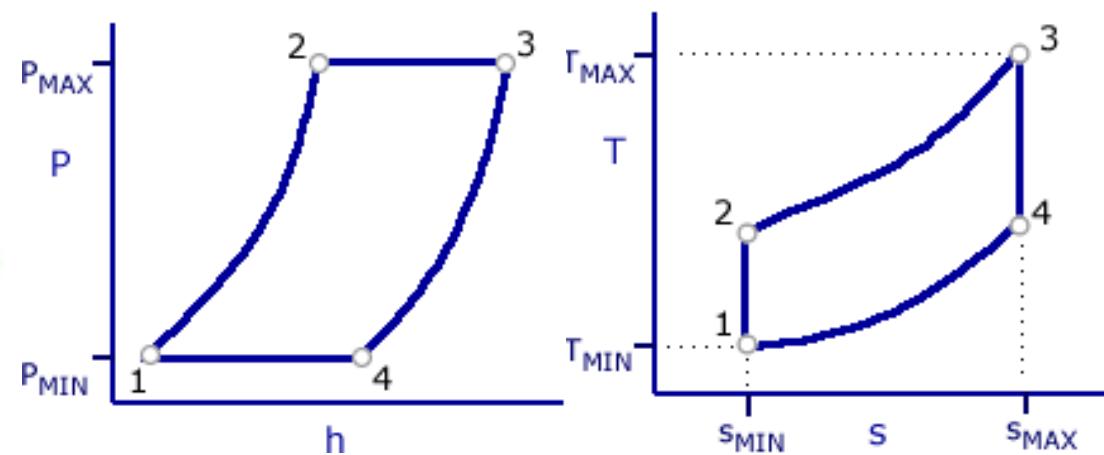
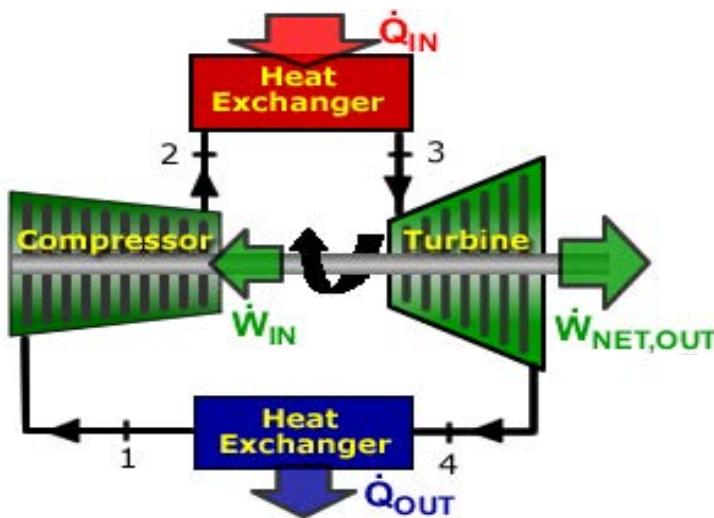
Heat rejection at constant low pressure, in a closed cycle a heat exchanger is used to cool the gases till the inlet temperature, **in an open cycle the gases are feed into the air**



Ideal Brayton Cycle Analysis

- Closed ideal Brayton cycle (Reversible $\rightarrow s_{\text{GEN}} = 0$)

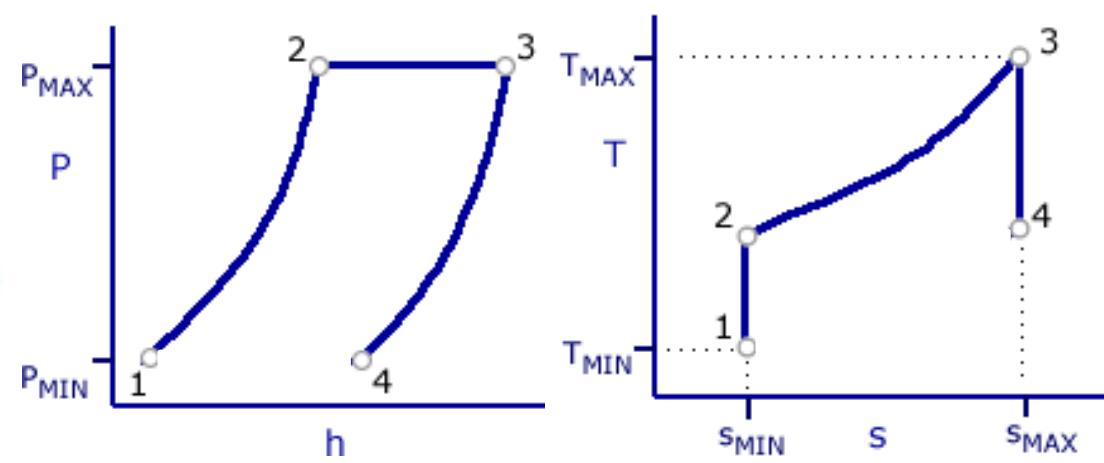
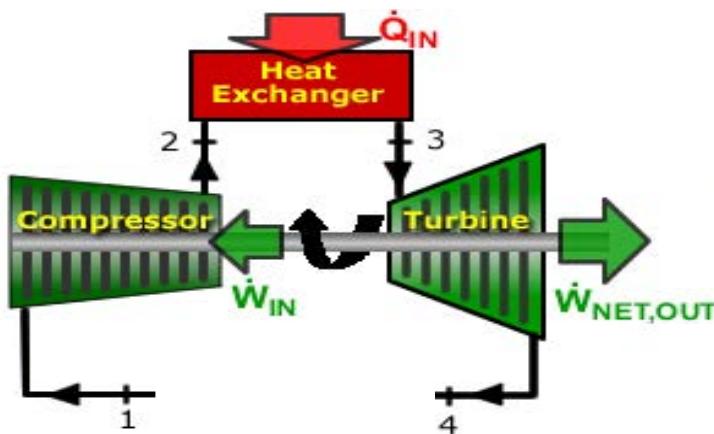
Process	Component	q	w	Const.
$1 \rightarrow 2$ Isentropic compression	Compressor	0	w_{IN}	s
$2 \rightarrow 3$ Isobaric heating	Heat Exchanger	q_{IN}	0	P
$3 \rightarrow 4$ Isentropic expansion	Turbine	0	w_{OUT}	s
$4 \rightarrow 1$ Isobaric cooling	Heat Exchanger	q_{OUT}	0	P



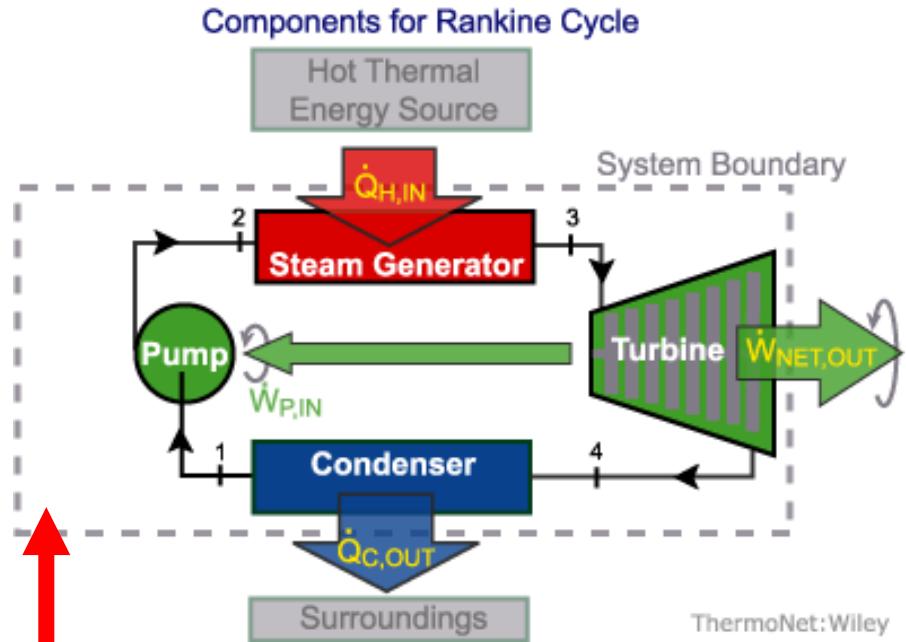
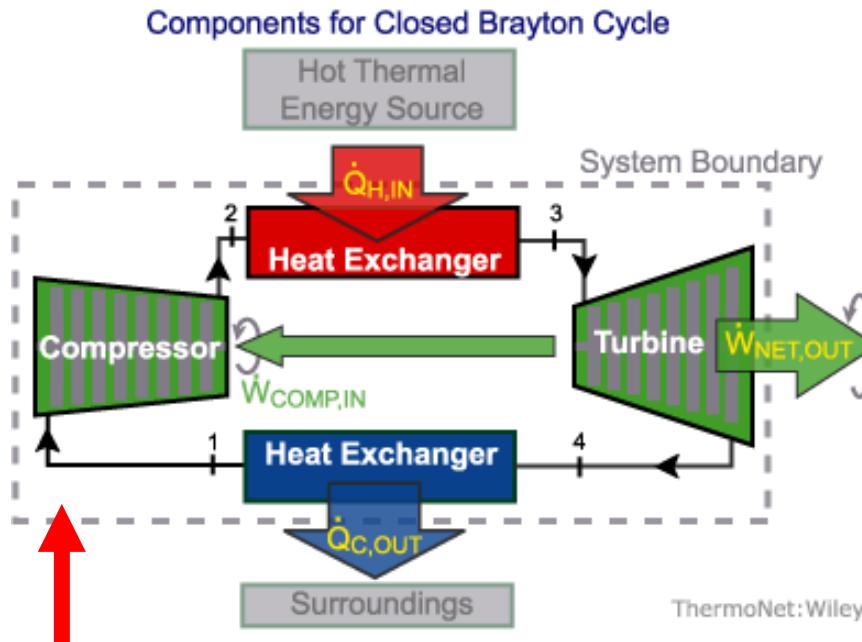
Ideal Brayton Cycle Analysis

- Open ideal Brayton cycle (Reversible $\rightarrow s_{GEN} = 0$)

Process	Component	q	w	Const.
$1 \rightarrow 2$ Isentropic compression	Compressor	0	w_{IN}	s
$2 \rightarrow 3$ Isobaric heating	Combustion chamber	q_{IN}	0	P
$3 \rightarrow 4$ Isentropic expansion	Turbine	0	w_{OUT}	s
$4 \rightarrow 1$ Isobaric cooling	Exhaust hot combustion gasses & intake fresh cold air	q_{OUT}	0	P



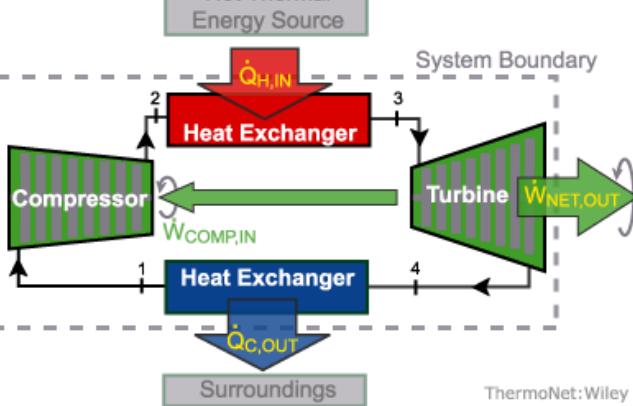
Comparison of Brayton to Rankine Cycle



- Brayton cycle
 - Air everywhere
 - Compressor instead of pump
- Compare the Rankine cycle to the Brayton cycle
 - The pump for liquid changed by a compressor for air
 - Condenser for phase transition changed by a heat exchanger for air
- Rankine cycle
 - Liquid at the pump
 - Vapor (gas) at the turbine
 - Phase change in steam generator and condenser

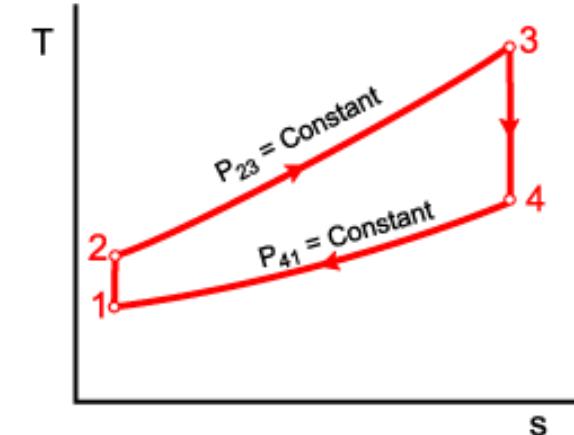
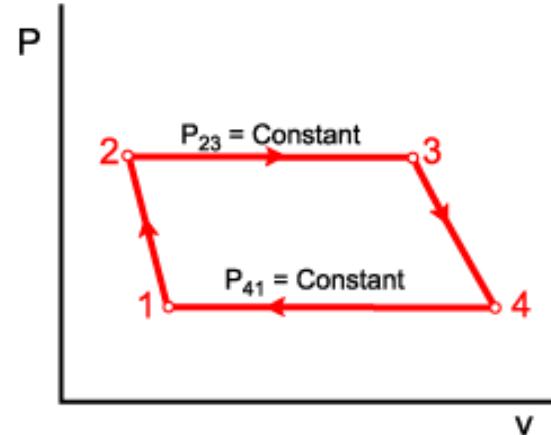
Comparison of Brayton to Rankine Cycle

Components for Closed Brayton Cycle



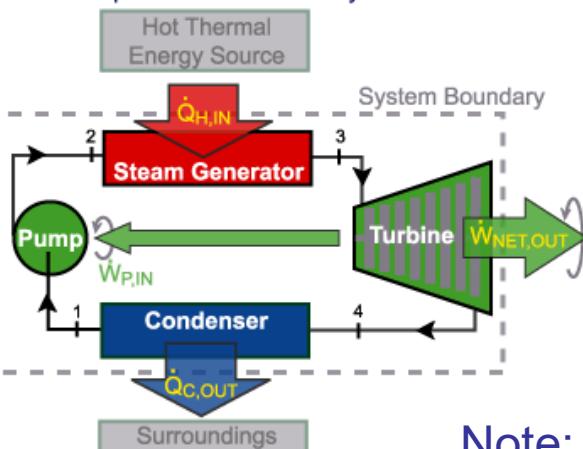
ThermoNet: Wiley

Simple Brayton Cycle

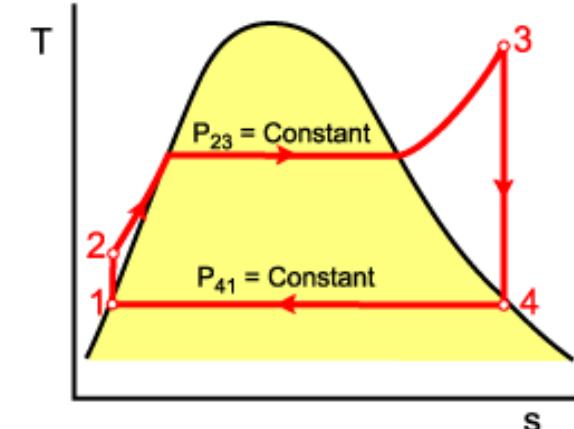
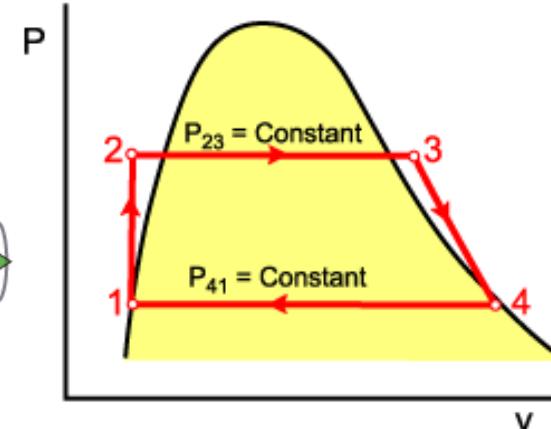


ThermoNet: Wiley

Components for Rankine Cycle



Rankine Cycle with Superheat



ThermoNet: Wiley

Note: in the Brayton cycle (gas turbine) no saturation region as the working fluid is in the gas phase during the whole cycle

Comparison of Brayton to Rankine Cycle

Process	States	Constant Property	Phase	
			Brayton	Simple Rankine
Pressure Increase	1→2	s	Ideal Gas	Liquid
Heat Transfer to Working Fluid	2→3	P	Ideal Gas	Liq.-Vapor
Expansion	3→4	s	Ideal Gas	Liq.-Vapor
Heat Transfer from Working Fluid	4→1	P	Ideal Gas	Liq.-Vapor
Property Source			Air Tables Air Diagram Ideal Gas Law	Steam Tables Steam Diagram No analytical relations

Comparison of Rankine to Brayton Cycle

- The **back work ratio** is the ratio of the compressor input work to the turbine output work → back work ratio = $\frac{w_{in-comp-or-pump}}{w_{out-turbine}}$,
 - **Modern Rankine cycle:** back work ratio = $\frac{w_{in-pump}}{w_{out-turbine}} \sim 0.01$
 - **Modern Brayton cycle:** back work ratio = $\frac{w_{in-comp}}{w_{out-turbine}} 0.50$
- **Why is this ratio so different?**
 - The input work is the work required to compress the working fluid
 - This work is proportional to the volume change → $\delta w = Pdv$
→ volume change liquid << volume change gas → $w_{in,liquid} \ll w_{in,gas}$
- Therefore, a Rankine cycle can operate with an inefficient pump and turbine: 1712 Thomas Newcomen's steam engine used in coal mines
- But for a Brayton cycle to work an efficient compressor and turbine is needed: 1939 First flight of turbojet engine using Hans von Ohain design

Ideal Brayton Cycle Analysis

- Modeling of the **ideal Brayton cycle** (note: ideal i.e., assumed to be reversible → $s_{GEN} = 0$)
- Model each component as an open system at SSSF like in the Rankine cycle
- Use standard air cycle assumptions
 - Neglect fuel and assume the working fluid to be pure air behaving as an ideal gas
 - Combustion is replaced by a heat transfer process in which heat is added
- Mass flow rate through each component in the cycle is constant
- Cycle can be analyzed analytical (use of formulas), graphical (Mollier diagram) or by using tables

Work and Power Output Brayton Cycle

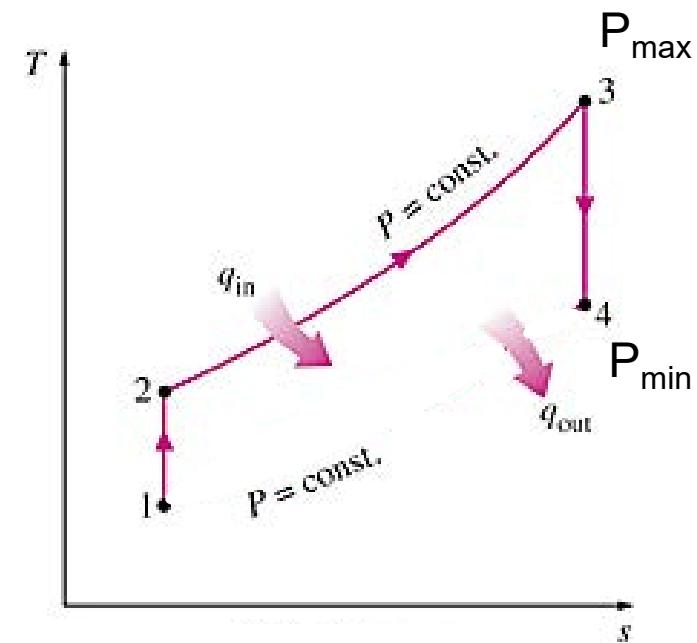
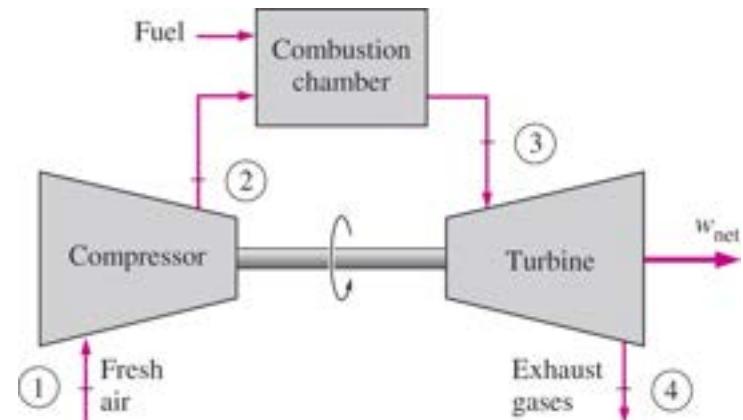
- The work of the Brayton cycle is produced by the turbine (3-4)
- However, the compressor consumes work (1-2)
- The work used by the compressor is taken from the produced work by the turbine

- The work produced by the turbine:**

$$w_{\text{turbine}} = w_{\text{out}} = w_{3-4} = h_3 - h_4 \quad (\text{kJ/kg})$$

- The work consumed by the compressor:**

$$w_{\text{compr}} = w_{\text{in}} = w_{1-2} = h_2 - h_1 \quad (\text{kJ/kg})$$



Work and Power Output Brayton Cycle

- The work produced by the turbine:

$$w_{\text{turbine}} = w_{\text{out}} = w_{3-4} = h_3 - h_4 \quad (\text{kJ/kg})$$

- The work consumed by the compressor:

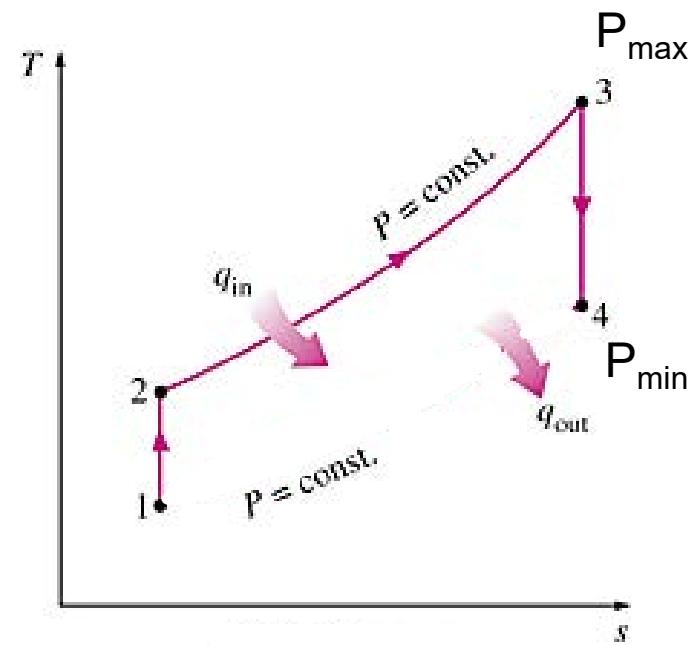
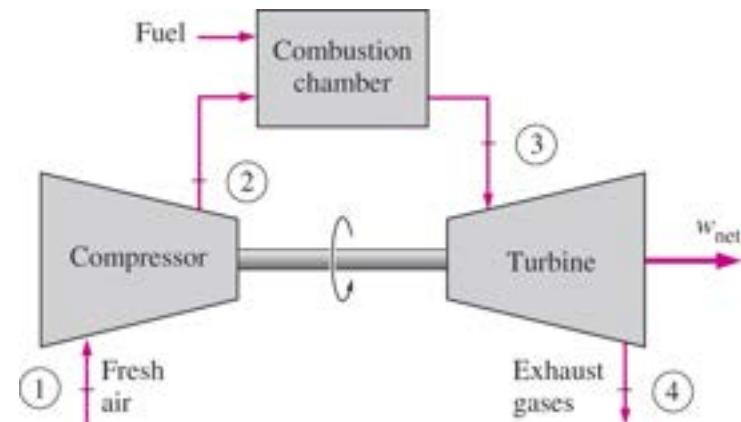
$$w_{\text{compr}} = w_{\text{in}} = w_{1-2} = h_2 - h_1 \quad (\text{kJ/kg})$$

- The net work output of the gas turbine per kg fluid is:

$$\begin{aligned} w_{\text{net}} &= w_{\text{out}} - w_{\text{in}} = w_{\text{turbine}} - w_{\text{compressor}} \\ &= (h_3 - h_4) - (h_2 - h_1) \quad (\text{kJ/kg}) \end{aligned}$$

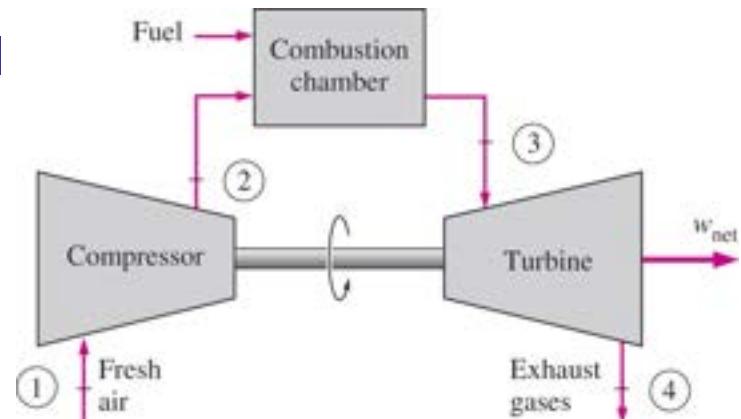
- The total net power is:

$$\dot{W}_{\text{net}} = \dot{m}w_{\text{net}} = \dot{m}[(h_3 - h_4) - (h_2 - h_1)] \quad (\text{kg/s} \cdot \text{kJ/kg} = \text{kJ/s} = \text{kW})$$



Heat and Power Input Brayton Cycle

- Heat is added to the Brayton cycle in the combustion chamber by combustion of fuel (2-3)
- Heat is rejected to the environment (4-1)

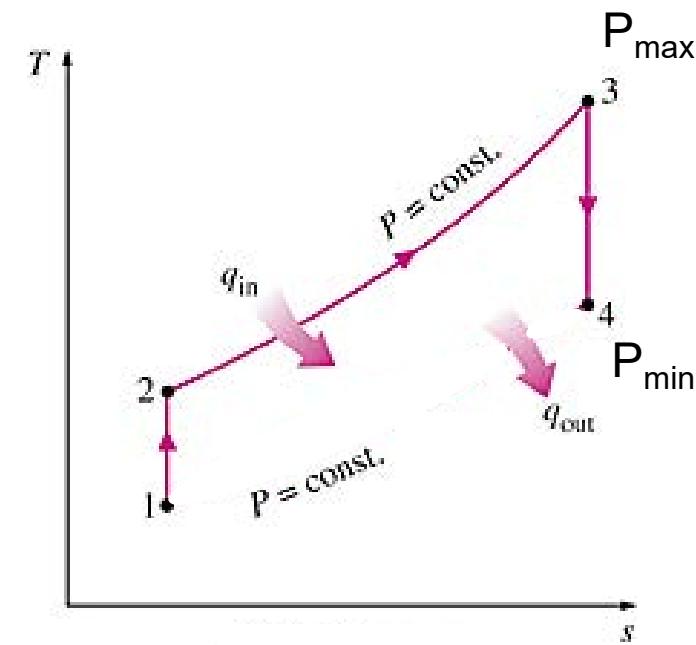


- **The heat input to the cycle:**

$$q_{\text{combustion}} = q_{\text{in}} = q_{2-3} = h_3 - h_2 \quad (\text{kJ/kg})$$

- **The heat rejected by the cycle:**

$$q_{\text{out}} = q_{4-1} = h_4 - h_1 \quad (\text{kJ/kg})$$



Heat and Power Input Brayton Cycle

- The heat added to the cycle:

$$q_{\text{combustion}} = q_{\text{in}} = q_{2-3} = h_3 - h_2 \quad (\text{kJ/kg})$$

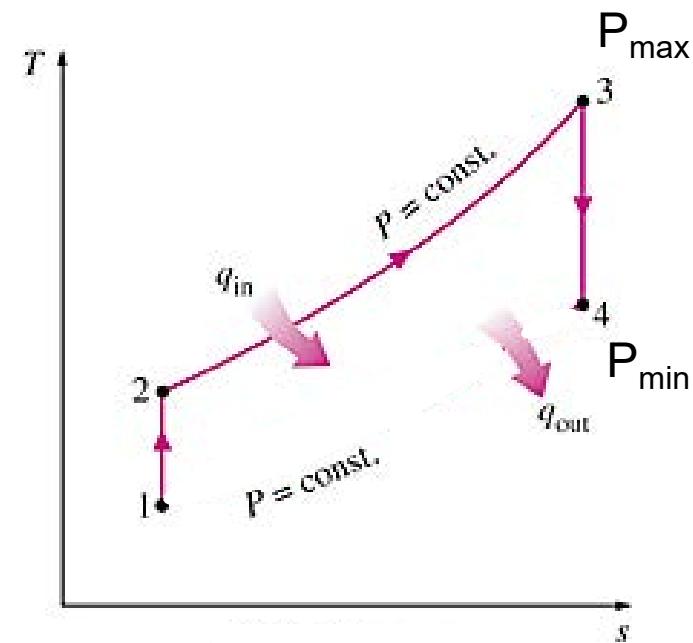
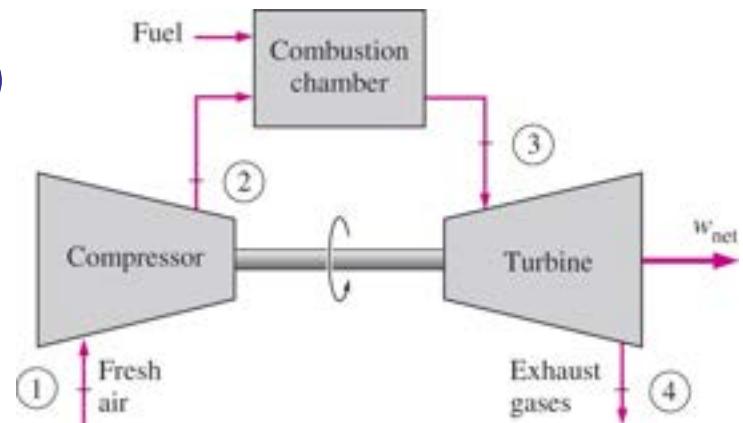
- The heat rejected by the cycle:

$$q_{\text{out}} = q_{4-1} = h_4 - h_1 \quad (\text{kJ/kg})$$

- The power input is:

$$\dot{Q}_{\text{in}} = \dot{m}q_{\text{in}} = \dot{m}(h_3 - h_2) \quad (\text{kJ/s} = \text{kW})$$

- Values of h can be looked up in the tables or in a graph (Mollier diagram) or can be calculated for ideal cycles (analytical)



Brayton Cycle Efficiency

- The **net work output** of the gas turbine per kg fluid is:
 - $w_{net} = w_{out} - w_{in} = w_{turbine} - w_{compressor} = (h_3 - h_4) - (h_2 - h_1)$ (kJ/kg)
- The **heat added** to the cycle:
 - $q_{combustion} = q_{in} = q_{2-3} = h_3 - h_2$ (kJ/kg)
- **Efficiency Brayton cycle:**

$$\eta_{Brayton} = \frac{\text{Wanted}}{\text{Payed for}} = \frac{\dot{w}_{net}}{\dot{q}_{in}} = \frac{\dot{m}w_{net}}{\dot{m}q_{in}}$$

$$\eta_{Brayton} = \frac{w_{net}}{q_{in}} = \frac{w_{out} - w_{in}}{q_{in}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)}$$

Brayton Cycle Efficiency

- Efficiency Brayton cycle:

$$\eta_{Brayton} = \frac{w_{net}}{q_{in}} = \frac{w_{out} - w_{in}}{q_{in}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)}$$

- For a Brayton cycle with **ideal air standard assumptions** (ias) the efficiency can be rewritten as

$$\eta_{Brayton,ias} = \frac{c_p(T_3 - T_4) - c_p(T_2 - T_1)}{c_p(T_3 - T_2)} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1}{T_2} \frac{(T_4/T_1 - 1)}{(T_3/T_2 - 1)} = 1 - \frac{1}{r_p^{(k-1)/k}}$$

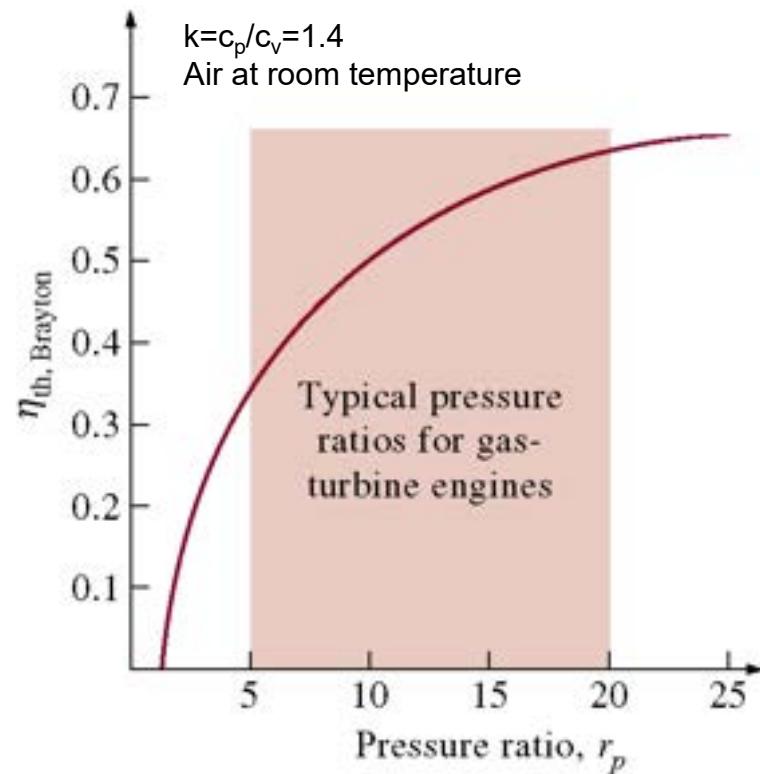
- In the evaluation relations derived for an ideal gas (class 9) are used
 - $dh = c_p dT$ and $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} = \left(\frac{P_3}{P_4}\right)^{(k-1)/k} = \frac{T_3}{T_4}$
 - Note that this relation is only valid under the assumption that C_p does not depend on the temperature and when the compressor and turbine are ideal
 - However, it can be used to determine the effect of different parameters on the efficiency

Brayton Cycle Efficiency

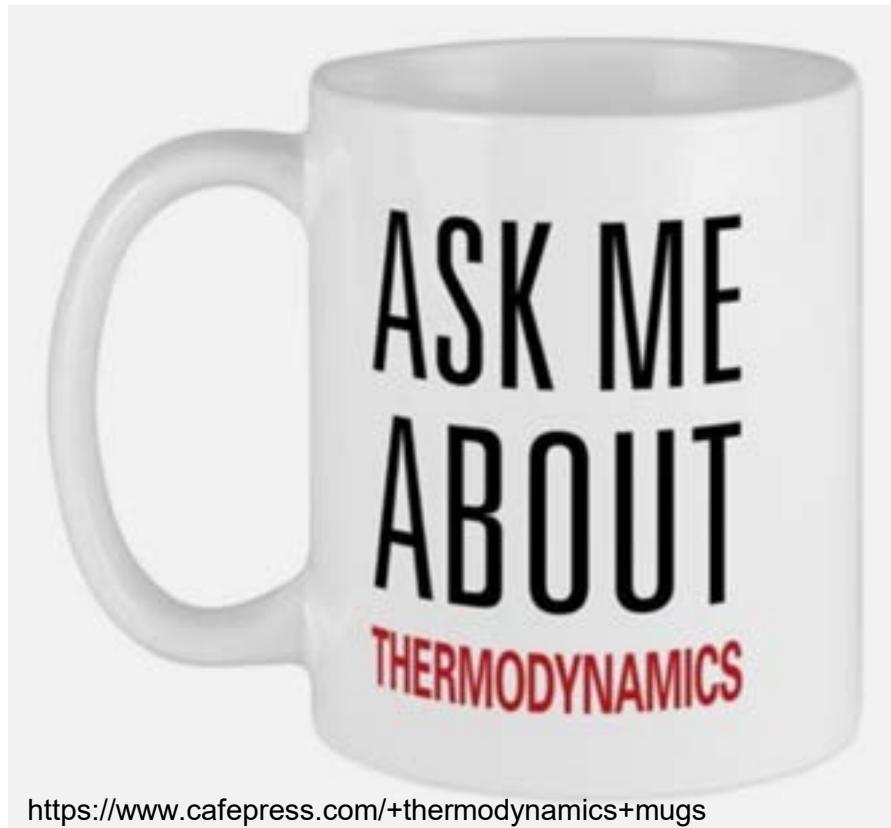
- Efficiency Brayton, ideal air standard cycle:

$$\eta_{Brayton,ias} = \frac{w_{net}}{q_{in}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)} = 1 - \frac{1}{r_p^{(k-1)/k}}$$

- The formula shows that the efficiency only depends on the pressure ratio across the compressor and k
- For fixed T_{Max} (turbine inlet temperature)
 - Efficiency increases with r_p
 - $w_{net} = w_{turb.out} - w_{compr.in}$ decreases with r_p
 - Compromise between efficiency and work output
- T_{MAX} limited by materials (material sciences !)



BREAK



<https://www.cafepress.com/+thermodynamics+mugs>

Design parameters Brayton Cycle

- How can the efficiency of the basic Brayton cycle be increased?

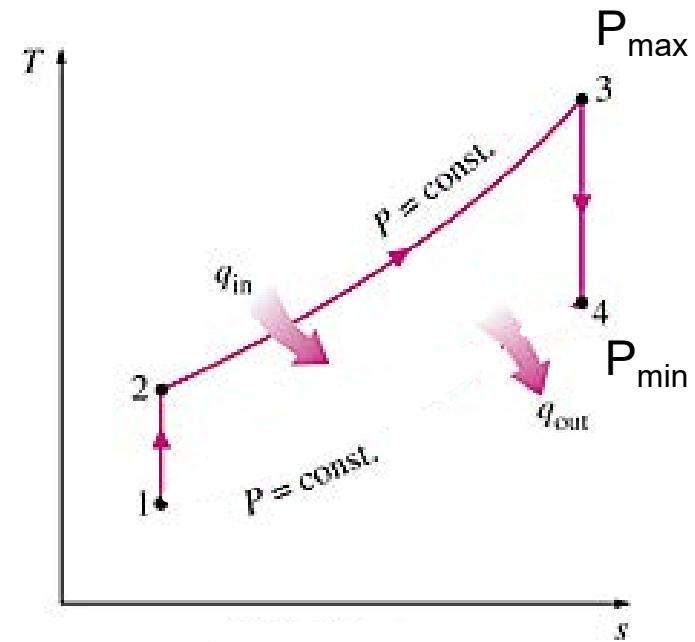
$$\eta_{Brayton} = \frac{w_{net}}{q_{in}} = \frac{w_{out} - w_{in}}{q_{in}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)}$$

- Remember

- The net work output is the area enclosed by the cycle 1 – 2 – 3 – 4
- The net heat input is the area below the curve 2 – 3

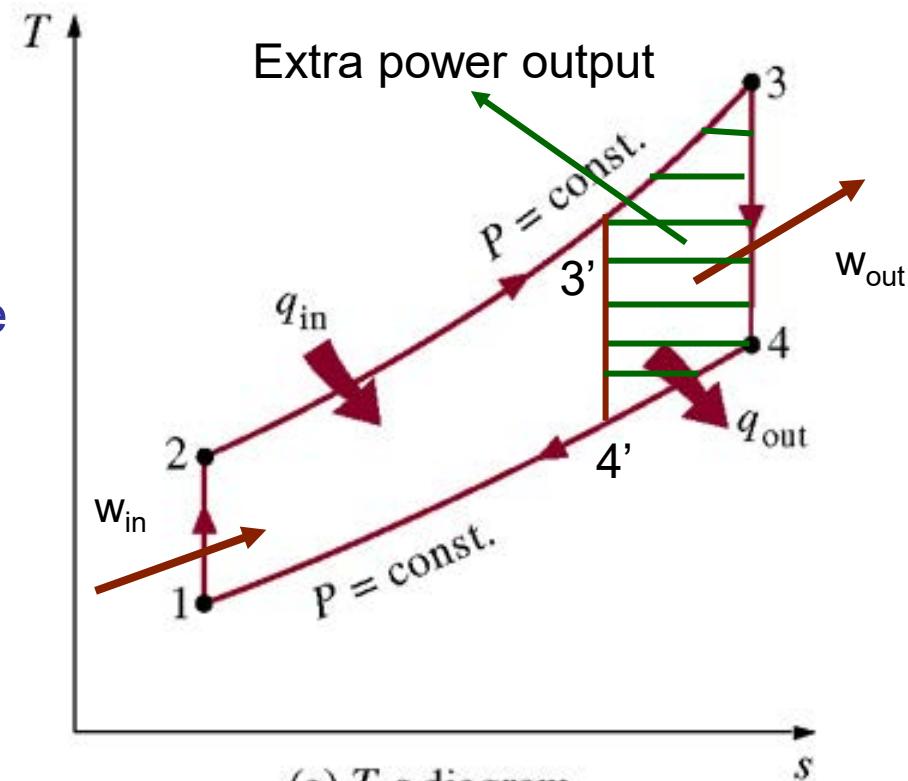
- This area can be enlarged by

- Increasing the turbine inlet temperature
- Increasing the pressure ratio
- Changing the type of working medium



Design parameters Brayton Cycle

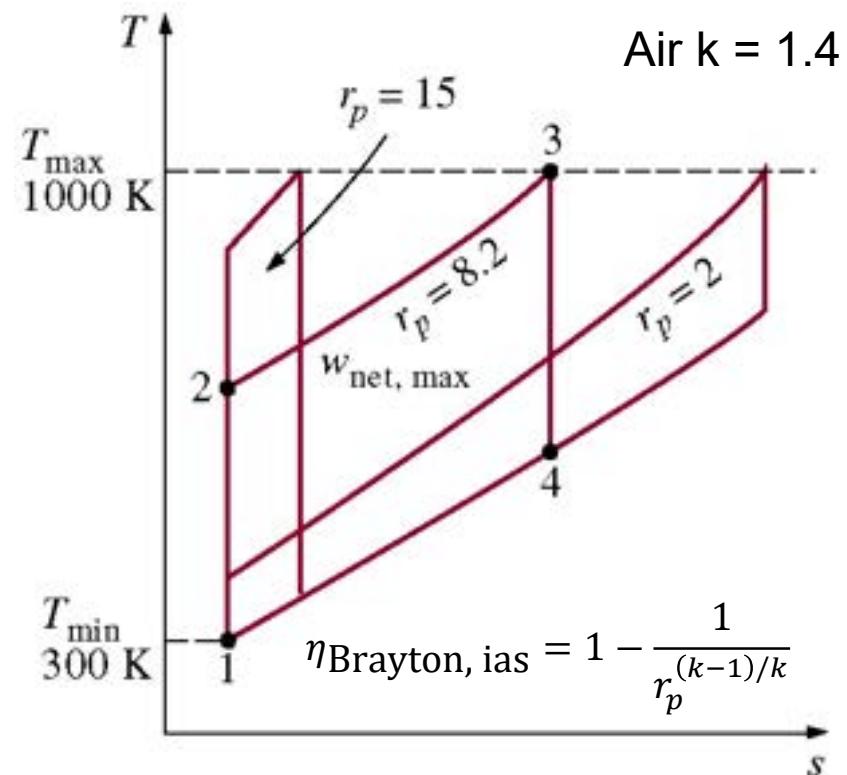
- The effect of increasing the turbine inlet temperature on the ideal Brayton cycle
- Increasing the turbine inlet temperature increases the area enclosed by the cycle 1-2-3-4 and W_{net} increases
- But the area below the curve 2-3, the heat input also increases
- However, the efficiency increases as the average temperature at which heat is added to the cycle increases
- T_{\max} is restricted by the materials, but sometimes blades are actively cooled to reach higher temperatures
- Nowadays temperatures vary between 1000-1600 K



(a) T - s diagram

Design parameters Brayton Cycle

- The effect of changing the compression ratio on the ideal Brayton cycle → optimal pressure ratio at a given T_{\max} and T_{\min}
- The efficiency increases with higher compression ratio
- However, the maximum compression ratio is restricted by the maximum temperature in the cycle
- For fixed values of T_{\min} and T_{\max} the net work of the Brayton cycle first increases with pressure ratio, then reaches a maximum at
$$r_p = \left(\frac{T_{\max}}{T_{\min}} \right)^{k/2(k-1)}$$
and finally decreases
- In most common designs, the pressure ratio of gas turbines ranges from about 11 to 16

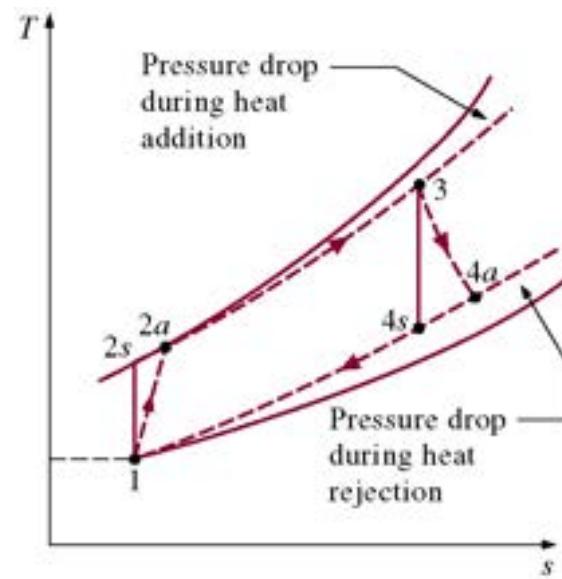
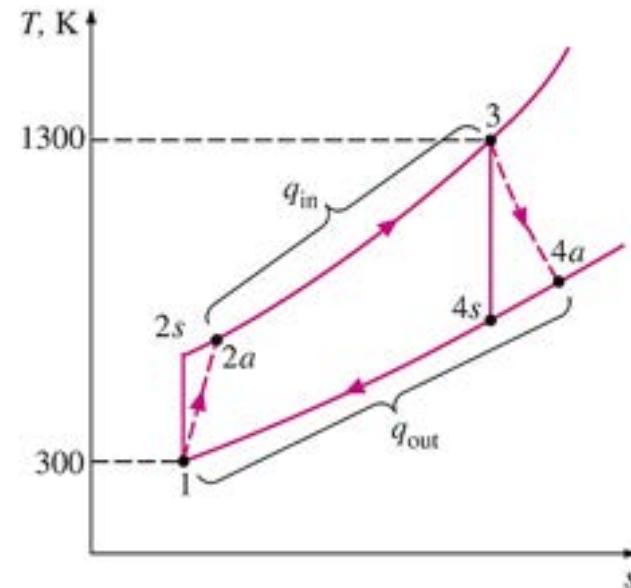


Design parameters Brayton Cycle

- The effect of changing the working fluid on the ideal Brayton cycle
- The efficiency depends on k , the ratio of the specific heats of the working fluid, $k = c_p/c_v$:
$$\eta_{Brayton,ias} = 1 - \frac{1}{r_p^{(k-1)/k}}$$
- The formula shows that the efficiency increases with increasing value of k
- At room temperature (300 K)
 - Air, nitrogen, oxygen: $k = 1.4$
 - Helium, argon, neon: $k = 1.66$
- Note: gasses like He, Ar and Ne are only possible in closed systems and no internal combustion can be applied

Effect of Component Efficiencies

- Thus far the modeling assumed a reversible (ideal) Brayton cycle
- However, there is a major departure from the ideal cycle due to irreversibilities in the compressor and turbine
- In process 1-2 and 3-4 the entropy increases
- Take the isentropic efficiency of the compressor and the turbine into account
- In a real gas turbine also, pressure drop occurs in the heat addition and rejection processes, however this can be neglected in the analysis



Effect of Component Efficiencies

- Model non-ideal cycle using isentropic efficiencies (class 5)

- For the turbine:

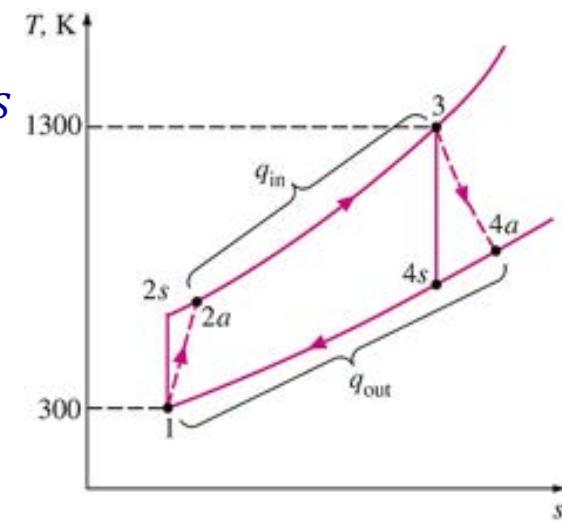
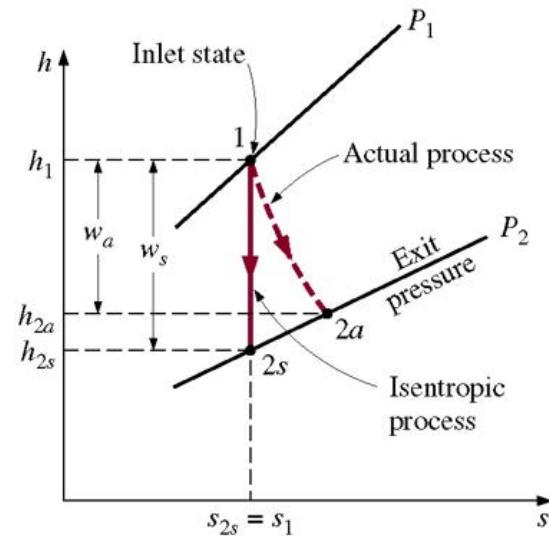
$$\eta_{S,Turbine} = \frac{h_{IN} - h_{OUT,A}}{h_{IN} - h_{OUT,S}} = \left(\frac{T_{IN} - T_{OUT,A}}{T_{IN} - T_{OUT,S}} \right)_{IAS}$$

$dh = c_p dT$ and c_p is constant

- For the compressor:

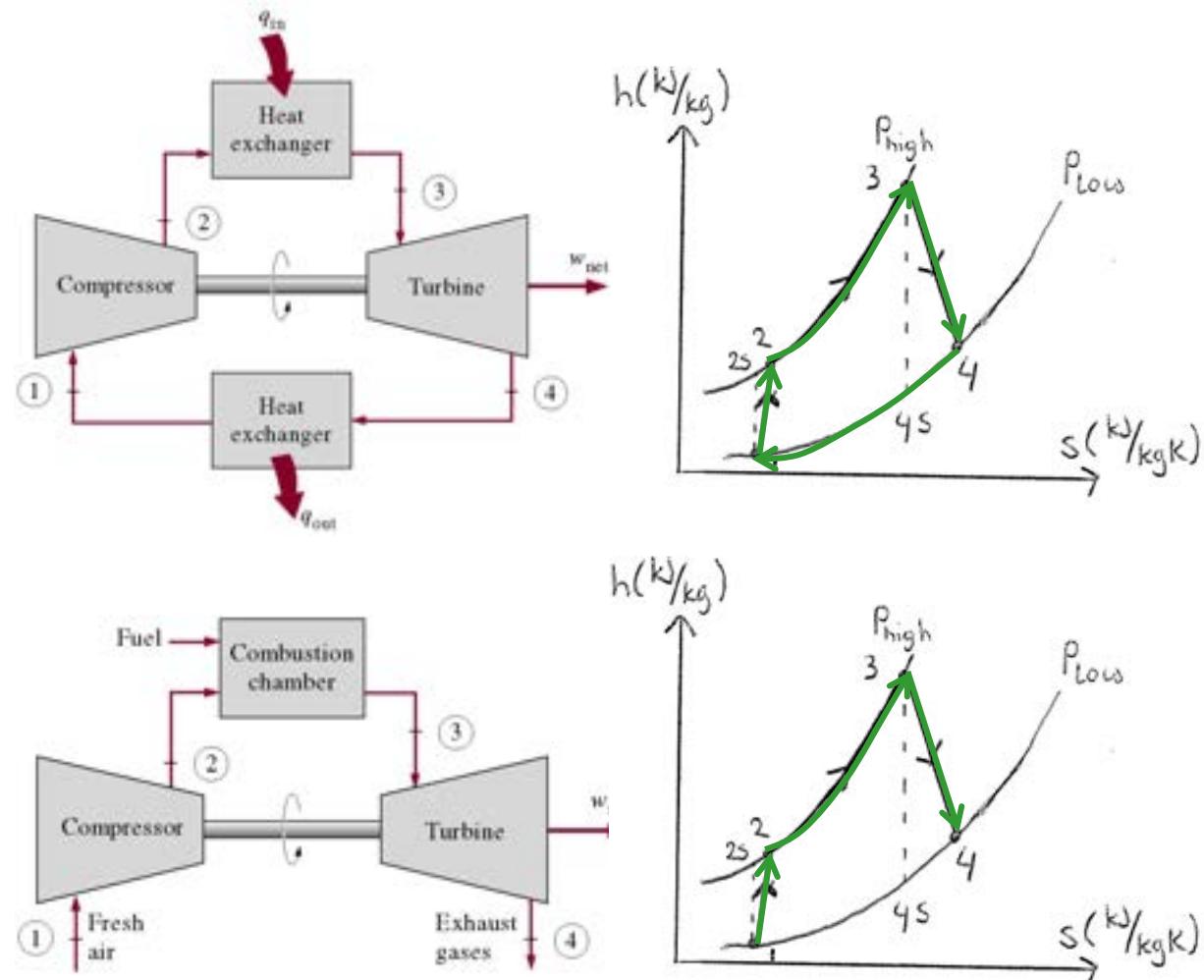
$$\eta_{S,Compressor} = \frac{h_{OUT,S} - h_{IN}}{h_{OUT,A} - h_{IN}} = \left(\frac{T_{OUT,S} - T_{IN}}{T_{OUT,A} - T_{IN}} \right)_{IAS}$$

- The entropy must increase
- To calculate the thermal efficiency the actual h values must be used



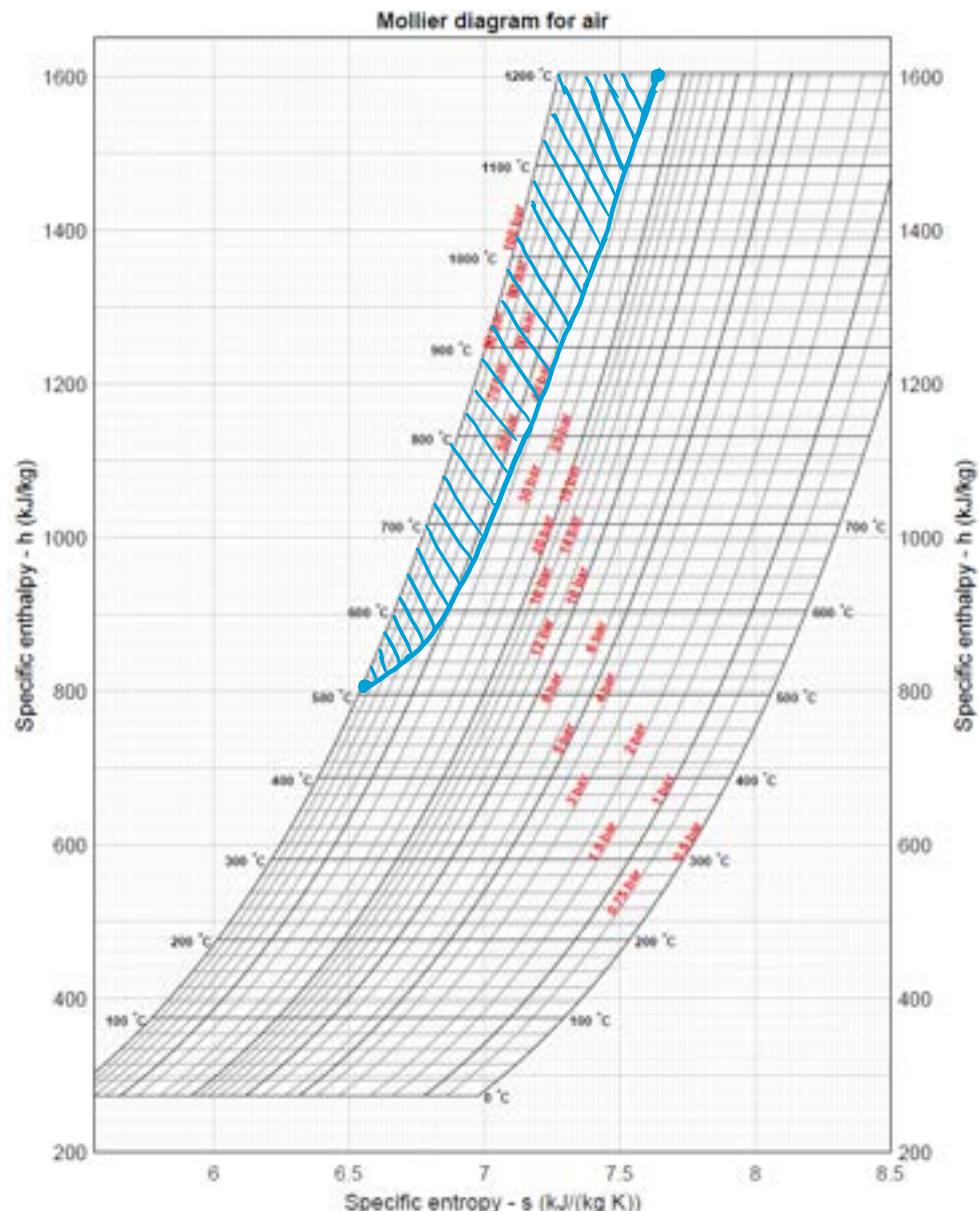
Closed versus Open Brayton Cycle

- The difference between the open and closed Brayton cycle is the presence of the heat exchanger to reject heat
- In the open cycle the air passed through the turbine is blown in the surroundings and fresh air for the compressor is taken from the surroundings
- In the diagram for the open cycle the line 1 to 4 is NOT connected
- Most real gas turbines are open cycles



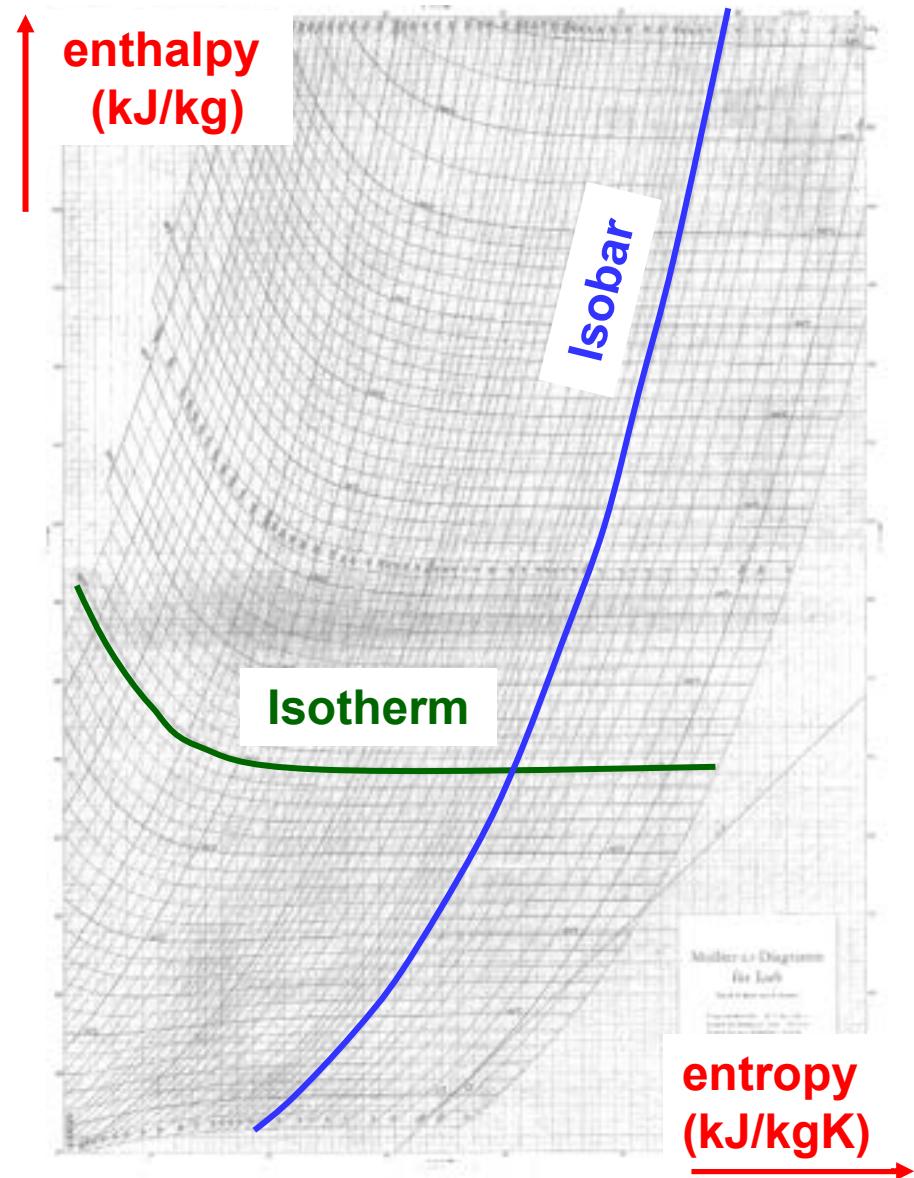
Mollier Diagram Air for Brayton Cycle

- Enthalpy values for air can also be found using the Mollier diagram
- Diagram is less exact, but gives a good overview of the process
- This diagram is made using Matlab
- In the program some assumptions are made, the most important one is that air is assumed to be an ideal gas, however the dependence of the specific heats on temperature is taken into account
- So, the diagram is valid for air assumed to be an ideal gas
- If the air cannot be assumed ideal (high P and high T indicated in blue) the values slightly deviate
- We will use this diagram to analyse the gas power cycles (next class)



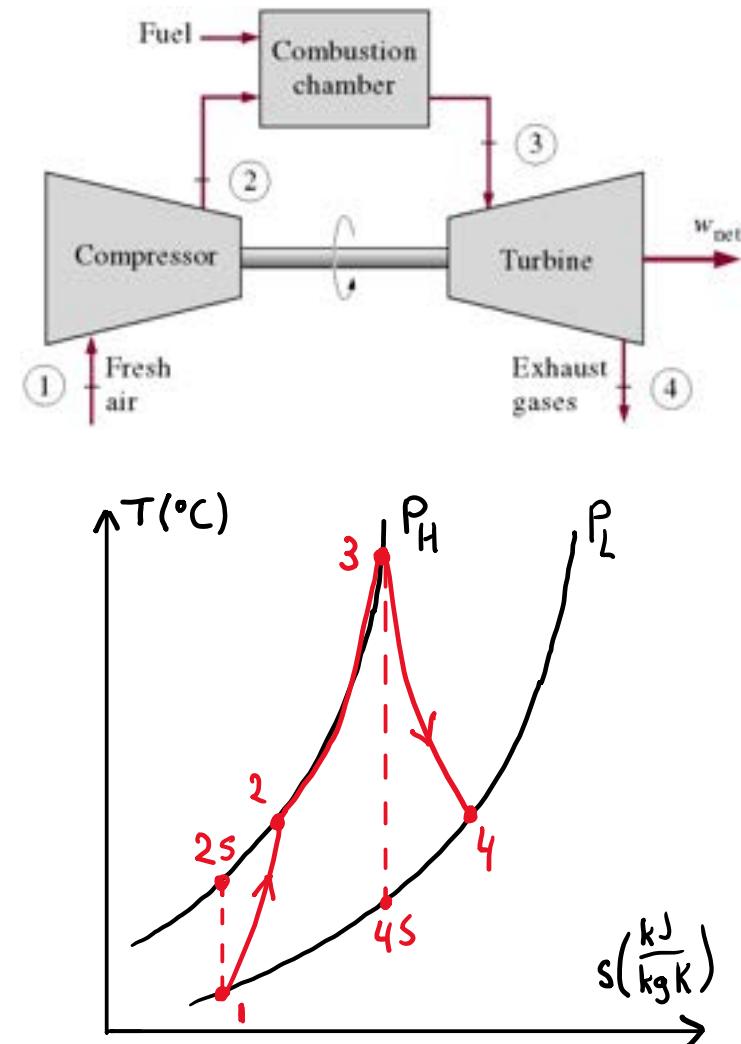
Mollier diagram air

- Scanned version of a Mollier diagram for real air
 - Enthalpy (kJ/kg) on the y-axis, horizontal line → $dh = 0$
 - Entropy (kJ/kgK) on the x-axis, vertical line → $ds = 0$
 - Isobars (in Bar !!)
 - Isotherms (in degree Celsius)
- The main difference with the one in which the air is assumed to be an ideal gas (previous page) is that the isotherms bend upwards in the high T and high P region where the air cannot be approximated as an ideal gas anymore
- This diagram is mostly used in the answers for the assignments



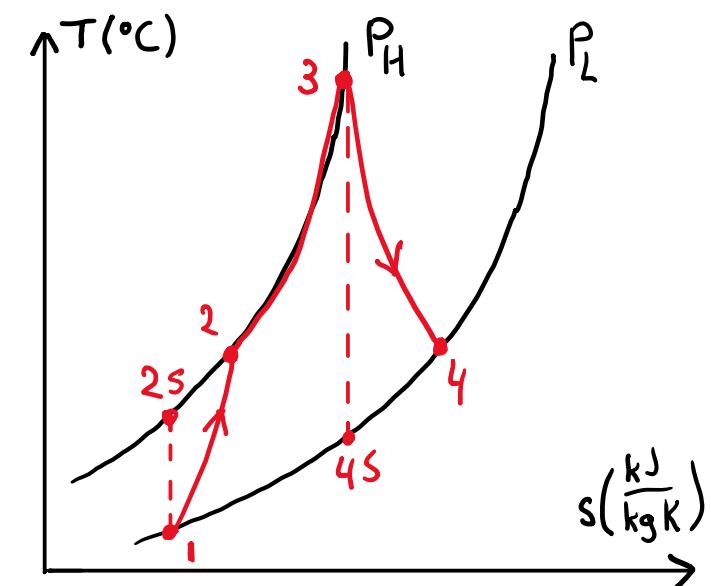
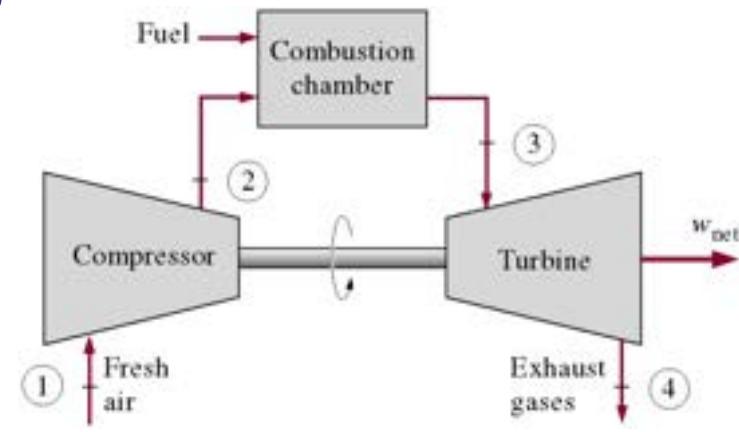
Systematic Analysis of Problems

- Large problems for cycles should be analyzed systematically
 - Tables, diagrams or formulas can be used
1. Make a schematic diagram of the setup
 2. Number the characteristic points connecting the different devices
 3. Sketch the Ts – diagram
 4. Collect the two known properties per point in a table (e.g., P, T, s, isentropic efficiency,), if known give mass flow or power output
 5. Determine the **enthalpy per point** and add it also to the table
 6. Now all interesting data, like power in- and output and efficiency can be determined



Note on Ts - diagram

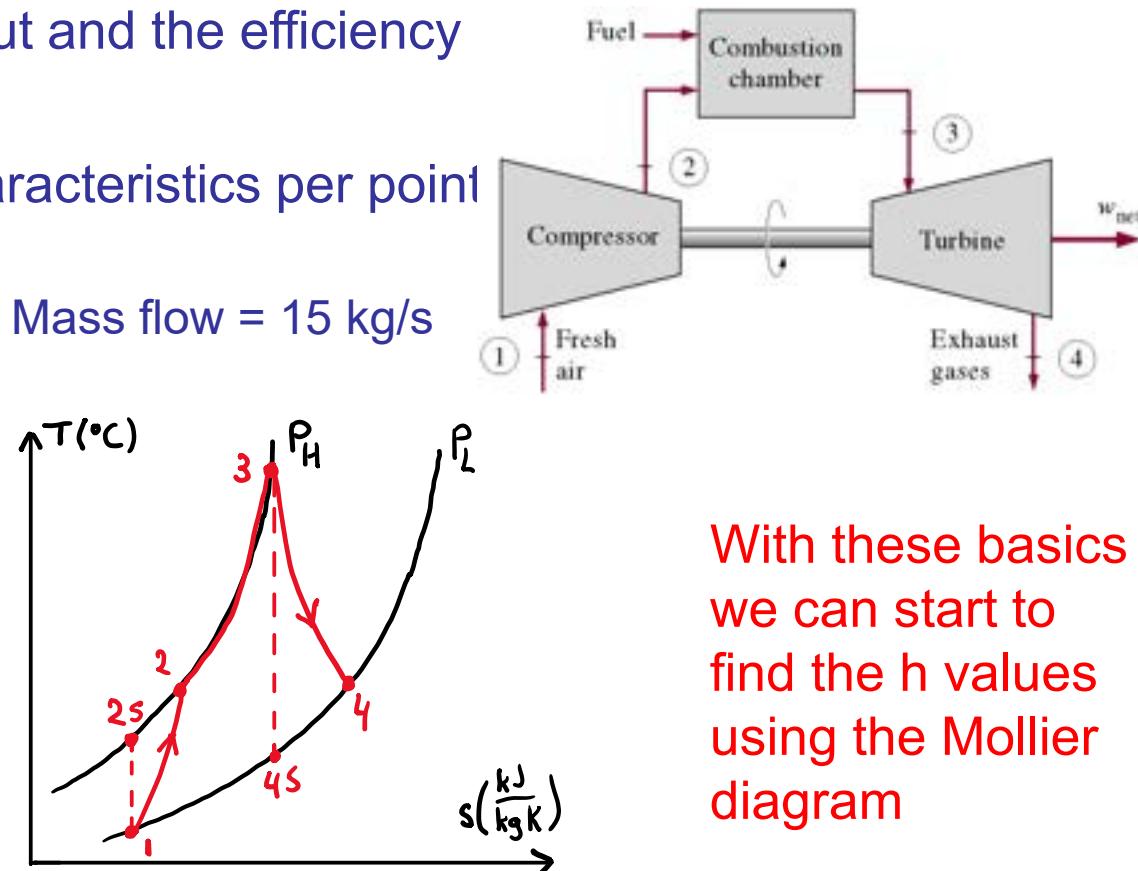
- Put parameters along the axis (T and s)
- Add the units along the axis ($^{\circ}\text{C}$ and kJ/kgK)
- Draw the isobars and put the value or indicate P_{high} / P_{low} / P_{medium}
- Indicate the points with the right number
- Put arrows in the direction of the processes
- Use $- - -$ for isentropic processes
- Use $---$ for real processes
- Add values along the axis if you know them
- Do not make them too small
- For air, no vapor dome (I do not want to see that on the exam)



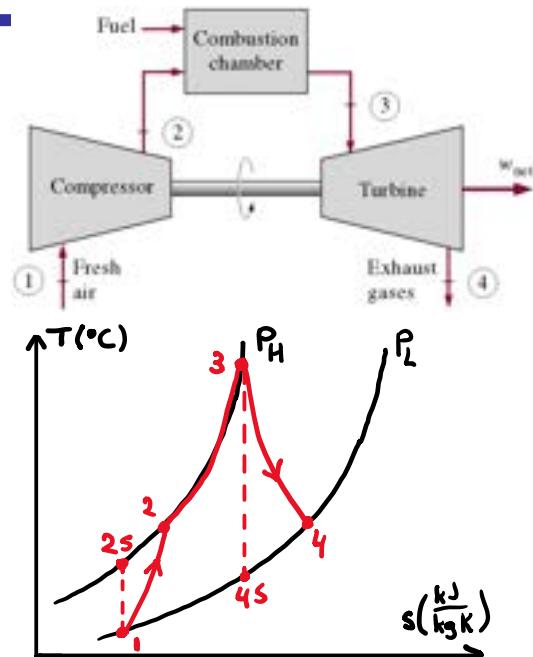
Example Simple Brayton Cycle

- A gas turbine installation undergoes a Brayton cycle
- The inlet conditions are 1 bar and 15°C, the temperature after combustion is 900°C, the pressure ratio is 8, the isentropic efficiencies of the turbine and the compressor are 80% and the mass flow rate is 15 kg/s
- Determine the power output and the efficiency
- Solution start with:
- Scheme, diagram, two characteristics per point

	First	Second
1	$P_1 = 1 \text{ bar}$	$T_1 = 15^\circ\text{C}$
2s	$P_{2s} = 8P_1$	$s_{2s} = s_1$
2	$P_2 = 8P_1$	$\eta = 0.8$
3	$P_2 = P_3$	$T_3 = 900^\circ\text{C}$
4s	$P_{4s} = P_1$	$s_{4s} = s_3$
4	$P_4 = P_1$	$\eta = 0.8$



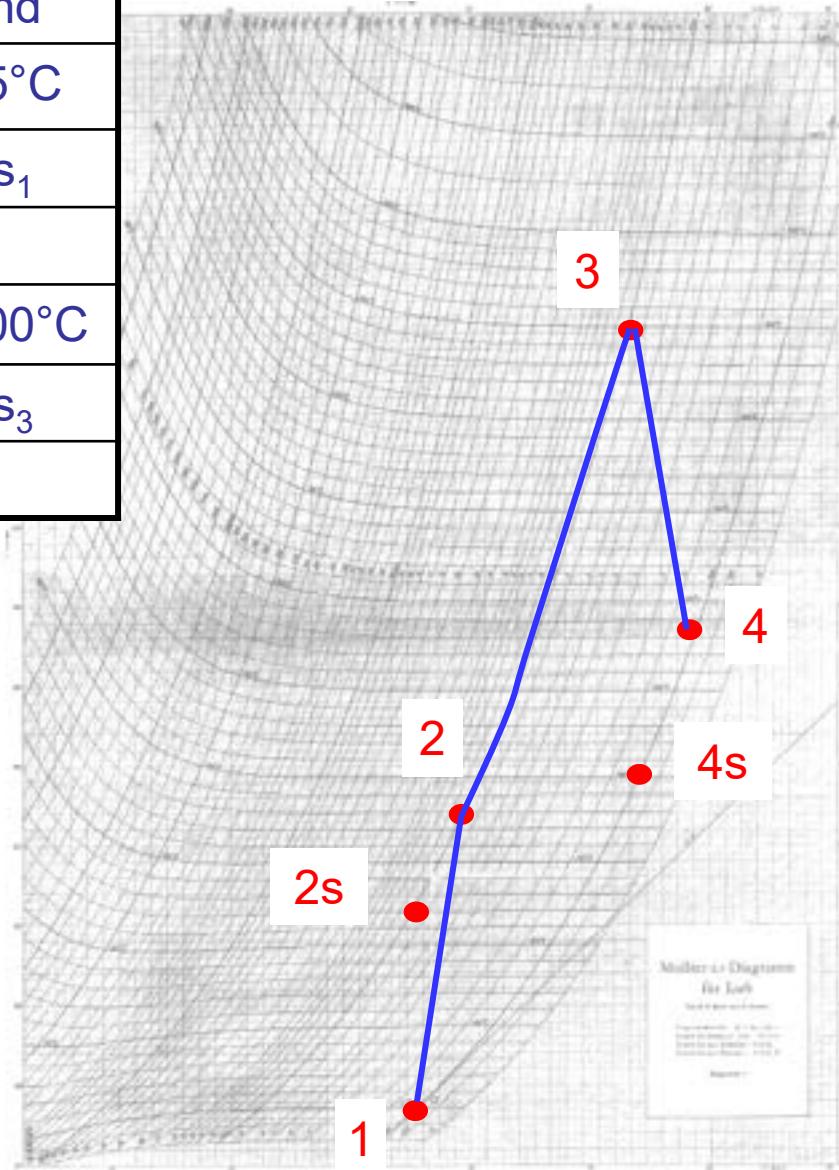
Example Simple Brayton Cycle



	First	Second
1	$P_1 = 1 \text{ bar}$	$T_1 = 15^\circ\text{C}$
2s	$P_{2s} = 8P_1$	$s_{2s} = s_1$
2	$P_2 = 8P_1$	$\eta = 0.8$
3	$P_2 = P_3$	$T_3 = 900^\circ\text{C}$
4s	$P_{4s} = P_1$	$s_{4s} = s_3$
4	$P_4 = P_1$	$\eta = 0.8$

Mass flow = 15 kg/s

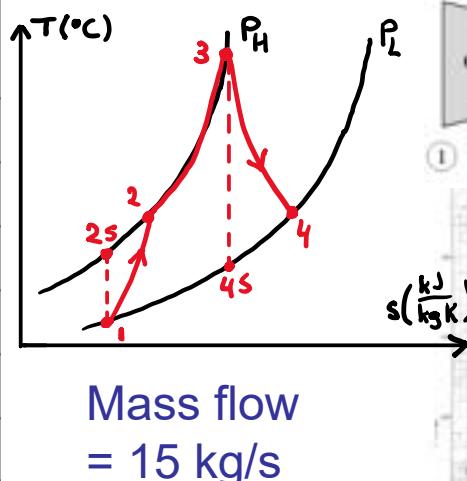
- Point 1: h_1 diagram $P_1=1 \text{ bar}$, $T_1=15^\circ\text{C}$
- Point 2s: h_{2s} diagram $P_2=8 \text{ bar}$, $s_1 = s_{2s}$
- Point 2: h_2 from $\eta_{S,COMP} = \frac{h_{2s}-h_1}{h_2-h_1}$
- Point 3: h_3 diagram $P_3=8 \text{ bar}$, $T_3=900^\circ\text{C}$
- Point 4s: h_{4s} diagram $P_4=8 \text{ bar}$, $s_3 = s_{4s}$
- Point 4: h_4 from $\eta_{S,TURB} = \frac{h_3-h_4}{h_3-h_{4s}}$



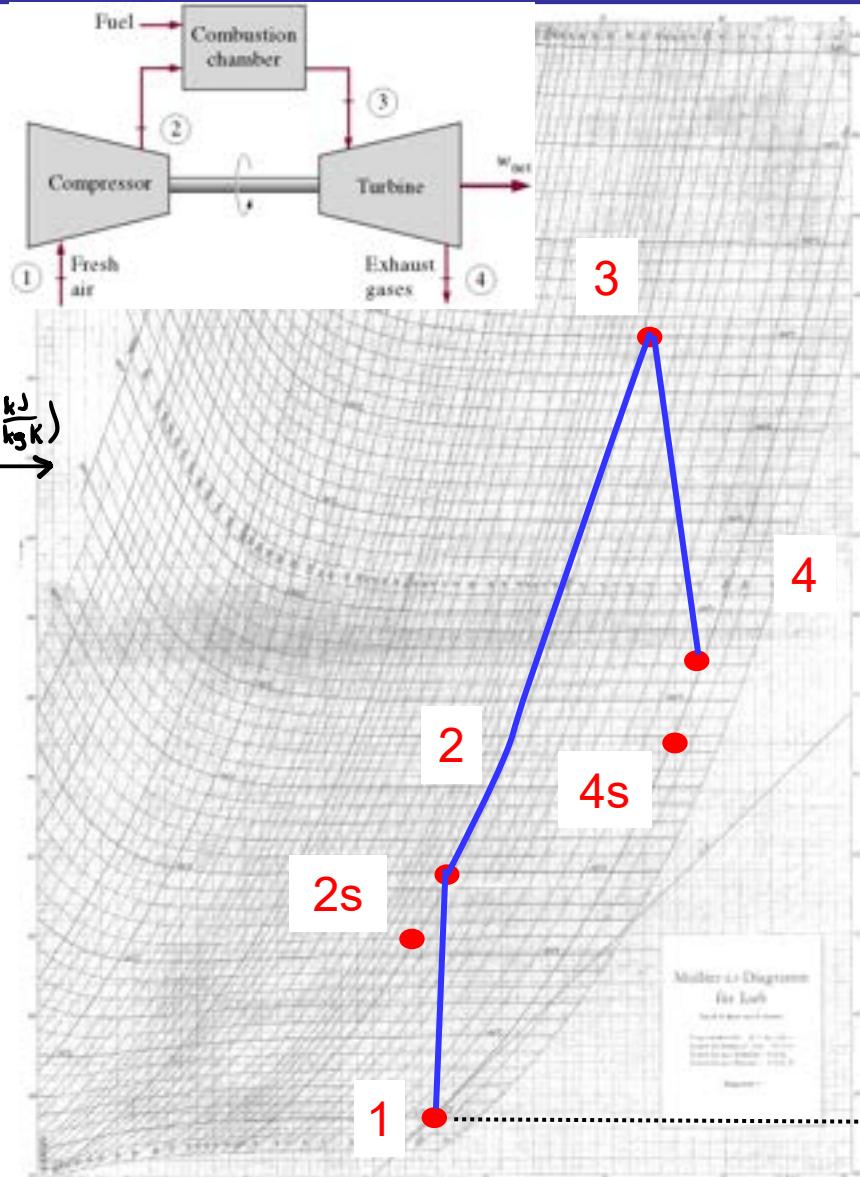
Example Simple Brayton Cycle

- Find the h value of every point

	P (bar)	T (°C)	h (kJ/kg)
1	1	15	290
2s	8	220	490
2	8	300	540
3	8	900	1250
4s	1	450	710
4	1	540	818



- $w_{in} = h_2 - h_1 = 250 \text{ kJ/kg}$
- $q_{in} = h_3 - h_2 = 710 \text{ kJ/kg}$
- $w_{out} = h_3 - h_4 = 432 \text{ kJ/kg}$
- $w_{net} = w_{out} - w_{in} = 182 \text{ kJ/kg}$
- $\dot{W}_{net} = \dot{m}(w_{out} - w_{in}) = 15 \cdot 182 = 2730 \text{ kW}$
- $\dot{Q}_{in} = \dot{m}q_{in} = 15 \cdot 710 = 10650 \text{ kW}$
- $\eta_{Brayton} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{w_{net}}{q_{in}} = \frac{(h_3-h_4)-(h_2-h_1)}{(h_3-h_2)} = 0.26 \rightarrow 26\%$



Example Simple Brayton Cycle

- Other characteristics to evaluate the cycle
- **Second law efficiency:** $\eta_{Second\ law,HE} = \frac{\eta_{HE}}{\eta_{CARNOT}}$ (second law efficiency,
not for the exam,
important for the project)

with $\eta_{Brayton} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)} = 0.26$

and $\eta_{CARNOT} = 1 - \frac{T_{MIN}}{T_{MAX}} = 1 - \frac{20+273}{900+273} = 0.75$

this gives $\rightarrow \eta_{Second\ law,HE} = \frac{\eta_{HE}}{\eta_{CARNOT}} = \frac{0.26}{0.75} = 0.35 \rightarrow 35\%$

- **Check the first law** (conservation of energy)
- $e_{in} = e_{out} \rightarrow q_{in} + w_{in} = q_{out} + w_{out} \rightarrow (h_3 - h_2) + (h_2 - h_1) = (h_4 - h_1) + (h_3 - h_4)$
 $\rightarrow 710 + 250 = 528 + 432! 960 = 960 \rightarrow$ right, energy conserved
- **Check the second law** (generation of entropy) $\sum_{i=1}^n \frac{q_{net,i}}{T_i} \leq 0$
$$\sum_{i=1}^n \frac{q_{net,i}}{T_i} = \underbrace{\frac{q_{in}}{T_{in}} - \frac{q_{out}}{T_{out}}}_{ds_{in} - ds_{out}} = \frac{710}{873} - \frac{528}{550} = 0.81 - 0.96 = -0.15 \leq 0 \rightarrow$$
 Right !
- Note: take the mean T_{in} and T_{out} (in Kelvin of course) !

Gas Turbine at UT (TE)

- Electricity for the apparatus in these tanks is delivered by a gas turbine
- A turbine of this type is used in our lab for research by Artur Pozarlik



Places where the tanks were used



Recapitulate class 10

- **Gas power cycles (Brayton cycles):** cycles using gas as working fluid throughout the whole cycle
 - Air-standard cycle, open and closed, ideal and real Brayton cycle
 - Heat and power in- and output simple Brayton

$$w_{\text{compressor,in}} = h_{\text{out}} - h_{\text{in}} = h_2 - h_1$$

$$q_{\text{in,combustion}} = h_{\text{out}} - h_{\text{in}} = h_3 - h_2$$

$$w_{\text{out,turbine}} = h_{\text{in}} - h_{\text{iut}} = h_3 - h_4$$

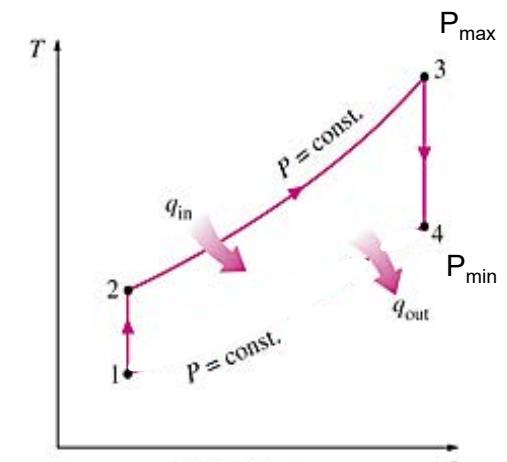
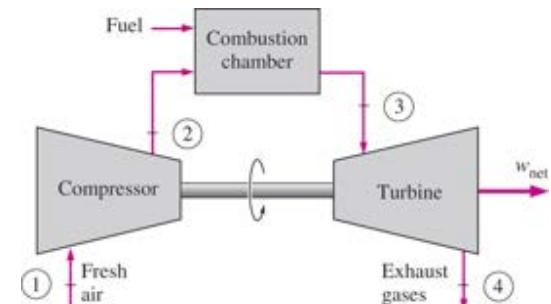
$$q_{\text{out,to environment}} = h_{\text{in}} - h_{\text{out}} = h_4 - h_1$$

$$w_{\text{net}} = w_{\text{out,turbine}} - w_{\text{comp,in}} = (h_3 - h_4) - (h_2 - h_1)$$

- Thermal efficiency simple Brayton cycle

$$\eta_{\text{Brayton}} = \frac{w_{\text{turbine,out}} - w_{\text{compr,in}}}{q_{\text{in,combustion}}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$

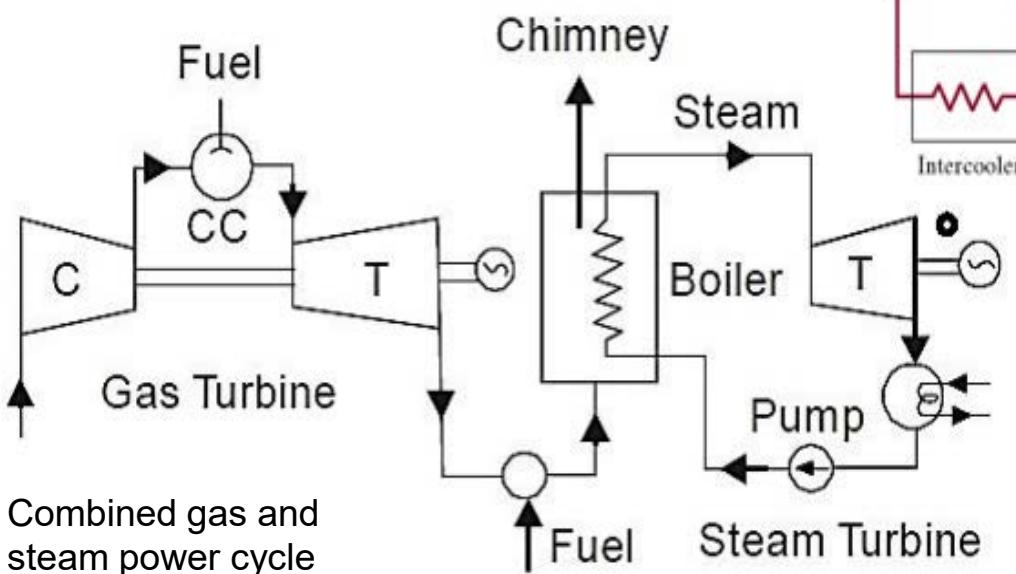
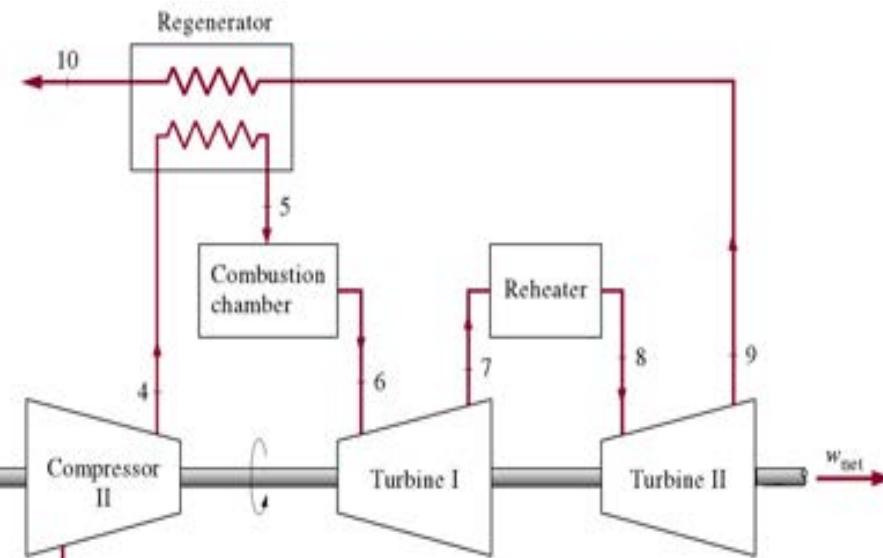
- Design parameters
 - Turbine inlet temperature
 - Pressure ratio
 - Working medium
- Mollier diagram for air



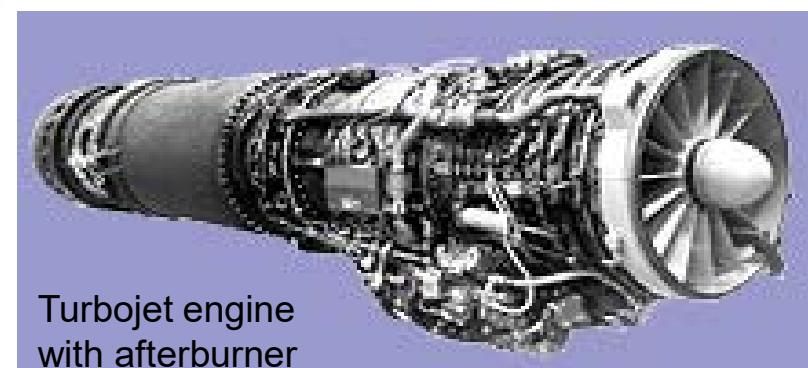
Simple open ideal Brayton cycle

Next Class 11: Gas Power Cycles - Advanced

- Extra devices improve the efficiency of a Brayton cycle
 - Reheating
 - Inter cooling
 - Regeneration
- Aircraft gas turbines
- Combined cycles

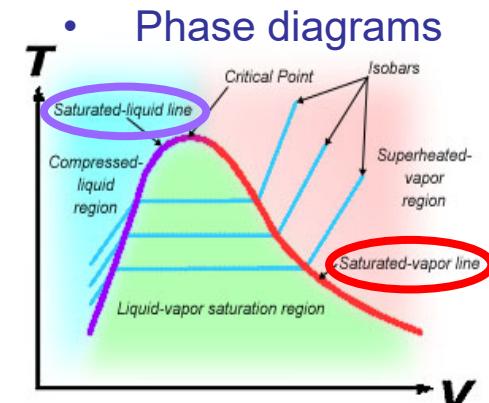


Brayton cycle with reheating, inter cooling and regeneration



Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal efficiency $\eta_{thermal} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Mixture fraction $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
- Ideal gas law $Pv = RT$, $c_p - c_v = R$
- For an ideal gas $du = c_v dT$ and $dh = c_p dT$
- Conservation of mass $m_{in} = m_{out}$, mass flow rate $\dot{m} = \rho v A$
- Conservation of energy, first law of thermodynamics
 - Closed system $du = \delta w - \delta q \rightarrow \Delta u = w - q$
 - 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 $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)
- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdP$
- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Isentropic processes ideal gas $Pv^k = \text{constant}$, $Tv^{k-1} = \text{constant}$, $P^{(k-1)/k}/T = \text{constant}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$ Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$



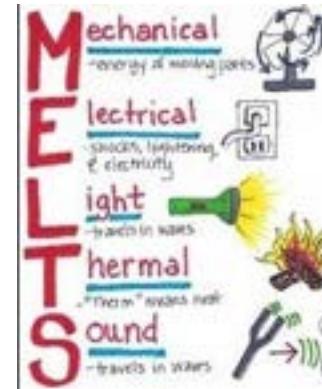
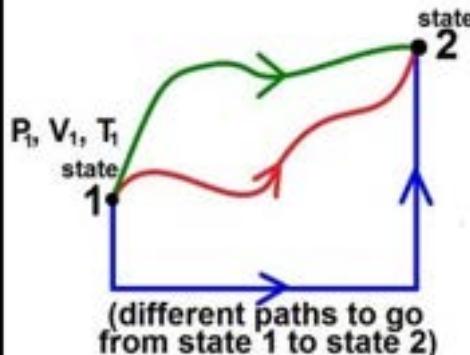
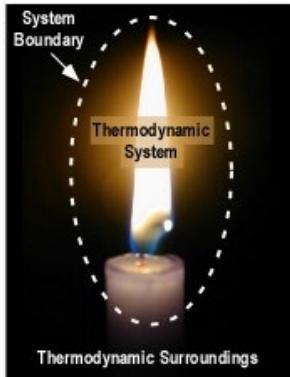
Class 11: Gas power cycles, advanced Brayton cycle and aircrafts



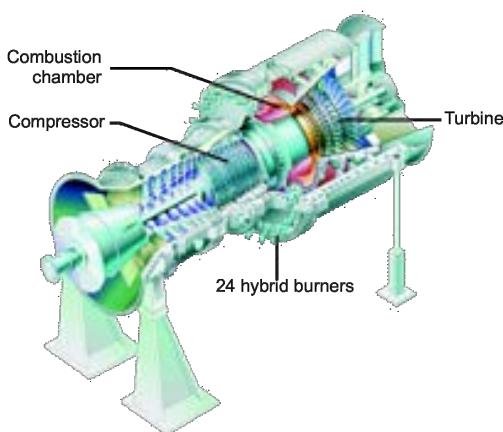
Turbojet-powered Raptor fighter aircraft

Roadmap Engineering Thermodynamics

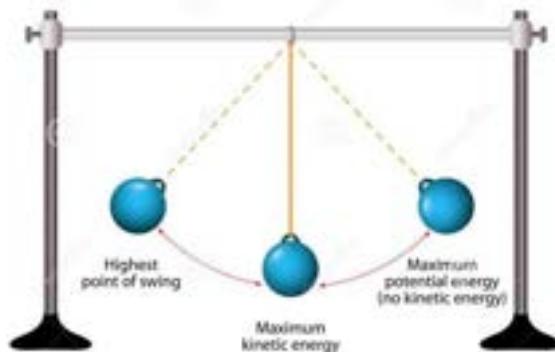
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



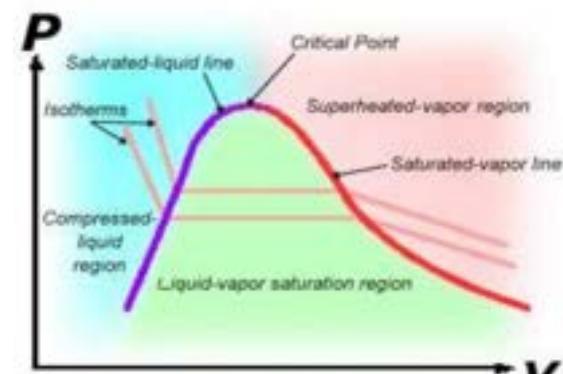
- Power cycles (Class 6 – 11)



- Laws of Thermo (Class 4 and 5)

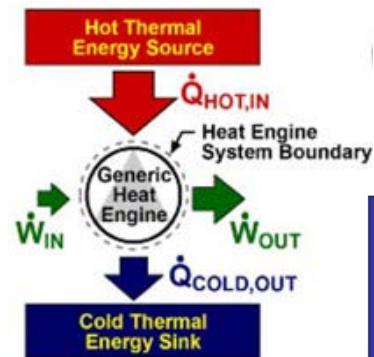


- Properties of Substances (Class 3, 9)

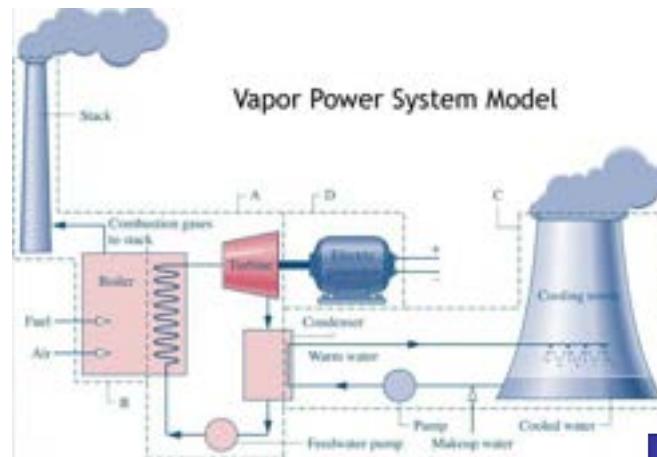


Roadmap Engineering Thermodynamics

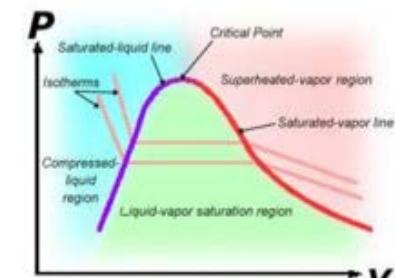
Thermodynamic cycles (Class 6)



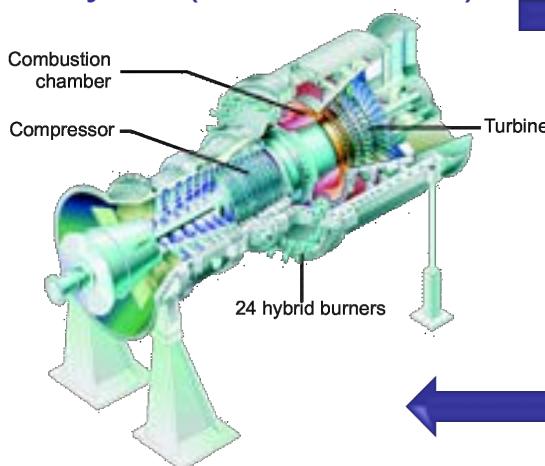
Vapor power cycles – Rankine cycle (Class 7, 8)



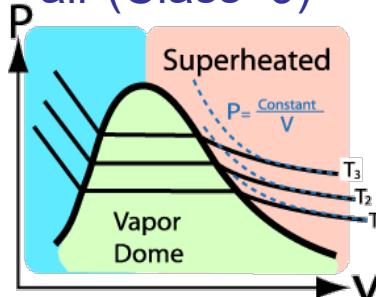
Properties of water (Class 3)



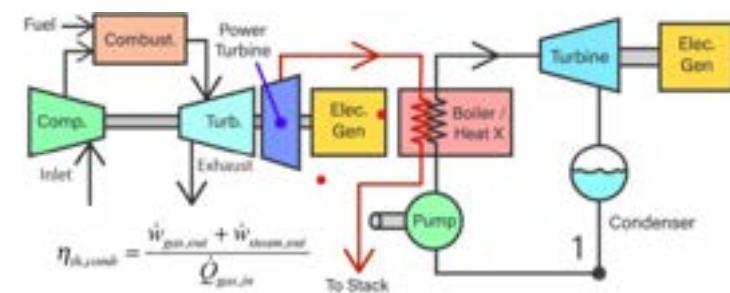
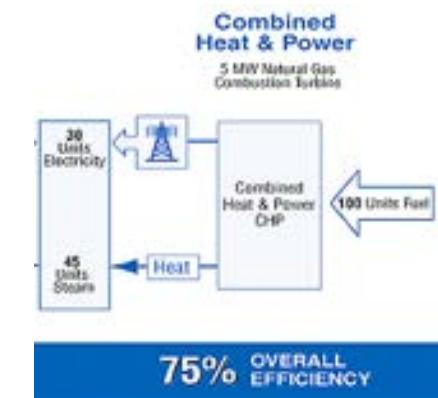
Gas power cycles – Brayton cycle (Class 10, 11)



Properties of air (Class 9)



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



Recapitulate class 10

- **Gas power cycles (Brayton cycles):** cycles using gas as working fluid throughout the whole cycle
 - Air-standard cycle, open and closed, ideal and real Brayton cycle
 - Heat and power in- and output simple Brayton

$$w_{\text{compressor,in}} = h_{\text{out}} - h_{\text{in}} = h_2 - h_1$$

$$q_{\text{in,combustion}} = h_{\text{out}} - h_{\text{in}} = h_3 - h_2$$

$$w_{\text{out,turbine}} = h_{\text{in}} - h_{\text{iut}} = h_3 - h_4$$

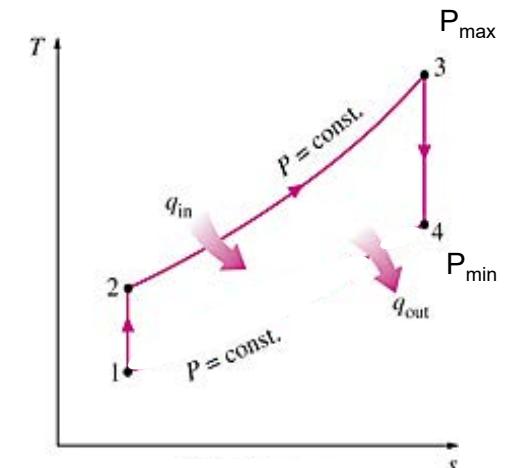
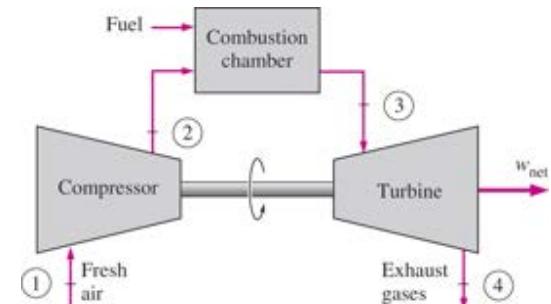
$$q_{\text{out,to environment}} = h_{\text{in}} - h_{\text{out}} = h_4 - h_1$$

$$w_{\text{net}} = w_{\text{out,turbine}} - w_{\text{comp,in}} = (h_3 - h_4) - (h_2 - h_1)$$

- Thermal efficiency simple Brayton cycle

$$\eta_{\text{Brayton}} = \frac{w_{\text{turbine,out}} - w_{\text{compr,in}}}{q_{\text{in,combustion}}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2}$$

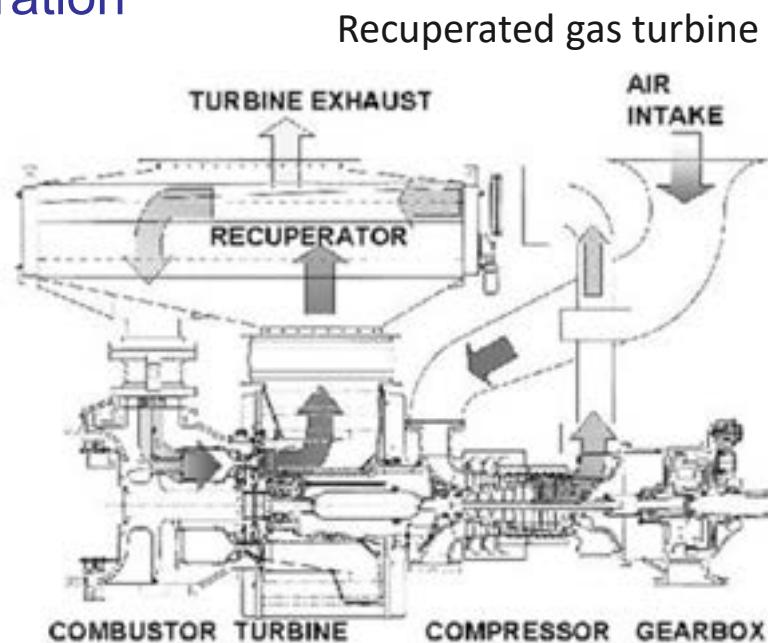
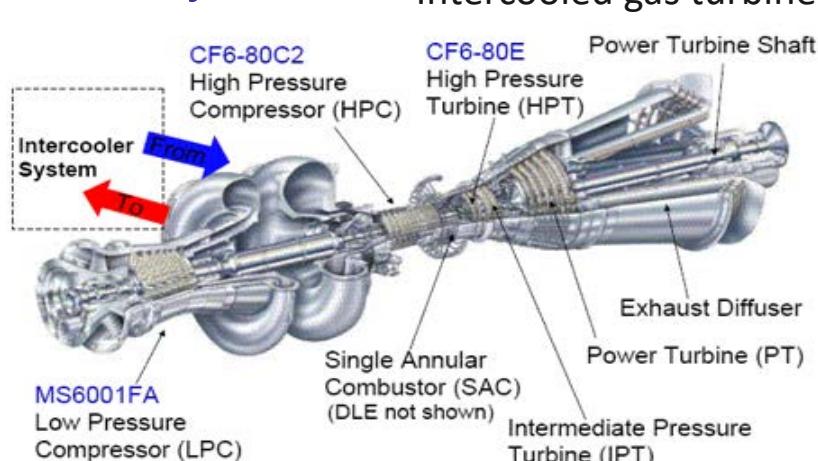
- Design parameters
 - Turbine inlet temperature
 - Pressure ratio
 - Working medium
- Mollier diagram for air



Simple open ideal Brayton cycle

Content Class 11

- Gas power cycles – Brayton cycles, advanced
- Adding extra devices → improves efficiency or power output
 - Extra heater & Intercooling & Regeneration
- Aircraft gas turbines
- Combined cycles



- Learning goal: recognize a **complicated** thermodynamic system to produce work, explain the configuration, analyse the thermodynamic aspects from the viewpoint of the first law of thermodynamics, interpret and evaluate the results and suggest improvements

Increasing the Brayton Cycle Performance

- In the previous class the simple Brayton cycle was explained and analysed
- It was discussed that the net power output or efficiency can be increased by
 1. Increasing the turbine output
 2. Decreasing the compressor input
 3. Decreasing the heat input
- The Brayton cycle can be further improved by adding extra devices, like in the Rankine cycle, for the Brayton cycle we can apply
 1. Reheating (comparable to reheating in the Rankine)
 2. Intercooling
 3. Regeneration (also called recuperation, comparable to feed water heating in the Rankine cycle)

Increasing the Brayton Cycle Performance

- For the (improved) design of the Brayton cycle designers are not only concerned with increasing the efficiency but also with increasing the net power output
 - Higher efficiency means a lower fuel / energy consumption
 - However, for some applications a minimum amount of power is needed, and efficiency can be considered less important
- The improved cycle can be more efficient and / or produce more power



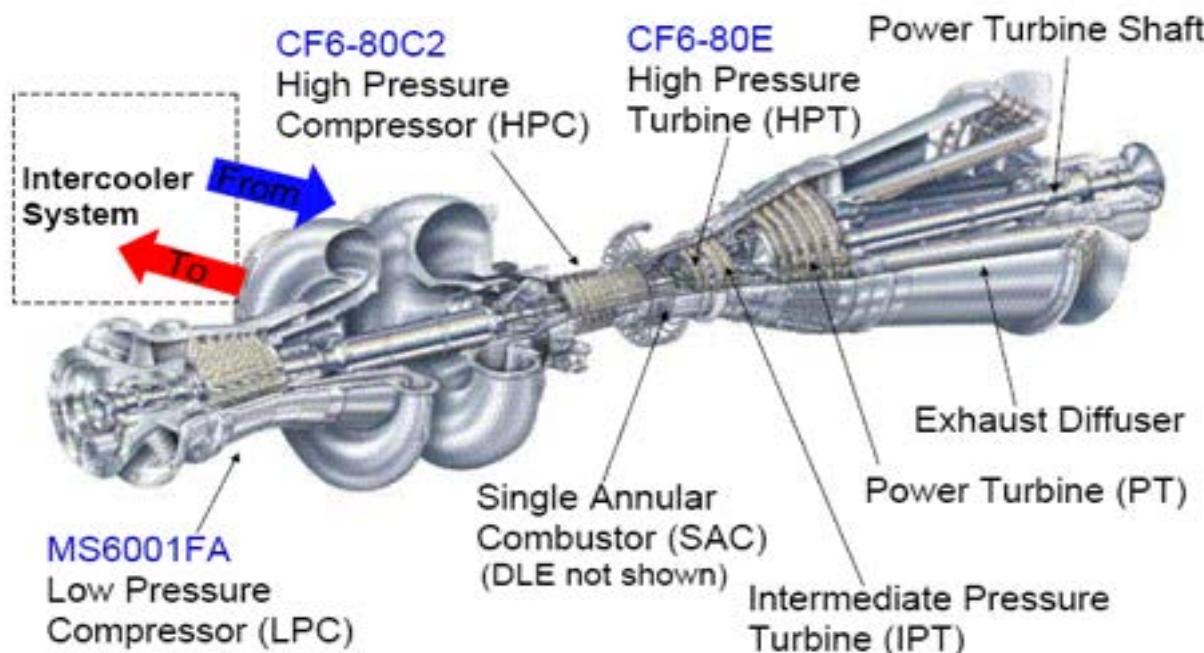
Airplane cruising: Long time, high efficiency is important but lower power output required



Airplane take off: High power output required, but short time and high efficiency is less important

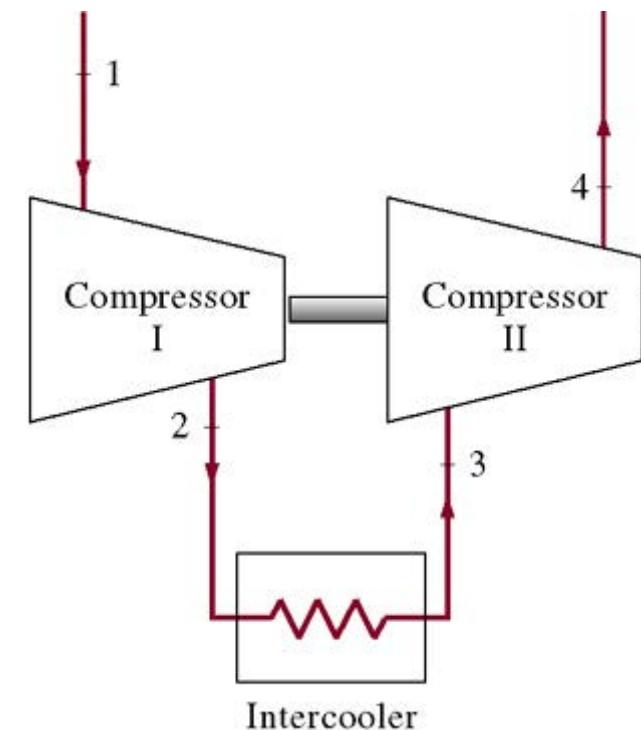
Brayton Cycle: Intercooling

- An **isothermal** compressor requires less power than an **isentropic** (adiabatic & reversible) compressor as $\delta w_{comp} = dh = c_p dT$
- The work input is 0 if $dT=0$, so if $T=\text{constant}$ as in an isothermal process
- However, an isothermal compressor is not practical (you should cool the fluid during compression)
- An adiabatic compressor is more practical



Brayton Cycle: Intercooling

- An isothermal compressor can be approximated by using inter cooling
 - Multiple adiabatic compressor stages are placed after each other
 - The working fluid is cooled in between the stages
- Intercooling
 - Increases the power output per unit mass flow as the power input decreases
 - Extra heat is rejected in the intercooler
 - Decreases the cycle efficiency without regeneration as the heat input increases (compression also heats the air so if the gas is cooled during compression it will have a lower temperature after compression and more energy is needed to end up with the same inlet turbine temperature as without compression)



Compressor Intercooling in h-s Diagram

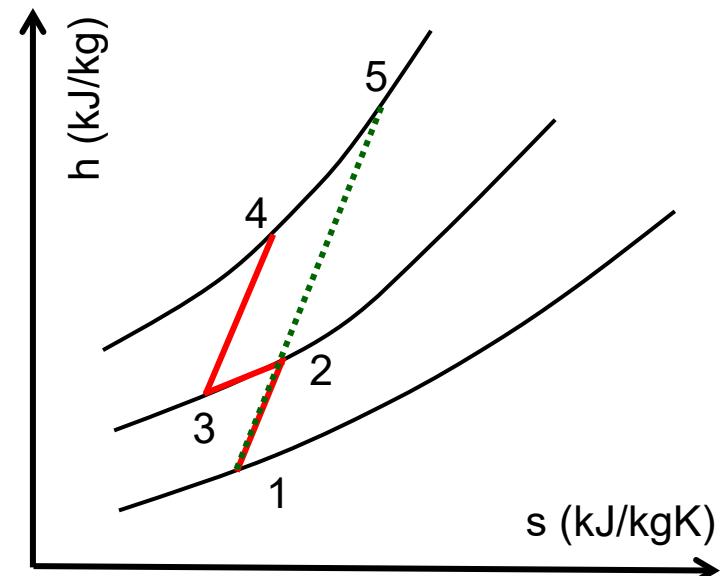
- The work input for the compressor without inter cooling is:

$$W_{\text{compressor}} = h_5 - h_1$$

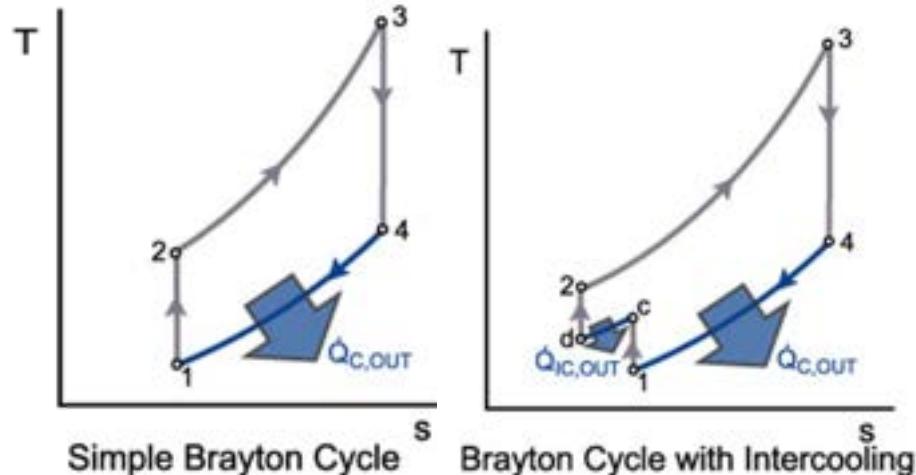
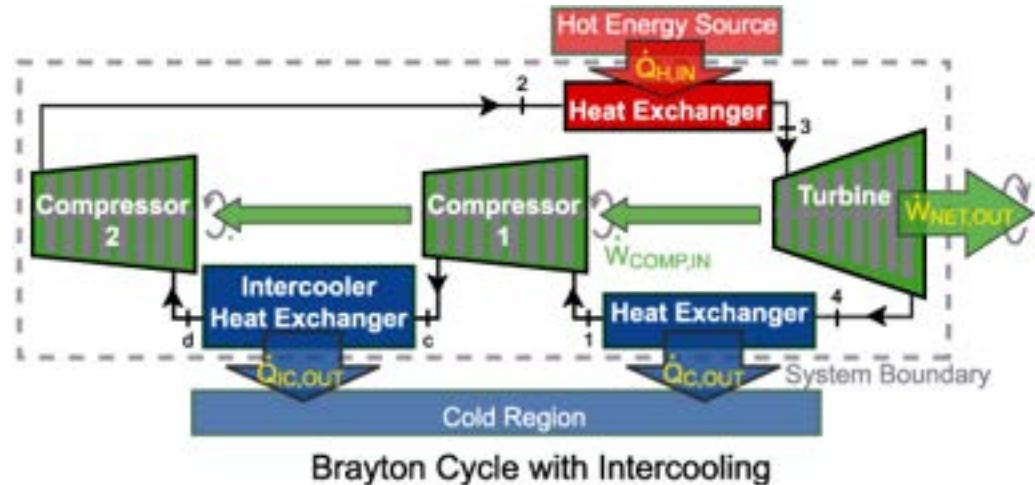
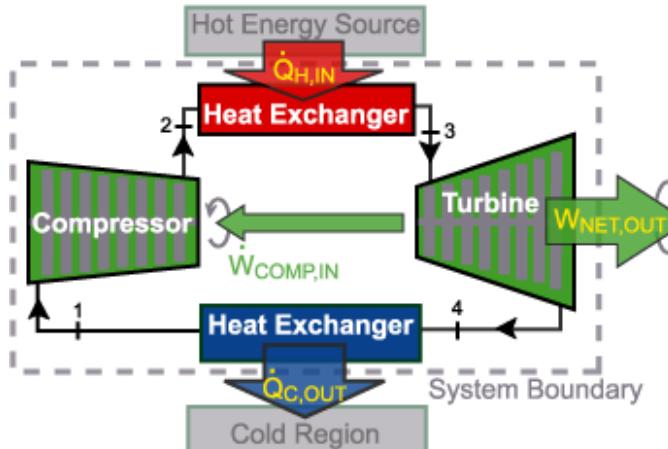
- With inter cooling the work input is less

$$\begin{aligned} W_{\text{compressor-intercooling}} &= \\ &(h_2 - h_1) + (h_4 - h_3) \end{aligned}$$

- Conclusion → the net work will increase
- However, there is big drawback, extra heat is needed as the gas leaves the compressor at a lower temperature: $q_{\text{extra-heat}} = h_5 - h_4$
- Extra disadvantageous is that this heat must be added at low temperature (remember, Carnot efficiency, it is better to add heat at high temperature)
- Inter cooling → compressor work reduced
→ thermal efficiency decreased (without regeneration)
- Inter cooling is applied as extra power output is required



Brayton Cycle: Intercooling

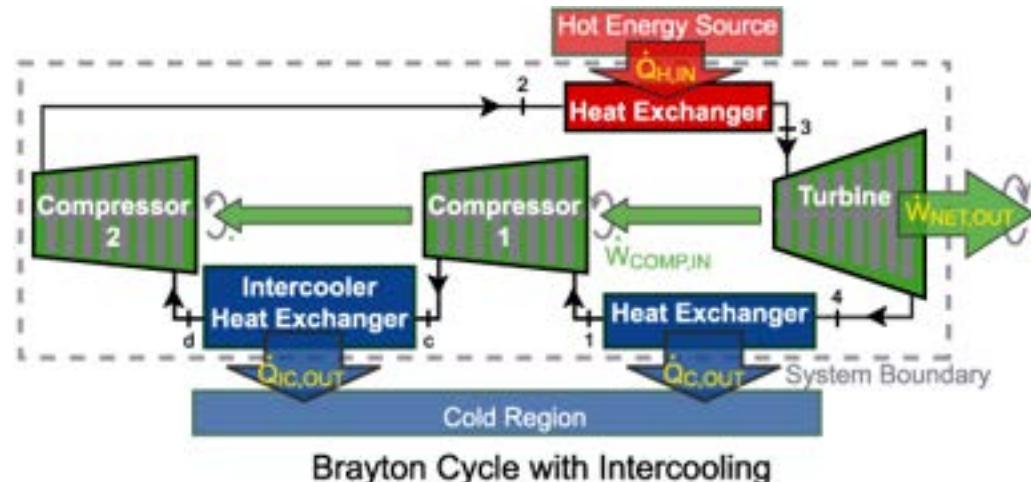
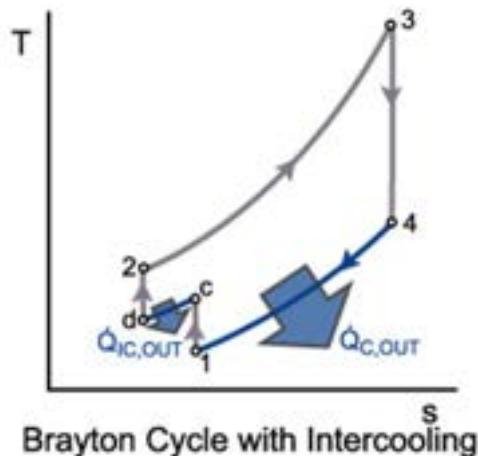


- To calculate the total work input the work input of all compressor stage should be added
- Work input (kJ/kg):

$$w_{in} = w_{compr1} + w_{compr2} = (h_c - h_1) + (h_2 - h_d)$$
- Intercooling results also in extra contributions to the heat output
- Heat output (kJ/kg):

$$q_{out} = q_{c,out} + q_{ic,out} = (h_4 - h_1) + (h_c - h_d)$$

Brayton Cycle: Intercooling



- Work input (kJ/kg):

$$w_{in} = w_{compr1} + w_{compr2} = (h_c - h_1) + (h_2 - h_d)$$

- Heat output (kJ/kg):

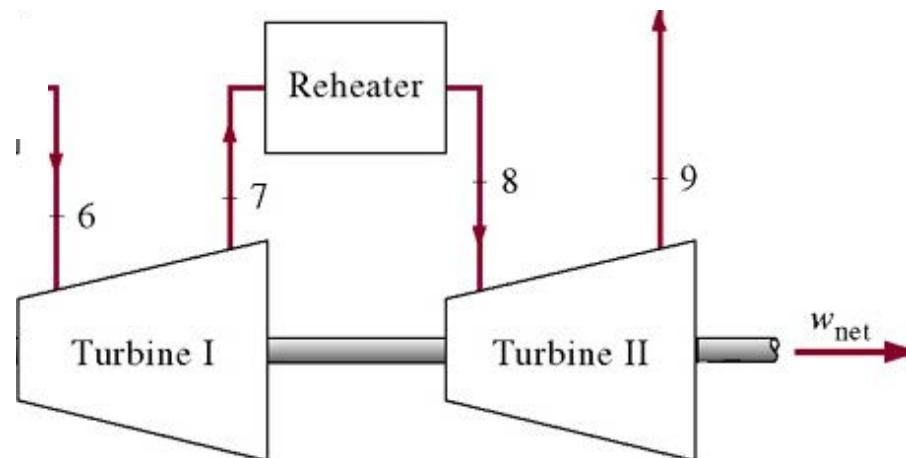
$$q_{out} = q_{c,out} + q_{ic,out} = (h_4 - h_1) + (h_c - h_d)$$

- Efficiency Brayton cycle with inter cooling

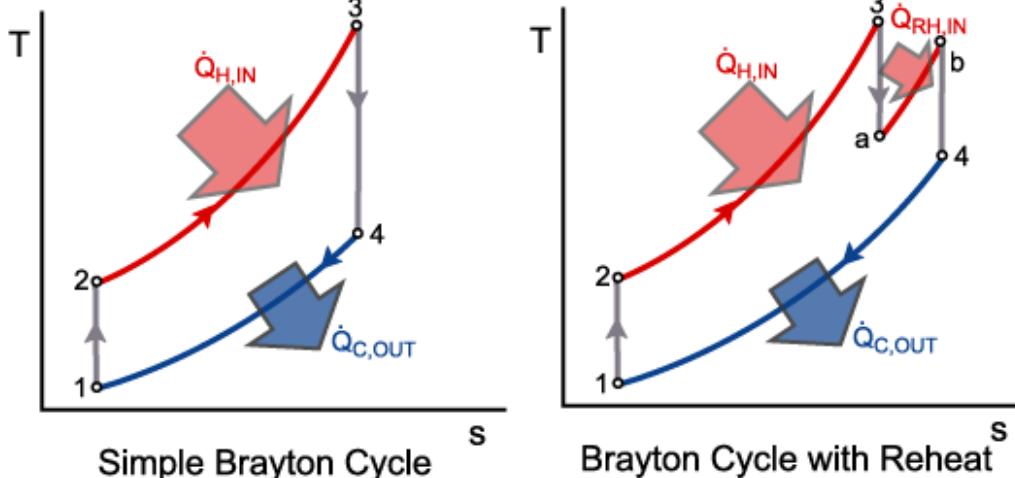
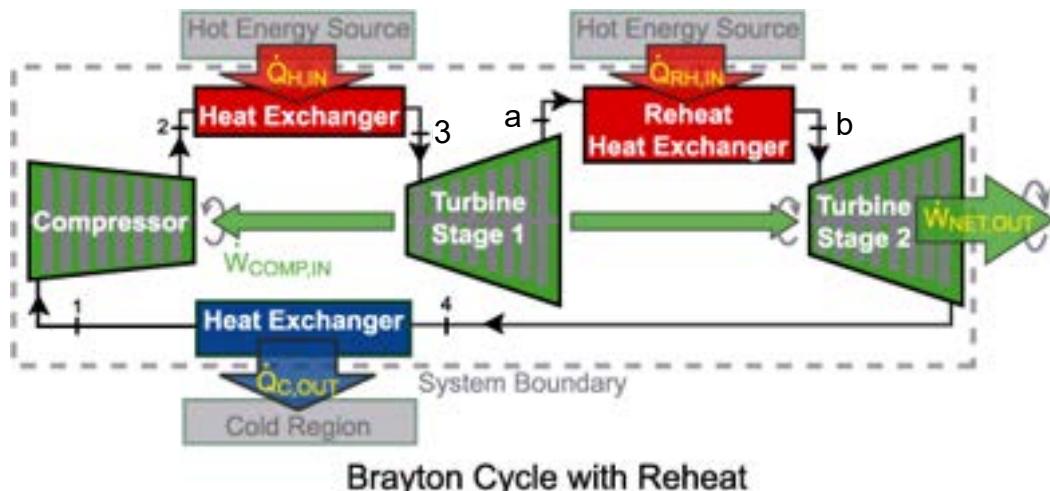
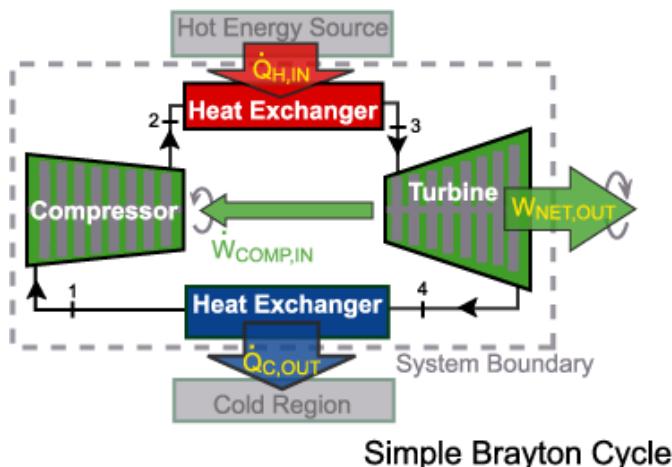
$$\begin{aligned} \eta_{th-Brayton-intercooling} &= \frac{w_{net}}{q_{in}} \\ &= \frac{w_{turb} - (w_{comp1} + w_{comp2})}{(h_3 - h_4) - [(h_c - h_1) + (h_2 - h_d)]} \end{aligned}$$

Brayton Cycle with Reheating

- An **isothermal** turbine produces more power than an **isentropic** (adiabatic & reversible) turbine
- However, an isothermal turbine is not practical (you should heat the fluid during the expansion)
- An adiabatic turbine is more practical
- An isothermal turbine can be approximated by using reheating
 - Multiple adiabatic turbine stages are placed after each other
 - The working fluid is reheated in between the stages
- Reheating
 - Increases the power output per unit mass flow
 - Increases the energy rejected at the turbine outlet
 - Decreases cycle efficiency without regeneration as extra heat is needed in the reheat



Brayton Cycle with Reheating



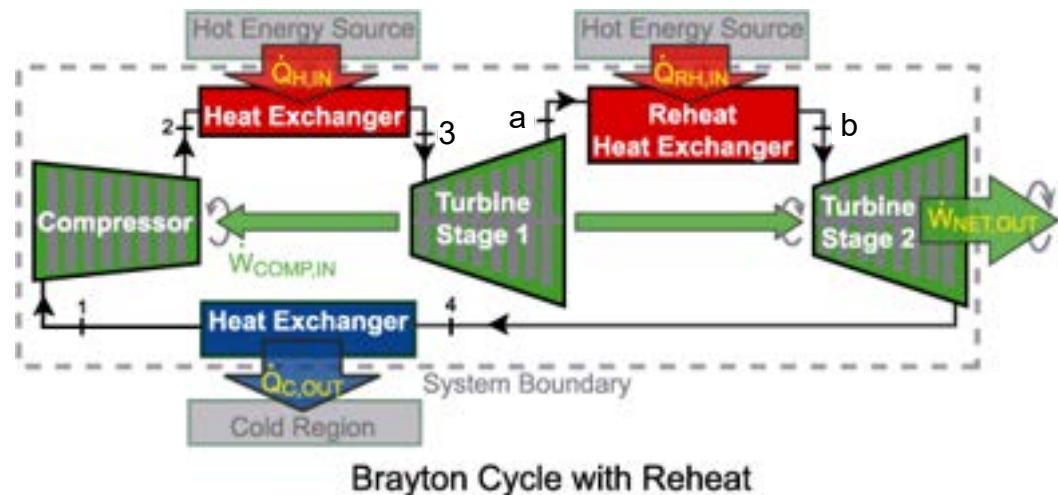
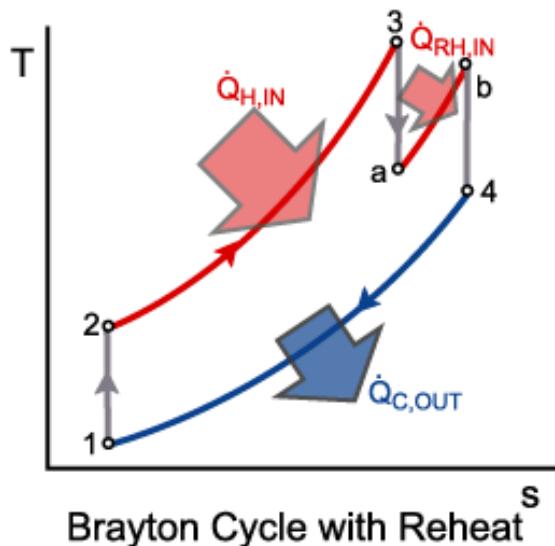
- Net output (kJ/kg):

$$W_{\text{net}} = W_{\text{out}} - W_{\text{in}} = \\ W_{\text{turb1}} + W_{\text{turb2}} - W_{\text{compr}} = \\ (h_3 - h_a) + (h_b - h_4) - (h_2 - h_1)$$

- Heat input (kJ/kg):

$$q_{\text{in}} = q_{\text{heat}} + q_{\text{reheat}} = \\ (h_3 - h_2) + (h_b - h_a)$$

Brayton Cycle with Reheating



- Net output (kJ/kg):

$$W_{net} = W_{out} - W_{in} =$$

$$W_{turb1} + W_{turb2} - W_{compr} =$$

$$(h_3 - h_a) + (h_b - h_4) - (h_2 - h_1)$$
- Heat input (kJ/kg):

$$q_{in} = q_{heat} + q_{reheat} =$$

$$(h_3 - h_2) + (h_b - h_a)$$

- Efficiency Brayton cycle with reheat

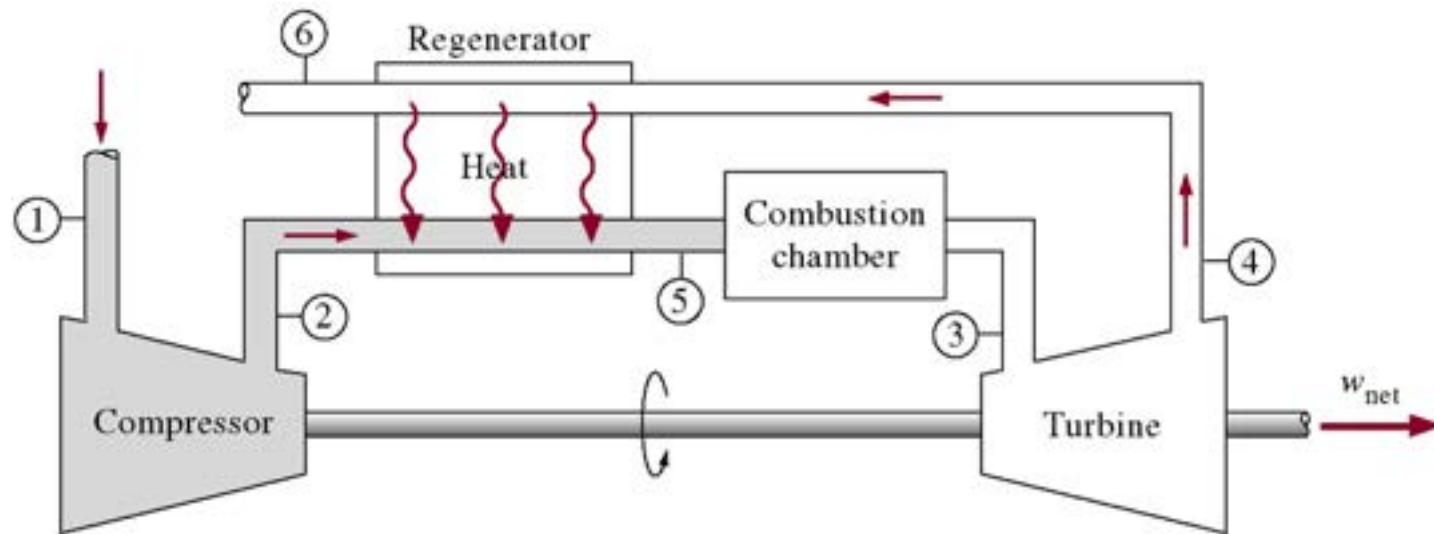
$$\begin{aligned}\eta_{th-Brayton-reheating} &= \frac{W_{net}}{q_{in}} \\ &= \frac{(w_{turb1} + w_{turb2}) - w_{comp}}{q_{heat} + q_{reheat}} \\ &= \frac{(h_3 - h_a) + (h_b - h_4) - (h_2 - h_1)}{(h_3 - h_2) + (h_b - h_a)}\end{aligned}$$

Brayton Cycle with Reheating / Intercooling

- **Reheating increases the net output of Brayton cycle** as the work output of the turbine increases
- **Inter cooling increases the net output of the Brayton cycle** as the work input of the compressor decreases
- However, **both modifications decrease the thermal efficiency** of the Brayton cycle
 - For intercooling more heat input is required to reach the same inlet temperature as without inter cooling
 - For reheating extra heat is necessary to reach the high temperature for the second turbine
- **Regeneration or recuperation** can increase the thermal efficiency of the Brayton cycle with inter cooling and / or reheating by decreasing the heat input

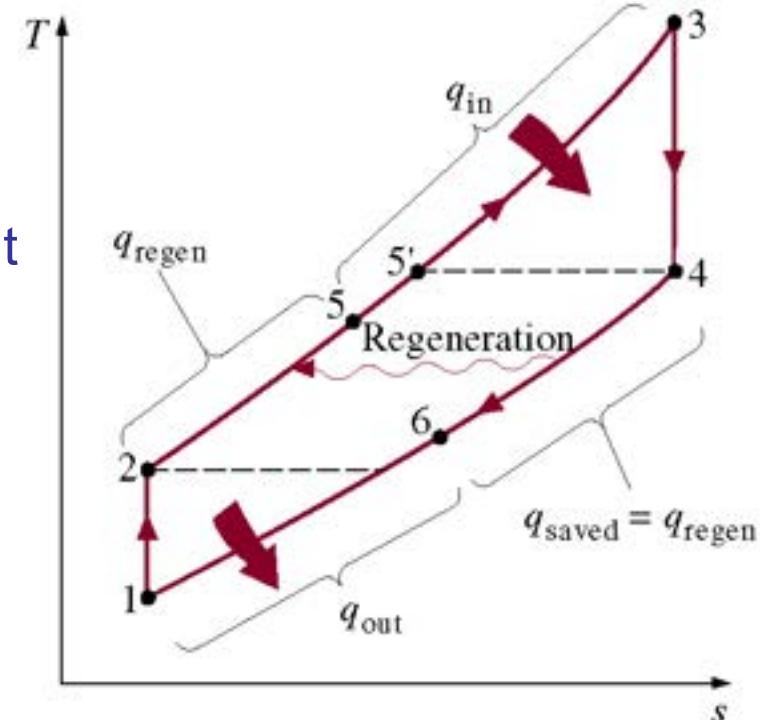
Brayton Cycle Regeneration

- Part of the heat input, q_{IN} is ‘lost’ to the surroundings as q_{OUT} with the exhaust gases, due to 2nd law limitations
- The Brayton cycle rejects relatively hot exhaust gases
- **Regeneration** (or recuperation)
 - The heat still present in the exhaust gasses leaving the turbine is used to pre heat the high-pressure air leaving the compressor in a counter flow heat exchanger which is known as a regenerator or recuperator



Brayton Cycle Regeneration

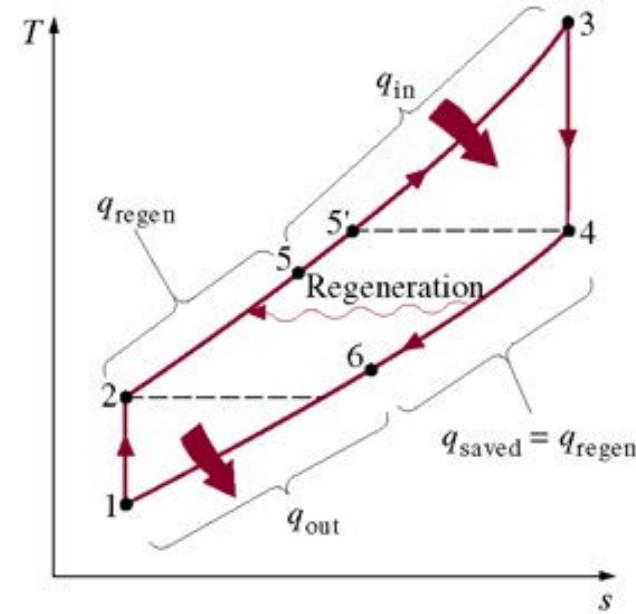
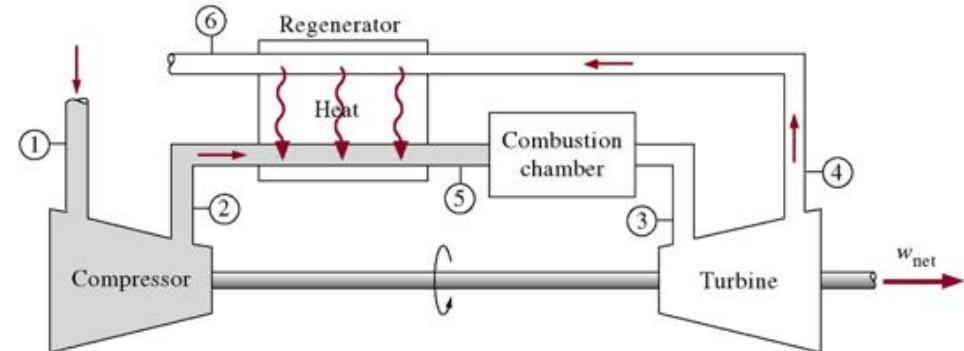
- With regeneration the energy of the relative hot turbine exhaust gases is used to pre heat the gas before combustion and therefore the heat input decreases
- The power output remains the same and therefore the thermal efficiency increases



- Regeneration is only possible if the turbine outlet temperature is higher than the compressor outlet temperature
 - Reheating: turbine outlet temperature (T_4) \uparrow
 - Intercooling: compressor outlet temperature (T_2) \downarrow
- So, reheating as well as inter cooling are advantageous for regeneration

Brayton Cycle Regeneration

- Regeneration → only possible if $T_{\text{turbine outlet}} > T_{\text{compressor outlet}}$
- $T_4 \rightarrow$ highest temperature within the regenerator
- High-pressure air (T_5) → can never be pre heated to a temperature above T_4
- Limiting (ideal) case → the air will exit the regenerator at the temperature of the exhaust gasses ($T_{5'} = T_4$)
- Actual case → air will exit the regenerator at a lower temperature T_5



$$q_{\text{reg-actual}} = h_5 - h_2$$

$$q_{\text{reg-max}} = h_{5'} - h_2 = h_4 - h_2$$

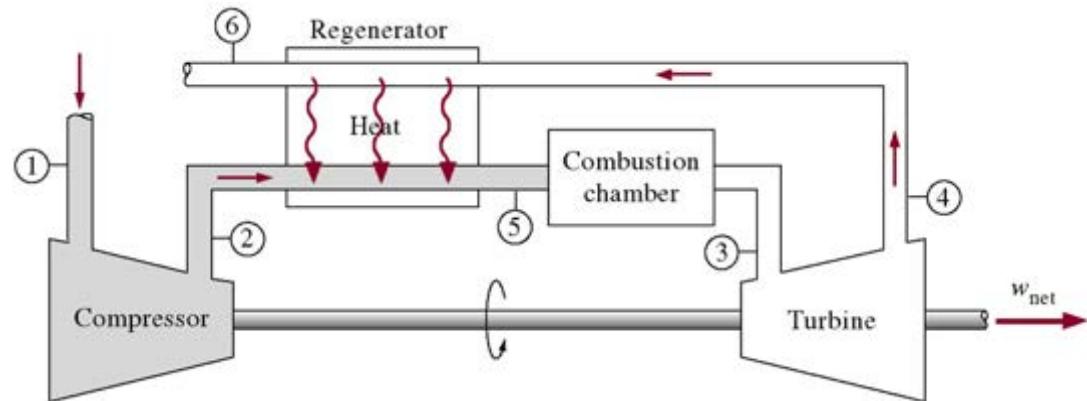
Brayton Cycle Regeneration

- Actual heat transferred:

$$q_{\text{reg-actual}} = h_5 - h_2$$

- Maximum heat transferred:

$$q_{\text{reg-max}} = h_{5'} - h_2 = h_4 - h_2$$

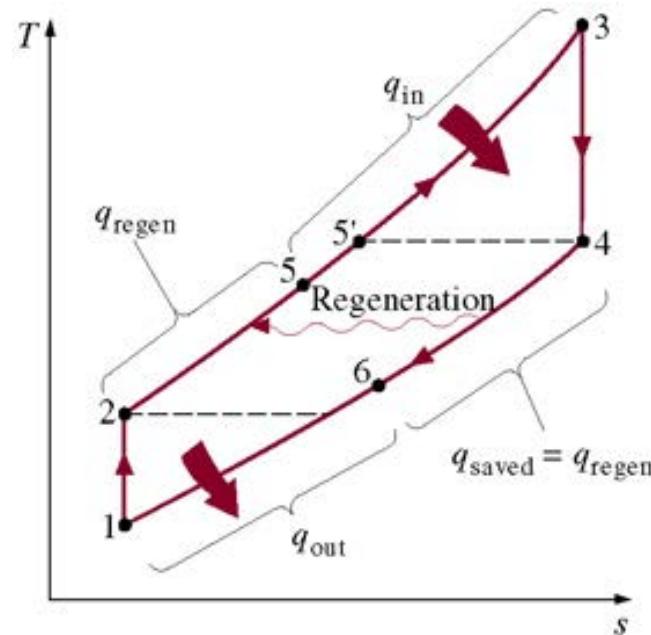


- Effectiveness regenerator (ε): the extend to which a regenerator approaches an ideal regenerator

$$\varepsilon = \frac{q_{\text{reg-actual}}}{q_{\text{reg-max}}} = \frac{h_5 - h_2}{h_4 - h_2}$$

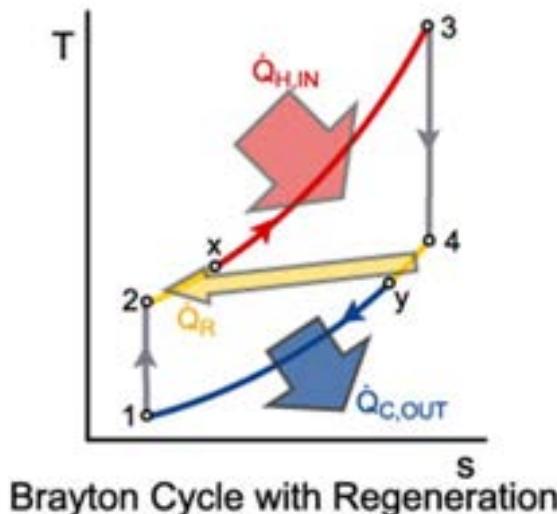
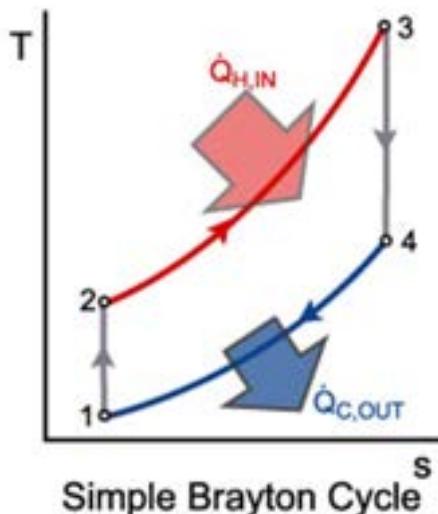
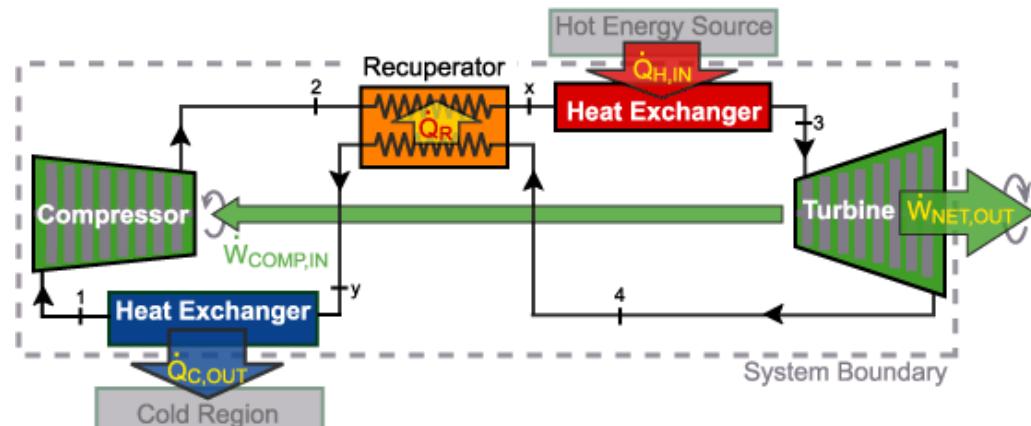
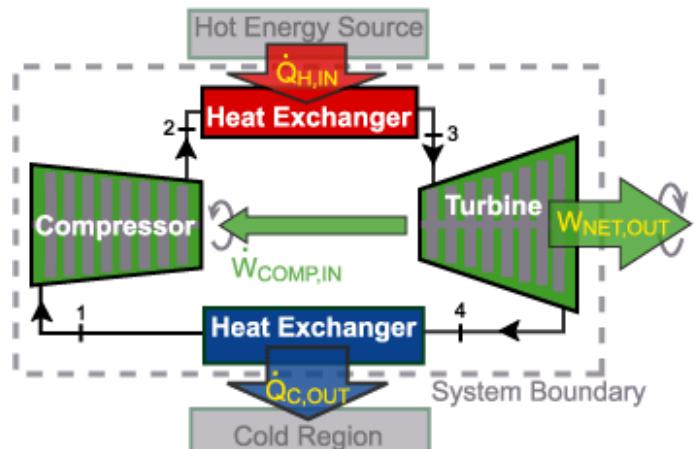
- Under cold-air-standard assumptions this reduces to:

$$\varepsilon \cong \frac{T_5 - T_2}{T_4 - T_2}$$



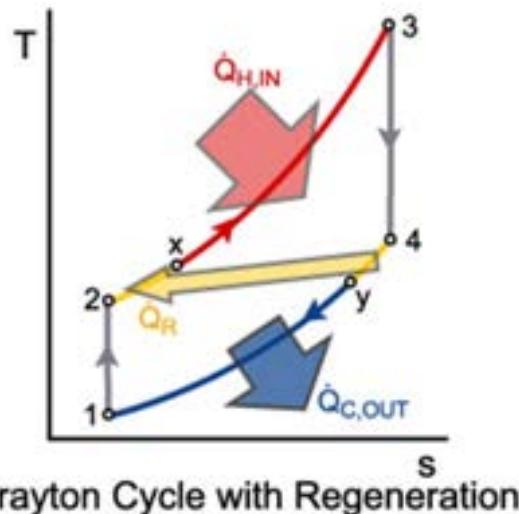
Note: $q_{\text{saved}} = q_{\text{regen}} \rightarrow h_4 - h_6 = h_5 - h_2$

Brayton Cycle Regeneration

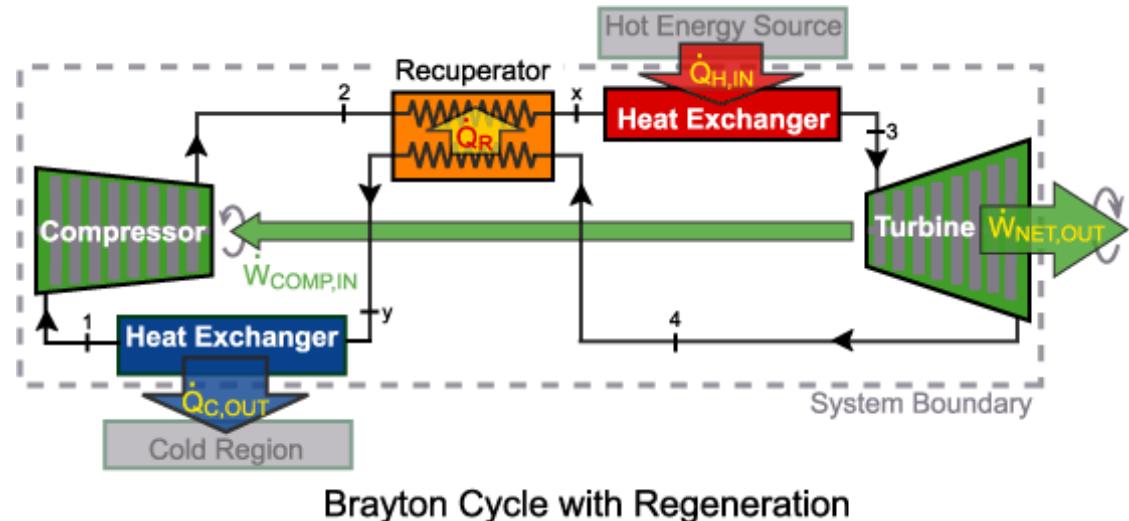


- Heat input (kJ/kg):
 $q_{in} = (h_3 - h_x)$
- Heat output (kJ/kg):
 $q_{out} = (h_y - h_1)$
- Heat regenerated (kJ/kg):
 $q_{reg} = (h_4 - h_y) = (h_x - h_2)$

Brayton Cycle Regeneration



Brayton Cycle with Regeneration



Brayton Cycle with Regeneration

- Heat input (kJ/kg):
 $q_{in} = (h_3 - h_x)$
- Heat output (kJ/kg)
 $q_{out} = (h_y - h_1)$
- Heat regenerated (kJ/kg)
 $q_{reg} = (h_4 - h_y) = (h_x - h_2)$
- Efficiency Brayton cycle with regeneration

$$\eta_{th-Brayton-regeneration} = \frac{\dot{W}_{net}}{q_{in}}$$

$$= \frac{\dot{W}_{turb} - \dot{W}_{comp}}{q_{heat}}$$

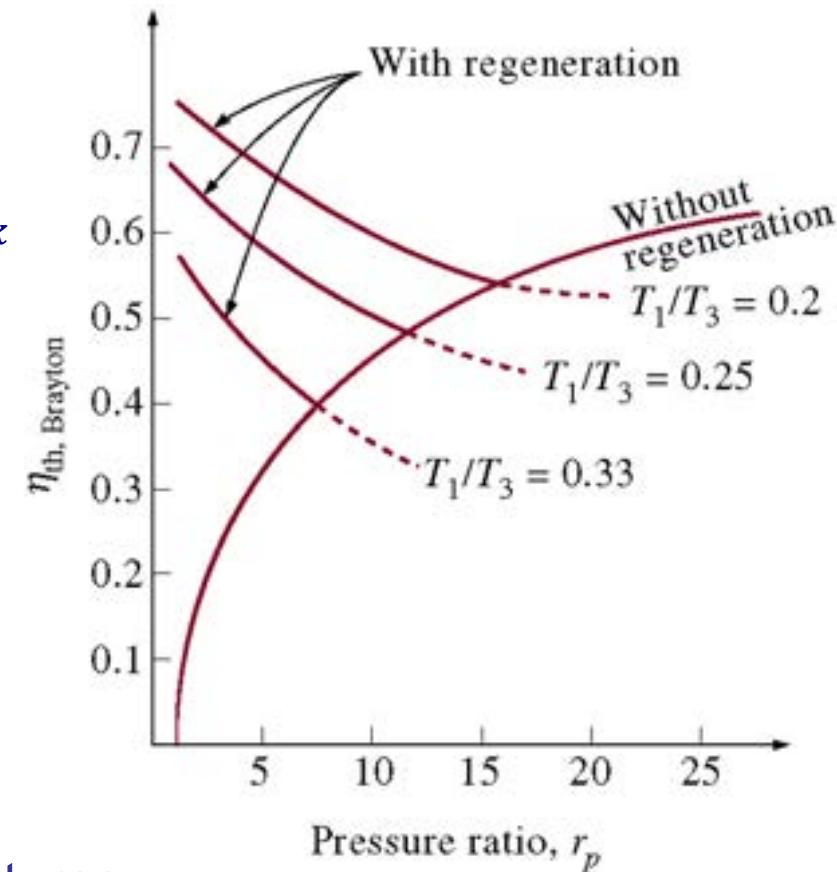
$$= \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_x)}$$

Pressure Ratio and Recuperation

- Thermal efficiency, ideal air standard Brayton cycle with regeneration:

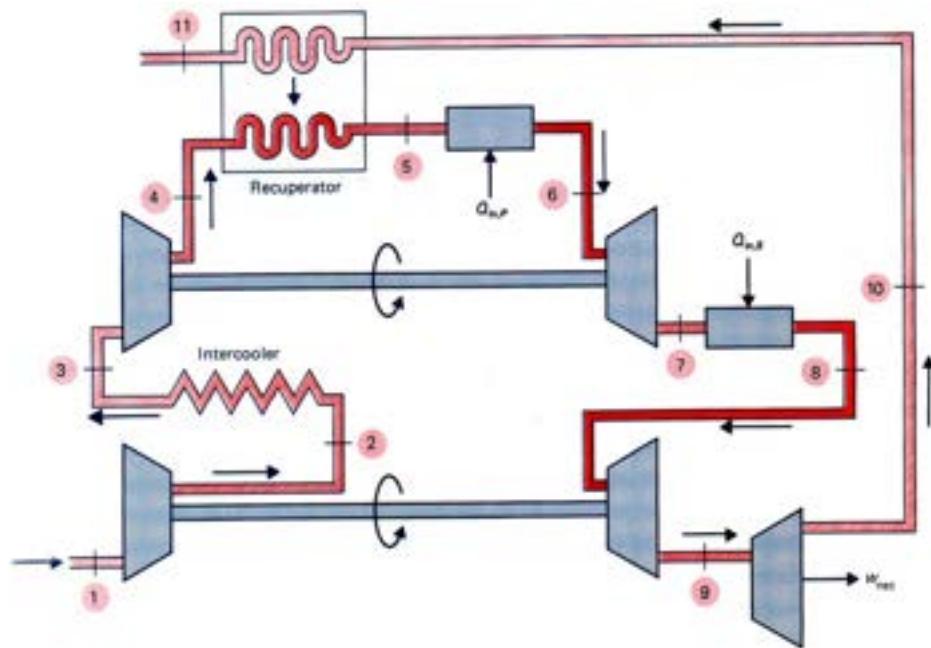
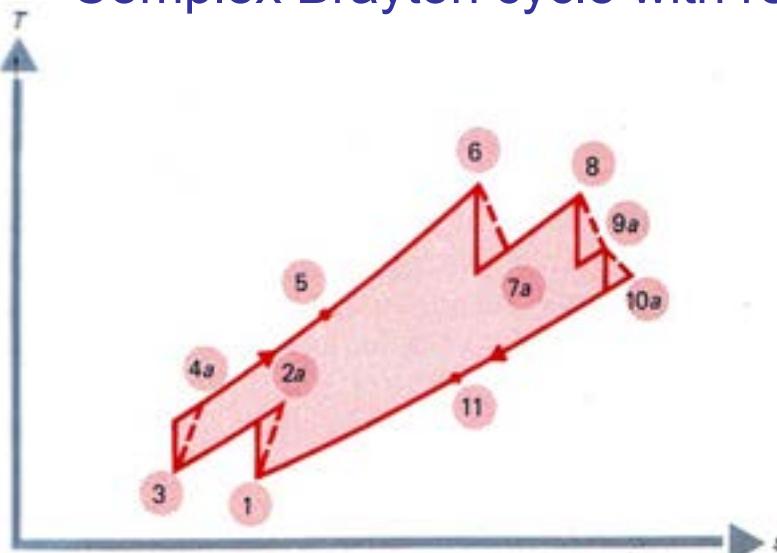
$$\eta_{th\text{-Brayton-reg-ias}} = 1 - \left(\frac{T_1}{T_3}\right) r_p^{(k-1)/k}$$

- For an ideal air standard cycle, the thermal efficiency depends on:
 - the pressure ratio (r_p)
 - the ratio of T_{\min} (T_1) and T_{\max} (T_3)
- Regeneration is most effective at:
 - lower pressure ratios
 - low minimum to maximum temperatures
- Regeneration is attractive as heat is added at a higher average temperature which increases the efficiency



Increasing Brayton Cycle Performance

- All the different improvements can be applied at once
- Complex Brayton cycle with reheat, inter cooling and regeneration



- Thermal efficiency: $\eta_{th-Brayton} = \frac{w_{net}}{q_{in}}$

$$= \frac{(w_{turb1} + w_{turb2} + w_{turb3}) - (w_{comp1} + w_{comp2})}{q_{heat} + q_{reheat}}$$

$$= \frac{[(h_6 - h_7) + (h_8 - h_9) + (h_9 - h_{10})] - [(h_2 - h_1) + (h_4 - h_3)]}{(h_6 - h_5) + (h_8 - h_7)}$$

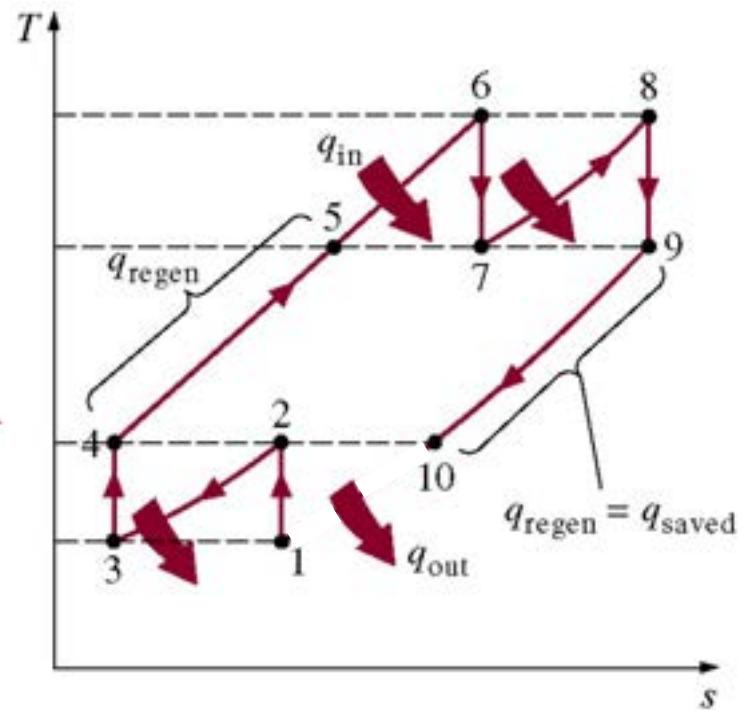
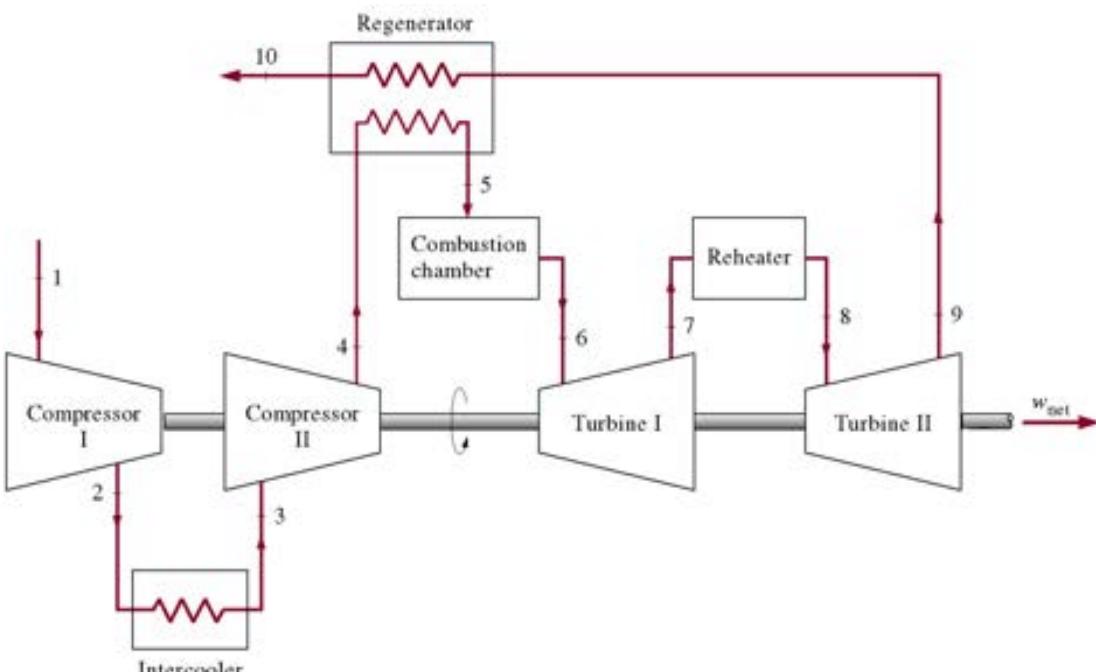
- In this case

$$w_{compr1} = w_{turb2}$$

$$w_{compr2} = w_{turb1}$$

$$w_{net} = h_9 - h_{10}$$

Inter Cooling, Reheating, Recuperation

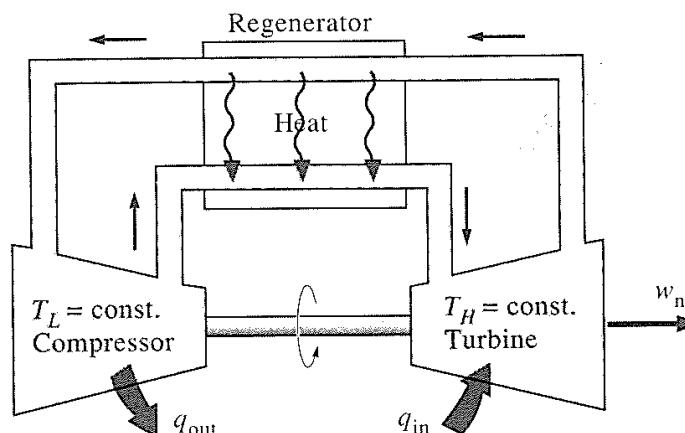
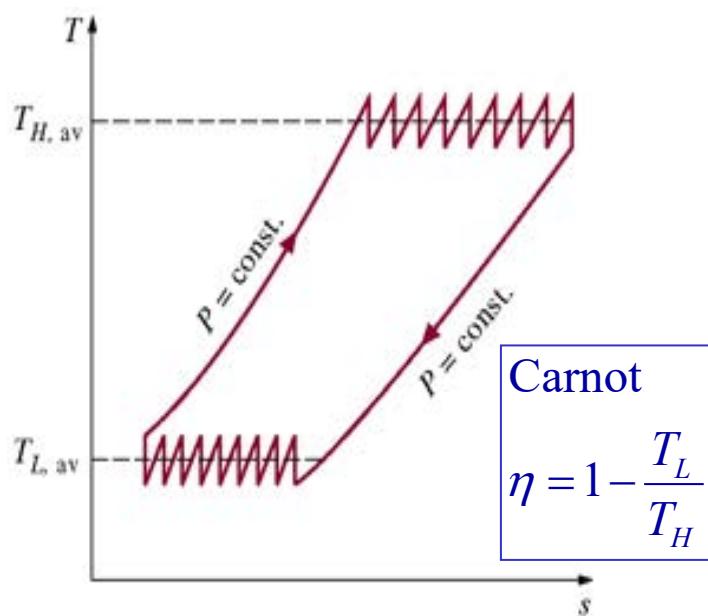


- For minimizing work input to compressor and maximizing work output from turbine:
- In principle infinite reheaters and intercoolers can be used to improve the efficiency, however the extra costs of those devices should be justified by the increased efficiency

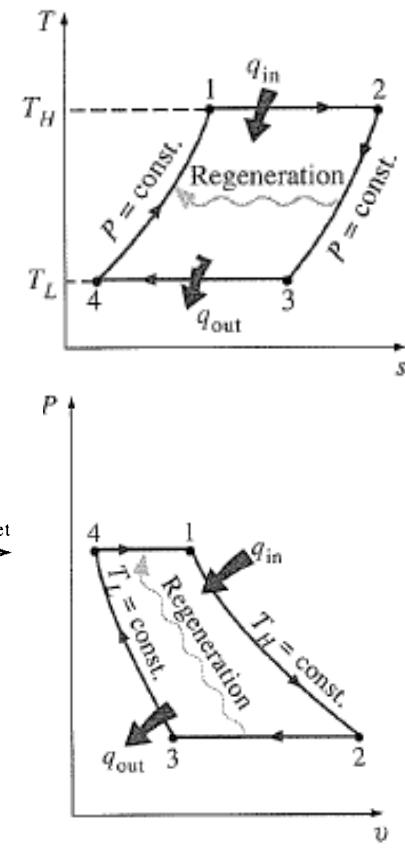
$$\frac{P_2}{P_1} = \frac{P_4}{P_3} \quad \text{and} \quad \frac{P_6}{P_7} = \frac{P_8}{P_9}$$

The Ericsson Cycle

- If the number of compression and expansion stages is increased, the ideal gas turbine cycle with reheating, inter cooling and regeneration will approach the Ericsson cycle
- Ericsson cycle → Ideal cycle, thermal efficiency approaches the theoretical limit: $\eta_{Carnot} = 1 - \frac{T_L}{T_H}$
- However, the use of more than 2 or 3 stages cannot be justified economically

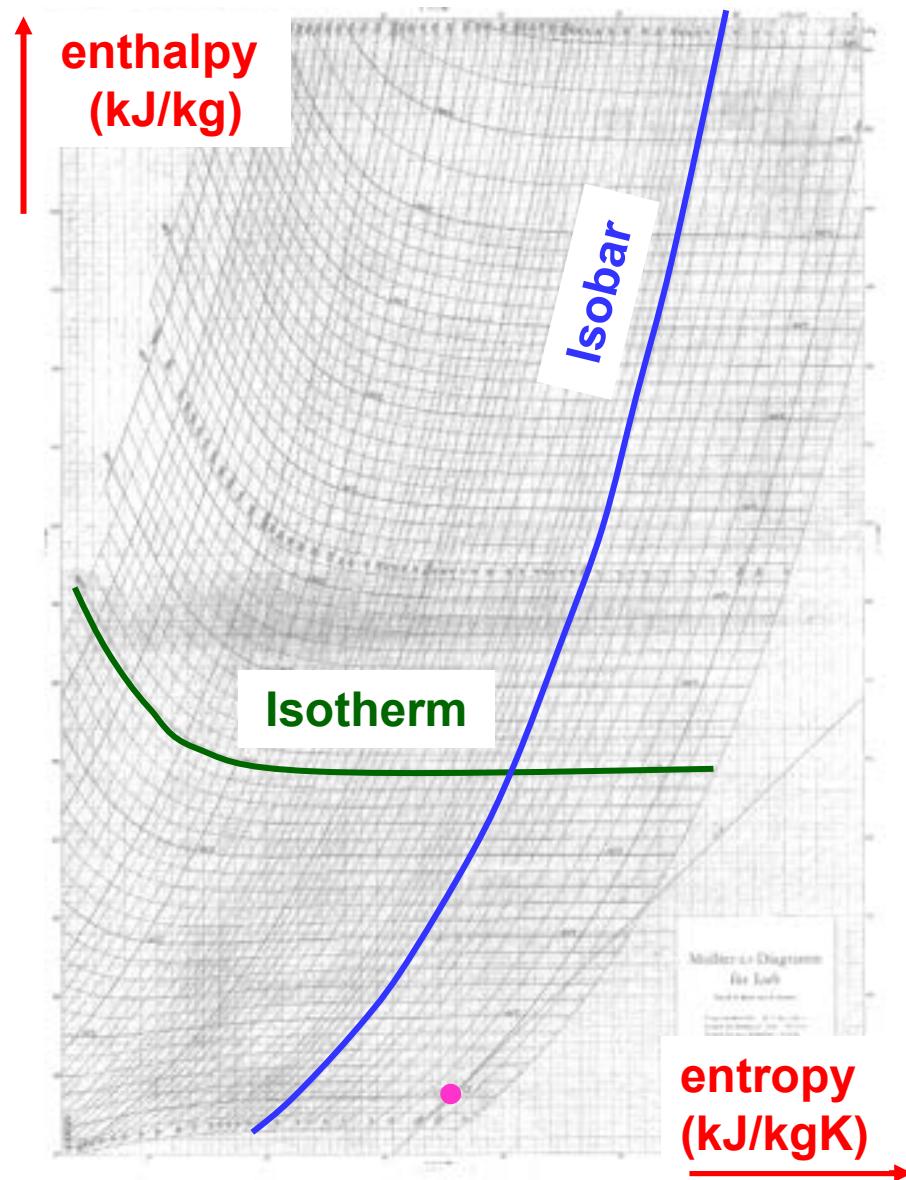


Ericsson cycle, all heat is recuperated



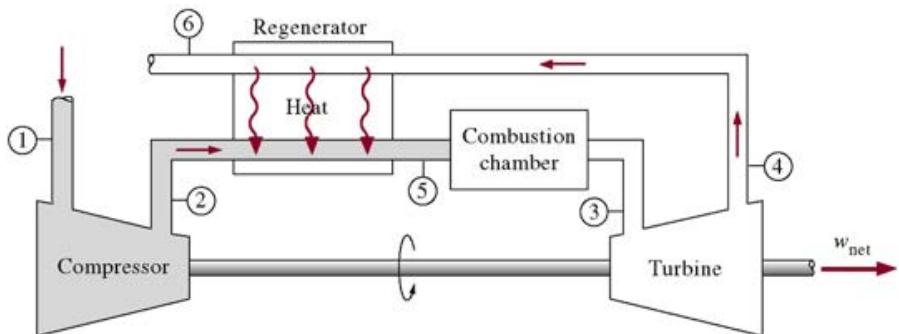
Example Gas Turbine with regeneration

- Consider a Brayton cycle with regeneration
- The pressure ratio is 8
- The air inlet temperature is 300K
- The temperature before the turbine inlet is 1300K
- The isentropic efficiency of the compressor is 80%
- The isentropic efficiency of the turbine 85%
- The effectiveness of the regenerator is 0.8
- Determine the thermal efficiency, the regenerated heat and the net work output using the Mollier diagram



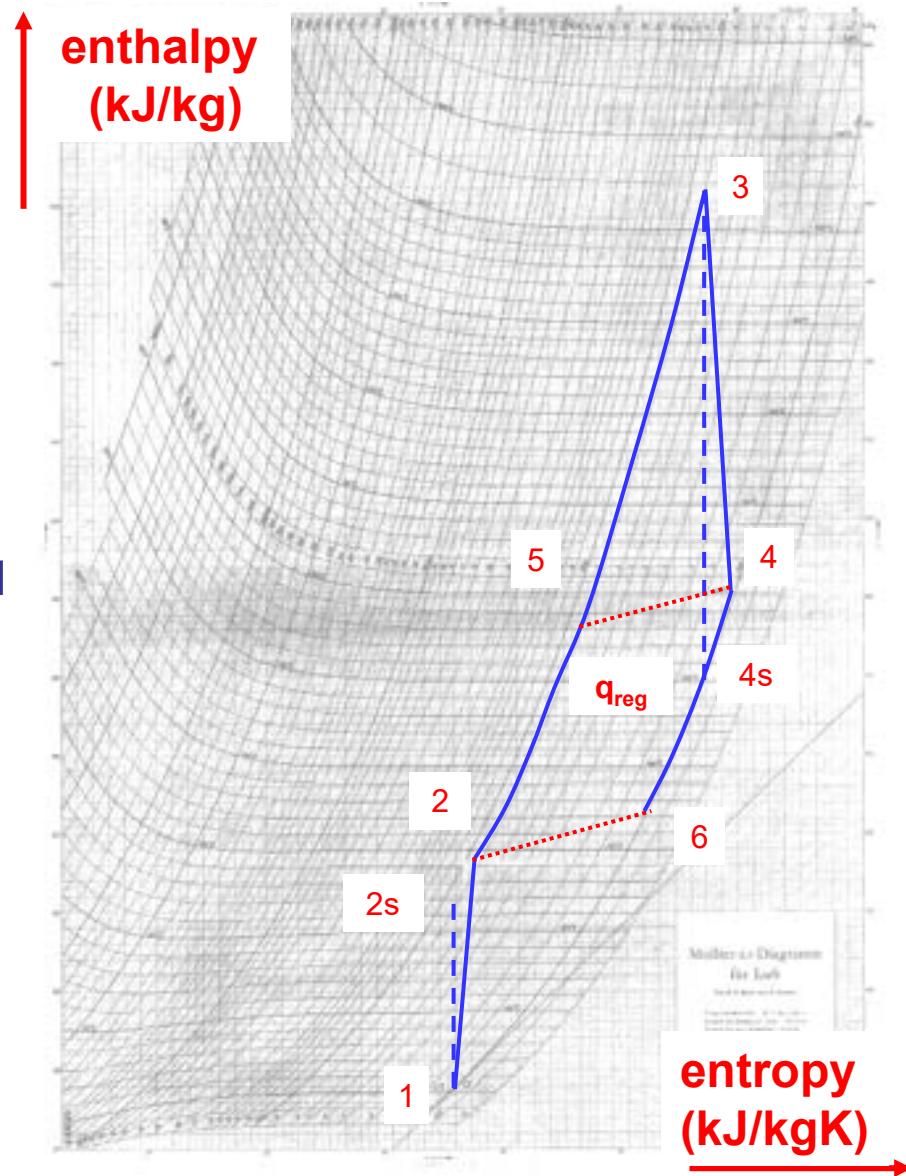
Example Gas Turbine with regeneration

- Solution, give first scheme, h-s diagram and two characteristics per point



	1 st	2 nd
1	1 bar	300 K
2s	8 bar	$s_1 = s_{2s}$
2	8 bar	$\eta_c = 0.8$
3	8 bar	1300 K
4s	1 bar	$s_3 = s_{4s}$
4	1 bar	$\eta_t = 0.85$
5	8 bar	$\varepsilon = 0.8$
6	1 bar	$h_4 - h_6 = h_5 - h_2$

- After this first analyses find all the h values from the diagram or from the known formulas for isentropic efficiencies or effectiveness and so on

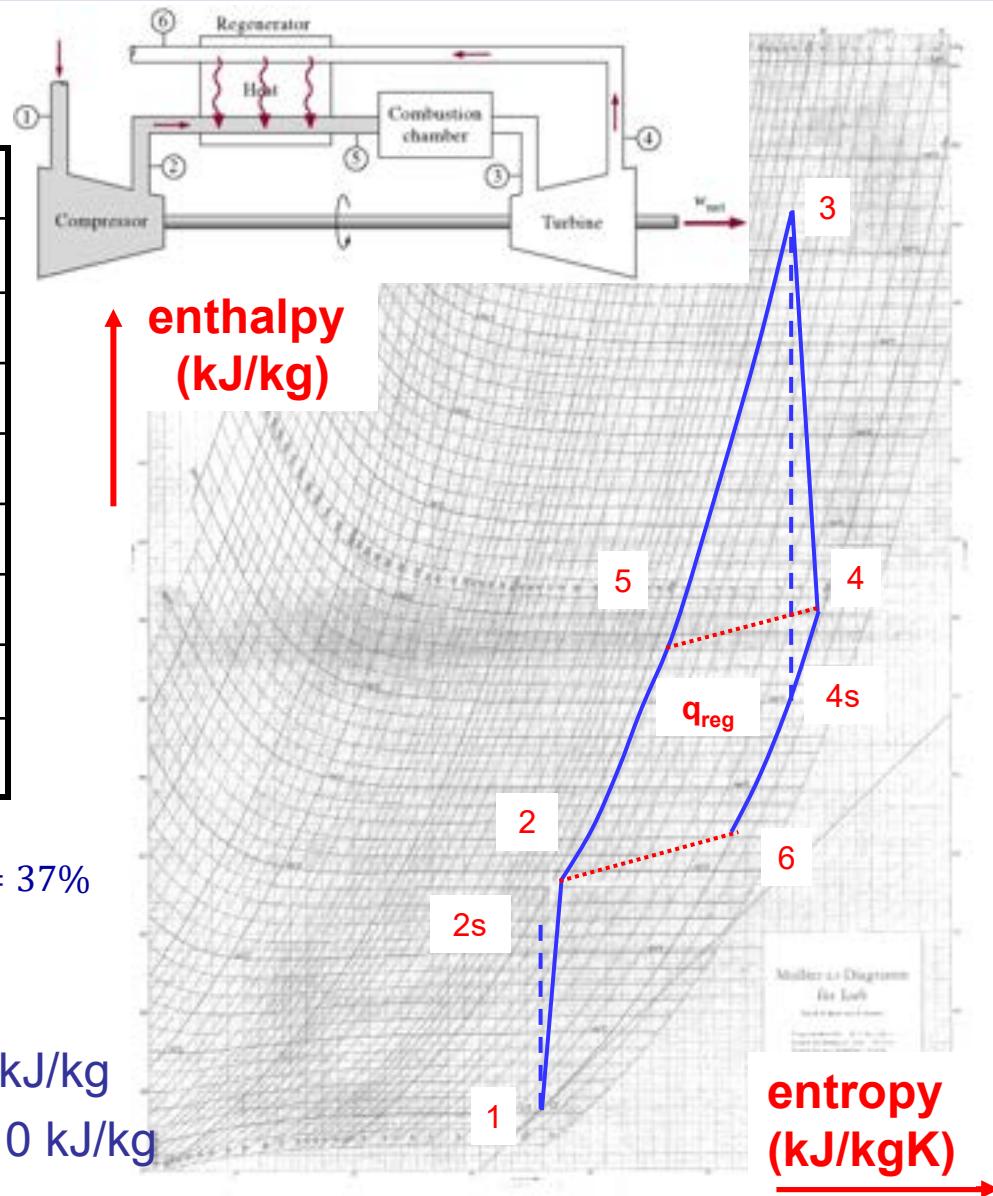


Example Gas Turbine with regeneration

- After this find all the h values from the diagram or from the known formulas

	$h(\text{kJ/kg})$	
1	300	Read from diagram
2s	545	Read from diagram
2	605	$h_2 = h_1 + 1/\eta_c(h_{2s} - h_1)$
3	1395	Read from diagram
4s	790	Read from diagram
4	880	$h_4 = h_3 - \eta_t(h_3 - h_{4s})$
5	825	$h_5 = h_2 + \varepsilon(h_4 - h_2)$
6	660	$h_6 = h_4 - (h_5 - h_2)$

$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_{\text{turb}} - w_{\text{comp}}}{q_{\text{heat}}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_5)} = 37\%$$



- With regeneration the efficiency is 37%
- Regenerated heat: $q_{\text{reg}} = h_5 - h_2 = 220 \text{ kJ/kg}$
- Net work: $w_{\text{net}} = (h_3 - h_4) - (h_2 - h_1) = 210 \text{ kJ/kg}$

Example Gas Turbine with regeneration

- Comparison of different efficiencies
- The Carnot efficiency is 77%

$$\eta_{Carnot} = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{300}{1300} \Rightarrow 77\%$$

- With regeneration the efficiency is 37%

$$\eta_{th-reg} = \frac{w_{net}}{q_{in}} = \frac{w_{turb} - w_{comp}}{q_{heat}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_5)} \Rightarrow 37\%$$

- Without regeneration the efficiency is 27%

$$\eta_{th} = \frac{w_{net}}{q_{in}} = \frac{w_{turb} - w_{comp}}{q_{heat}} = \frac{(h_3 - h_4) - (h_2 - h_1)}{(h_3 - h_2)} \Rightarrow 27\%$$

- The second law efficiency in the case with regeneration is 48%

$$\eta_{2nd-law-reg} = \frac{\eta_{th-reg}}{\eta_{Carnot}} = \frac{0.37}{0.77} \Rightarrow 48\% \text{ and}$$

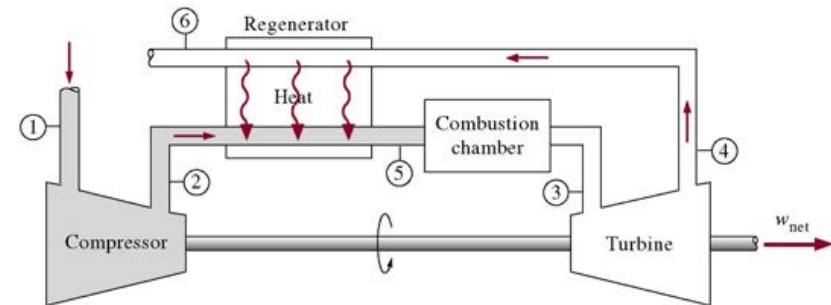
- The second law efficiency in the case without regeneration is 35%

$$\eta_{2nd-law-reg} = \frac{\eta_{th}}{\eta_{Carnot}} = \frac{0.27}{0.77} \Rightarrow 35\%$$

- In the ideal case, with an 100% efficient regenerator and 100% isentropic efficiencies of compressor and turbine, $h_5 = h_4$, it would have been 70%

$$\eta_{th-reg-ideal} = \frac{w_{net}}{q_{in}} = \frac{w_{turb} - w_{comp}}{q_{heat}} = \frac{(h_3 - h_{4s}) - (h_{2s} - h_1)}{(h_3 - h_4)} \Rightarrow 70\%$$

second law
efficiency not
for the exam



	$h(\text{kJ/kg})$
1	300
2s	545
2	605
3	1395
4s	790
4	880
5	825
6	660

BREAK



<https://www.cafepress.com/+thermodynamics+mugs>

Aircraft Gas Turbine Engines

- The first airplanes were powered using piston cylinder engines
- Around 1940 the jet engine, powered by a gas turbine, was invented
- From 1944 on the first military jet engines were used
- The first jet engine for passenger transport flew in January 1951

Modern airplane



One of the first airplanes
(Museu de Marinha, Lisbon)

Aircraft Gas Turbine Engines

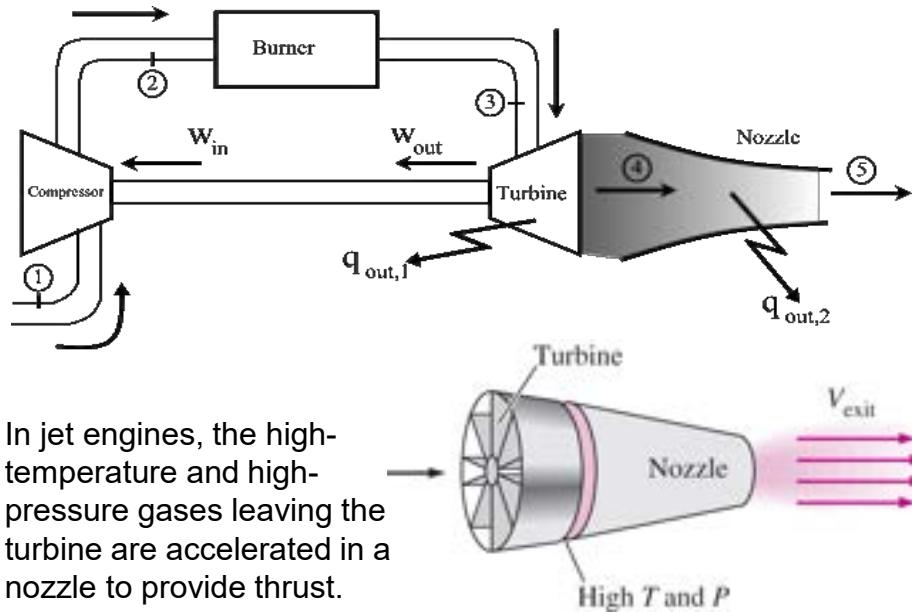
- The first airplanes were powered using piston cylinder engines like in an automobile
- The crank was connected to a propeller instead of to the wheels

(Pictures made in Museu de Marinha, Lisbon)

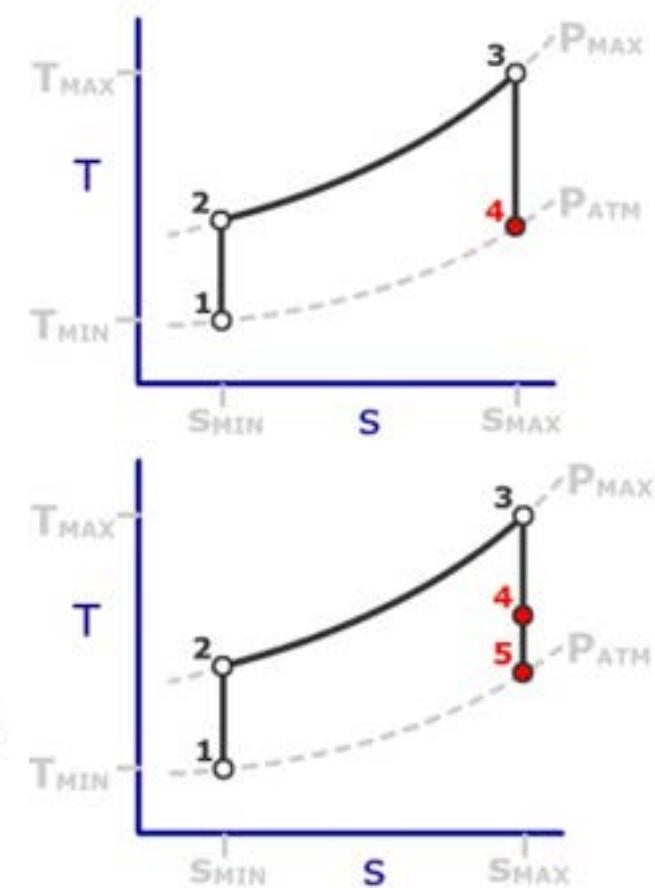
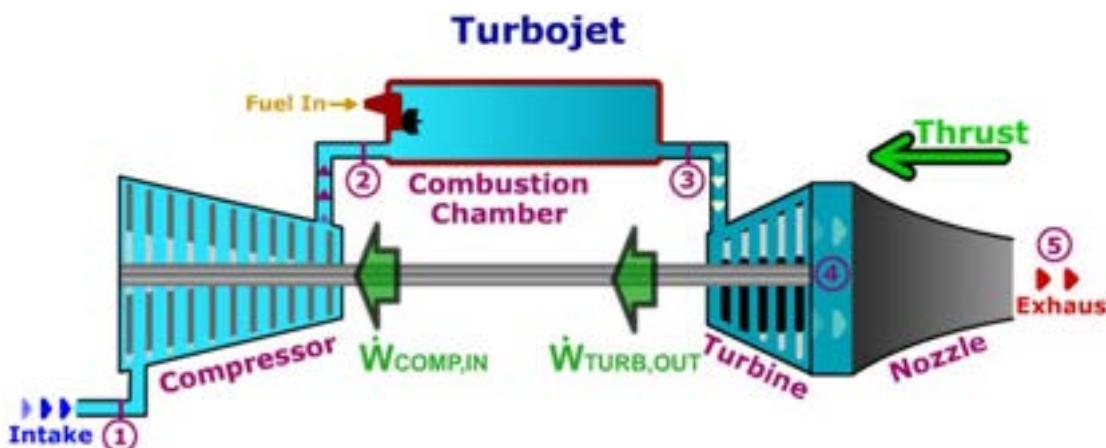
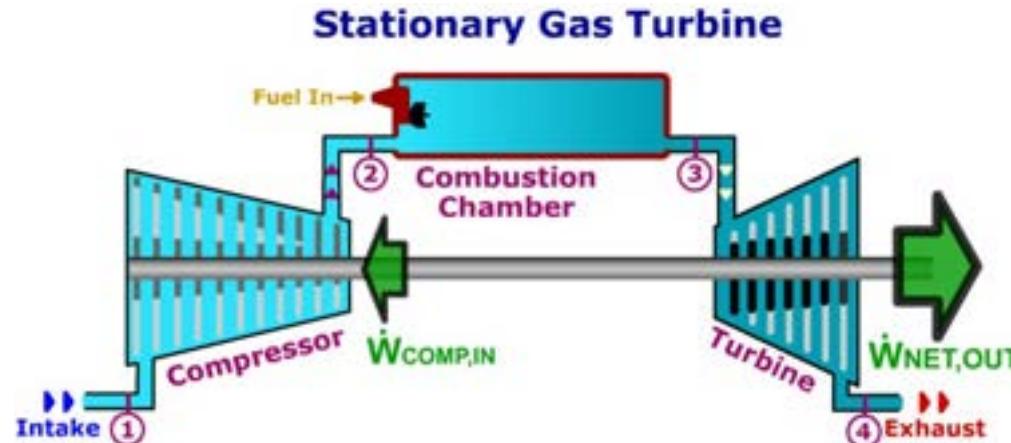


Aircraft Gas Turbine Engines

- The Brayton cycle is also used in engines that power aircraft
- Aircraft gas turbines operate on an open cycle called a **jet-propulsion cycle**
- In a **pure turbojet gas turbine**, a nozzle is added after the turbine
- The cycle differs from the Brayton cycle in that the gases are not expanded to ambient pressure, but to a pressure such that they produce just enough power to drive the compressor
- **The net work output is zero !**
- The gases that exit the turbine at a relative high pressure are accelerated in a nozzle to provide thrust ($F = ma$) to propel the aircraft
- Afterburner → Inject fuel after turbine & combust → extra thrust



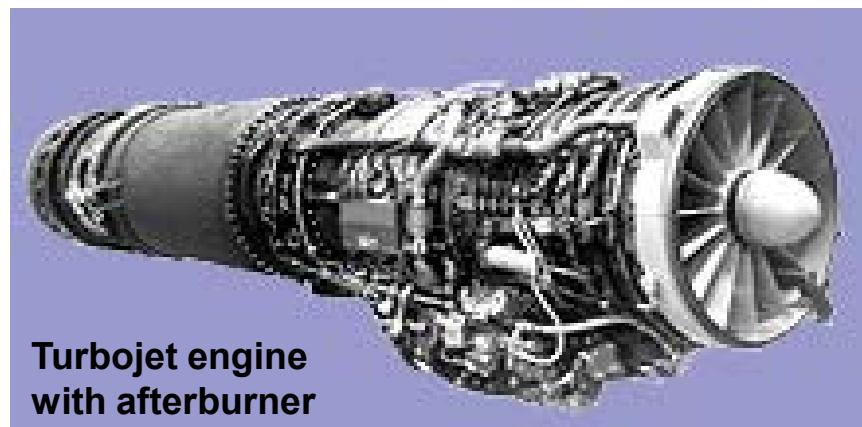
Stationary gas turbine - Turbojet



- Compare the stationary Brayton cycle with the turbojet, the turbojet does not produce net work output, only work is produced to drive the compressor the (3 – 4), the energy left is converted into thrust (4 – 5)

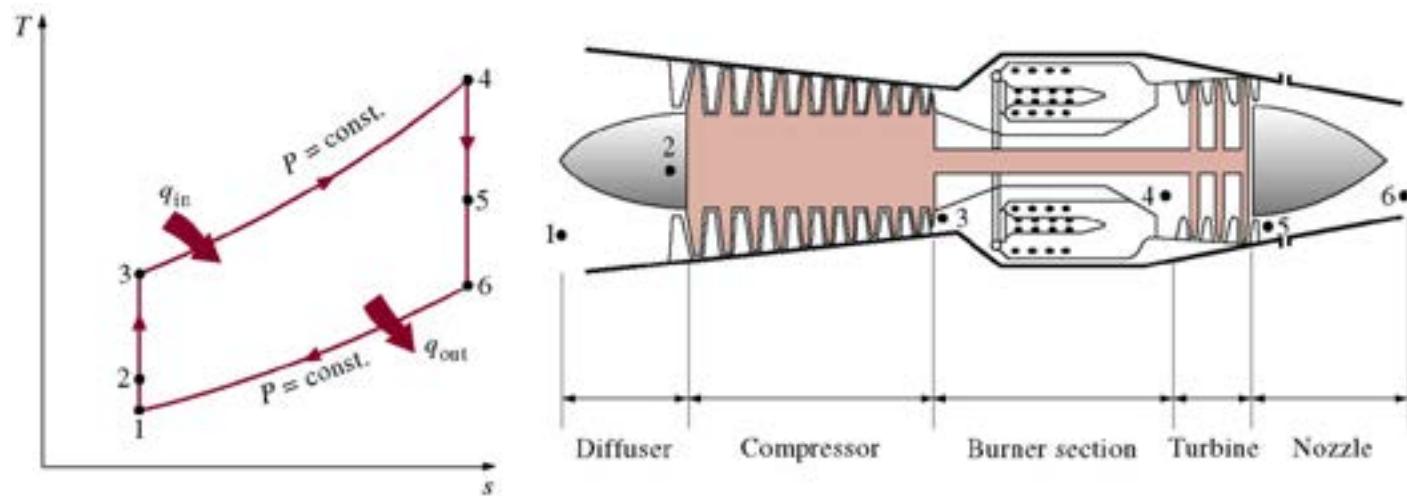
Turbojet Engine

- **Turbojet engines** are used to power high speed aircraft.
 - enthalpy of the combustion gasses is converted into shaft work by turbines to drive the engine's compressor
 - The rest of the enthalpy is converted into kinetic energy in a nozzle, which accelerates the gas resulting in thrust
- **In a turbojet engine with an afterburner:**
 - The hot gasses that are leaving the turbine are injected with more fuel and re-combusted, increasing the gasses' enthalpy before it enters the nozzle and therefore producing more thrust in the nozzle



Turbojet Engine Principle

- **Ideal jet-propulsion cycle**
- The pressure of the intake air rises slightly as it is decelerated in the diffuser (1-2) this does not require work
- Air is compressed in the compressor (2-3) requiring work
- The air is mixed with fuel in the combustion chamber and burned at a constant high pressure (3-4), heat is added to the air
- The high temperature, high pressure gases are partly expanded in a turbine (4-5), producing work to drive the compressor
- The gases finally expand in a nozzle to the ambient air pressure (5-6) and leave the aircraft at high velocity producing thrust



Turbojet Engine Analyses

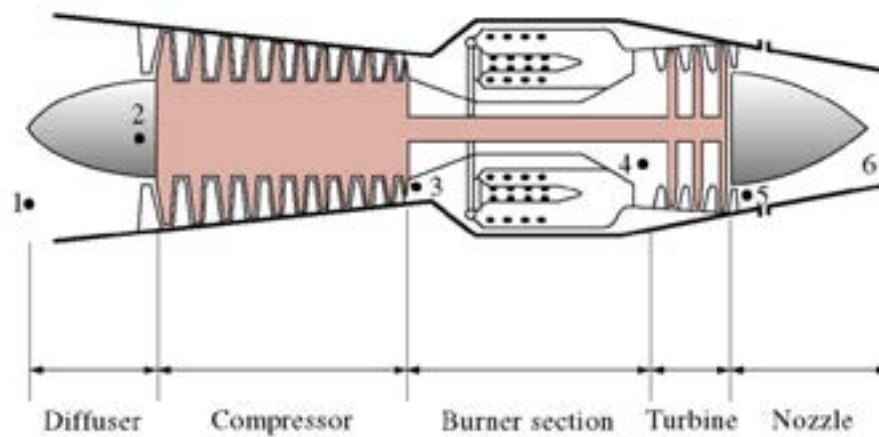
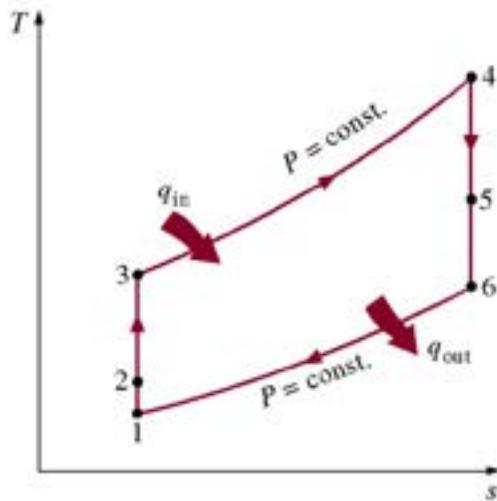
- Like all other cycles the ideal jet propulsion cycle is analyzed as a series of processes occurring in open devices
- The diffuser has no heat and power input, it can be assumed that $v_2 = 0$ and v_1 is v_{aircraft} , conversion of energy gives:

$$(h_2 + \frac{1}{2}v_2^2) - (h_1 + \frac{1}{2}v_1^2) = 0 \quad \text{and} \quad dh = c_p dT \Rightarrow h_2 = h_1 + \frac{v_1^2}{2} \Rightarrow T_2 = T_1 + \frac{v_1^2}{2c_p}$$

- Work produced by the turbine is used to drive the compressor:

$$w_{\text{comp}} = w_{\text{turb}} \rightarrow h_3 - h_2 = h_4 - h_5$$

- The heat added to the air is: $q_{\text{in}} = h_4 - h_3$

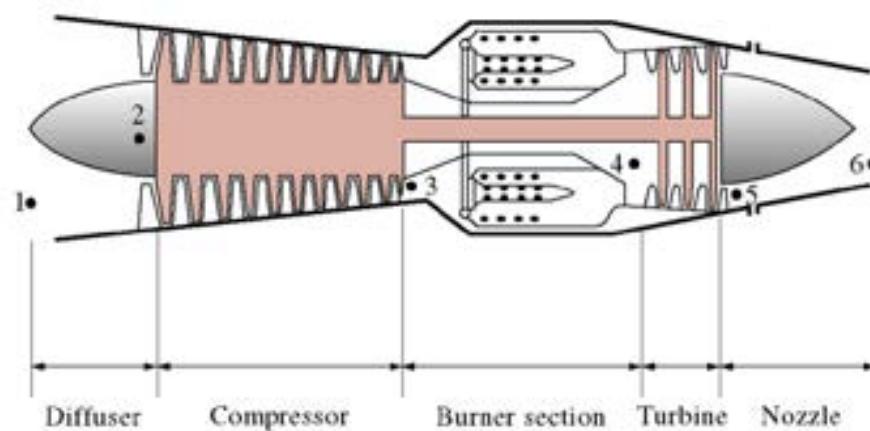
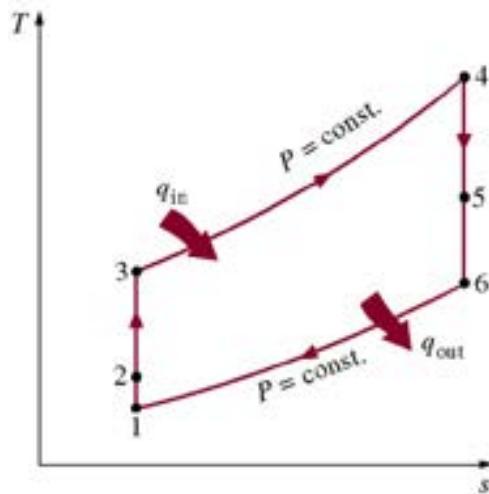


Turbojet Engine Analyses

- The enthalpy difference over the nozzle (no work, no heat) is converted to speed under the assumption that $v_5 = 0$ and the specific heat is constant

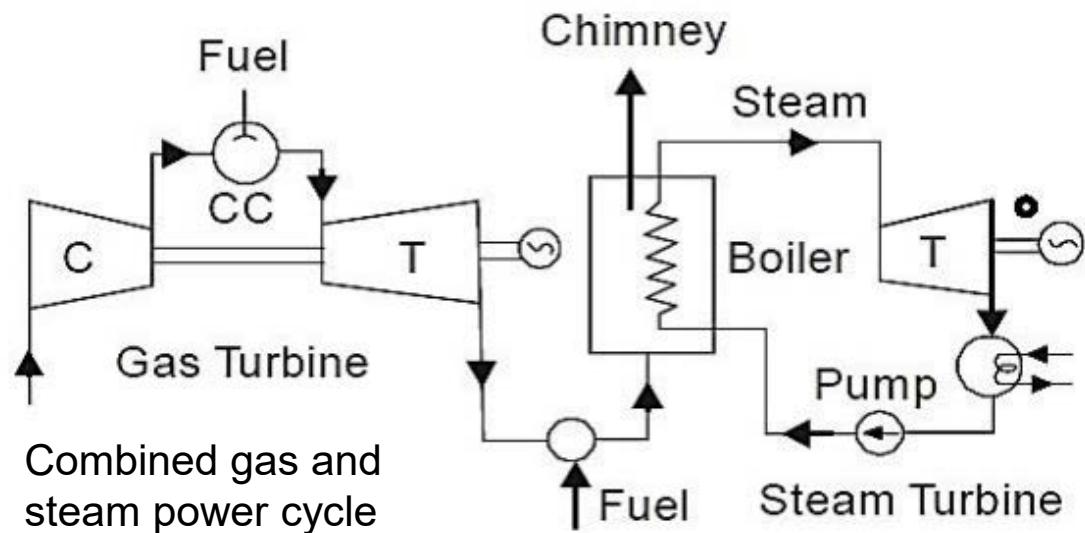
$$(h_5 + \frac{1}{2}v_5^2) - (h_6 + \frac{1}{2}v_6^2) = 0 \quad \text{and} \quad dh = c_p dT \quad \Rightarrow \quad v_6 = \sqrt{2(h_5 - h_6)} = \sqrt{2c_p(T_5 - T_6)}$$

- The **thrust** developed in a turbojet engine is the unbalanced force that is caused by the difference in the momentum of the low velocity air entering the engine and the high velocity exhaust gases leaving the engine
- Newton's law gives $F = \dot{m}(v_{exhaust} - v_{inlet}) = \dot{m}(v_6 - v_1) [N]$



Combined Cycles

- The continued quest for more power and higher thermal efficiencies has resulted in rather innovative modifications of conventional power plants
- A modification can be a first power cycle topping a second power cycle
- In such a **combined cycle** the rejected heat, q_{OUT} of the first cycle is used as input, q_{IN} for a second cycle
- **Combined gas-vapor cycle:** The combined cycle of greatest interest is the gas-turbine (Brayton) cycle topping a steam-turbine (Rankine) cycle, which has a higher thermal efficiency than either of the cycles executed individually

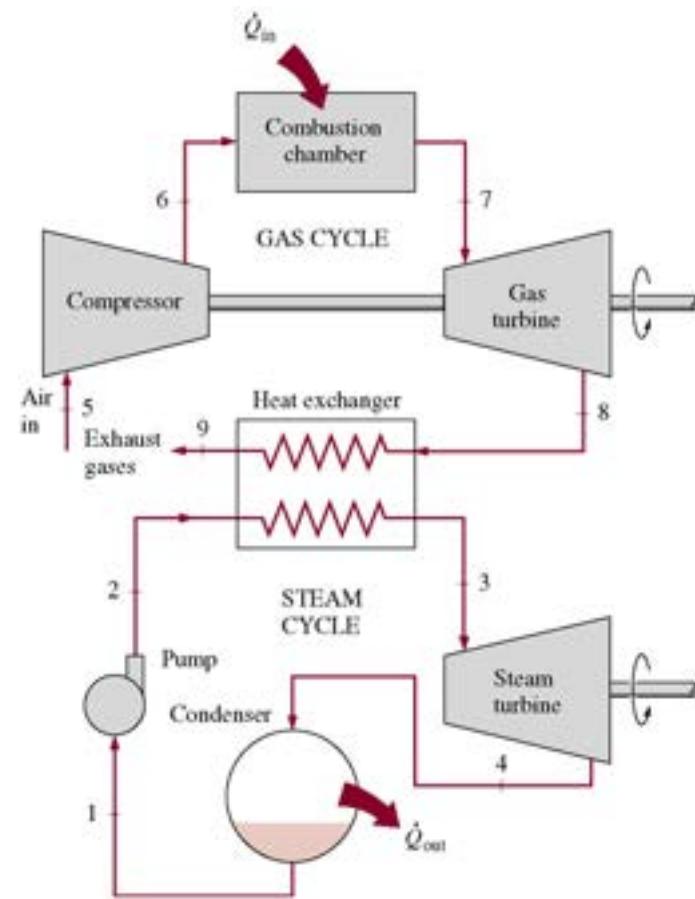
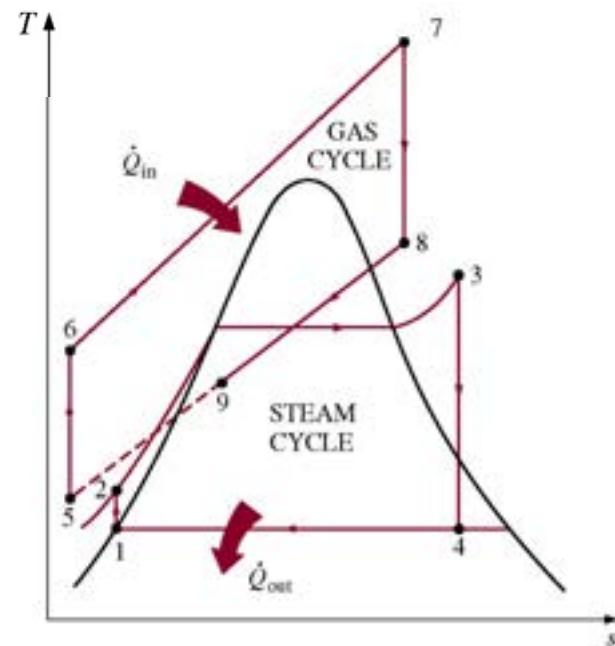


Combined Gas – Vapor power Cycles

- A combined cycle consisting of a gas power cycle (Brayton) topping a vapor power cycle (Rankine) will have a higher thermal efficiency than either of the cycles executed individually
- Gas turbine cycles operate at considerably higher temperatures than steam cycles, T_{\max} at the turbine inlet:
 - Modern steam power plants: 620°C
 - Modern gas turbine power plant: 1150°C
 - Modern turbo jet engine: over 1500°C
- Because of the higher average temperature at which heat is supplied gas-turbine cycles have a greater potential for higher efficiencies, however the exhaust gas leaves the gas turbine at relatively very high temperatures which reduces the efficiency a lot
- In a **combined gas – vapor power cycle** the relative hot exhaust gases of the Brayton cycle are used to heat the fluid in the Rankine cycle

Combined Gas – Vapor power Cycles

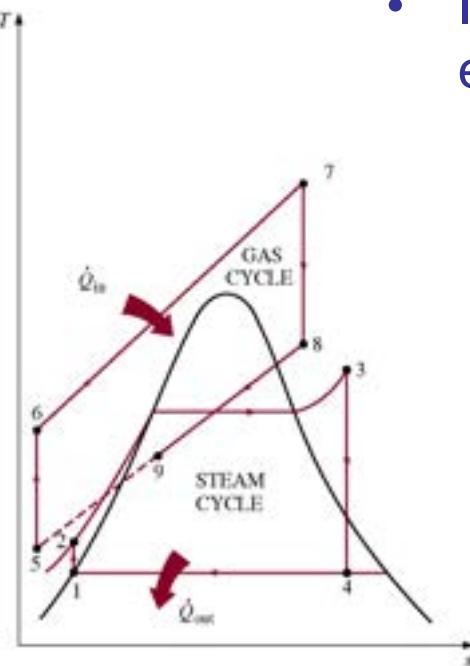
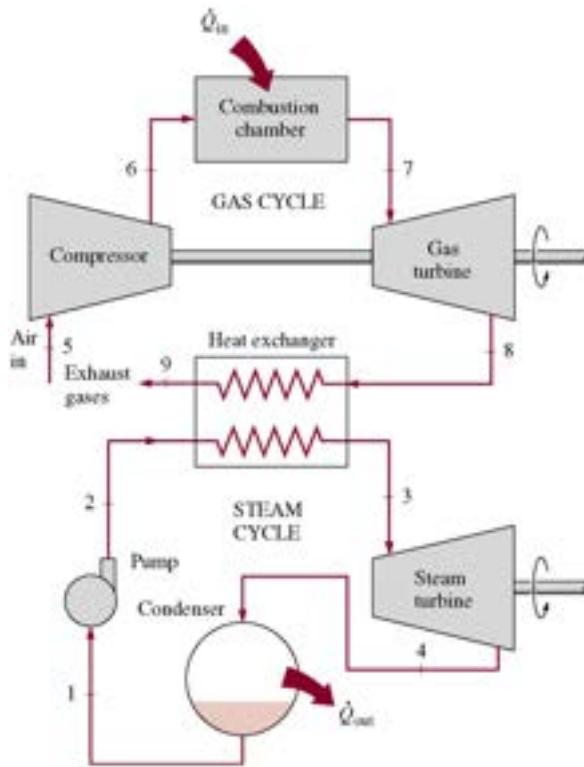
- In a combined gas – vapor power cycle the energy from the exhaust of the gas turbine is recovered by transferring it to the steam in a heat exchanger that serves as a boiler
- Generally, more than one gas turbine is needed to supply sufficient heat to the steam
- The steam cycle may involve regeneration as well as reheating
- The energy for reheating can be supplied by burning some additional fuel in the oxygen-rich exhaust gases



Combined Gas – Vapor power Cycles

- The cycles are connected by the heat exchanger, this gives a relation to connect both cycles in the analysis
- It relates the mass flow of the Rankine and the Brayton cycle
- The heat from the exhaust gases is transferred to the steam

$$\dot{Q}_{out_gas} = \dot{Q}_{in_steam} \rightarrow \dot{m}_{gas}(h_8 - h_9) = \dot{m}_{steam}(h_3 - h_2)$$



- In the heat exchanger the entropy increases (second law)

$$Q_{out_gas} = Q_{in_steam}$$

$$T_{out_gas} \Delta s_{out_gas} = T_{in_steam} \Delta s_{in_steam}$$

$$\Delta s_{in_steam} = \frac{T_{out_gas}}{T_{in_steam}} \Delta s_{out_gas}$$

$$\frac{T_{out_gas}}{T_{in_steam}} > 1 \rightarrow \Delta s_{in_steam} > \Delta s_{out_gas}$$

Combined Gas – Vapor power Cycles

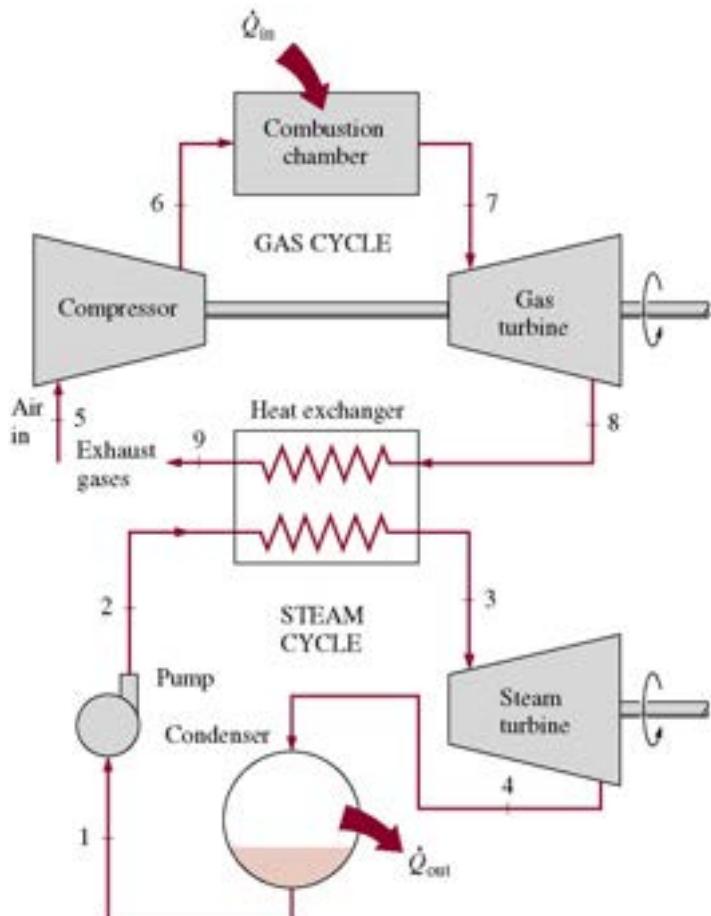
- Combined cycle: Brayton cycle and Rankine cycle
 - Thermal efficiency, add all outputs (note only one input)

$$\eta_{combined-cycle} = \frac{\dot{W}_{netto}}{\dot{Q}_{in}} =$$

$$\frac{\dot{w}_{out-gas} - \dot{w}_{in-gas}}{\dot{q}_{in-gas}} +$$

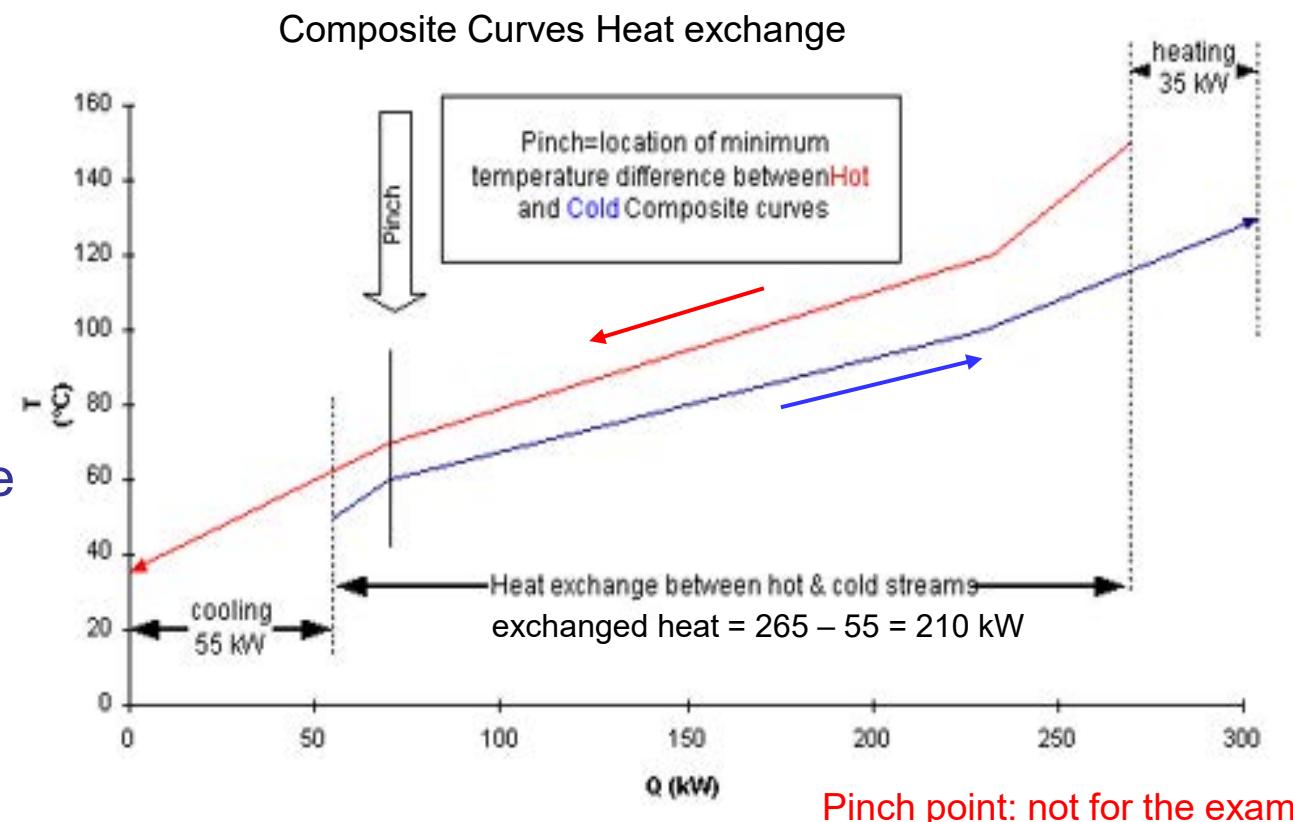
$$\frac{\dot{W}_{out-steam} - \dot{W}_{out-steam}}{\dot{q}_{in-gas}} =$$

$$\frac{\dot{w}_{out-turb-gas} - \dot{w}_{in-comp} + \dot{w}_{out-turb-gas} - \dot{w}_{in-pump}}{\dot{q}_{in-gas}}$$



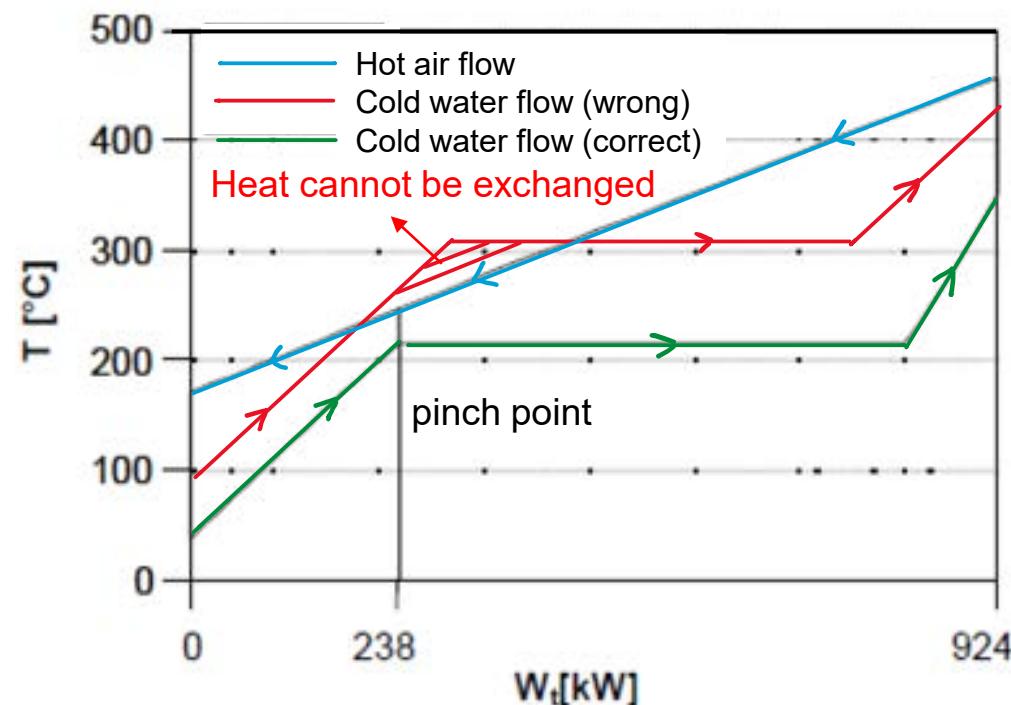
Pinch point analysis

- In combined cycles heat is exchanged in the heat exchanger, in the heat exchanger the temperature of the bottom cycle must always be lower than the temperature of the upper cycle
- In the figure the temperature of the hot and the cold flow is given as function of the exchanged heat (Tq-diagram) between 2 flows with *different inclination*
- The location with smallest temp difference is called the **pinch point**
- If the hot and the cold line touch each other heat exchange cannot occur any more



Pinch point analysis

- The pinch point should specially be considered in gas – vapor combined power cycles, in the heat exchanger the colder water should always have a lower temperature than the hotter air
- The water undergoes a phase change and part of the cold water curve is horizontal, therefore the begin and end temperature of the water can be lower than the end and begin temperature of the gas but still in the middle of the heat exchanger there can be a problem
- This is shown in the figure, for the red line the begin and end temperature are below the air temperature but somewhere in the middle of the heat exchanger they cross each other, and heat cannot be exchanged any more as the water temperature gets hotter
- The green line doesn't show this problem



Recapitulate Class 11

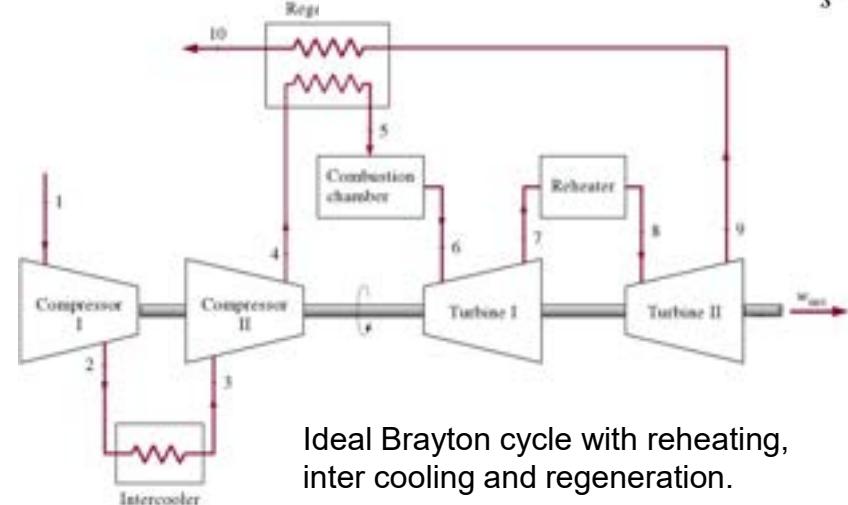
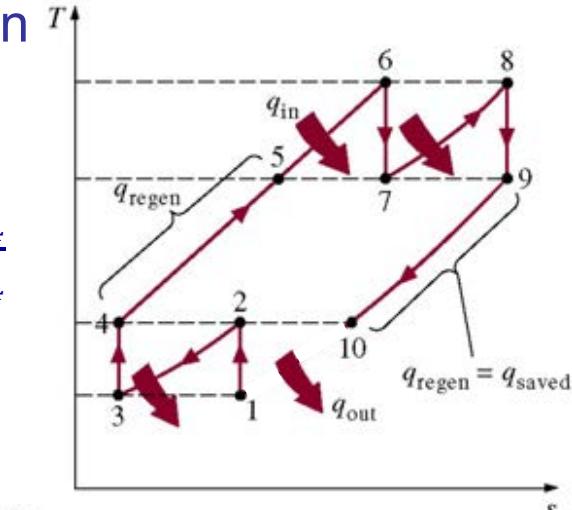
- Improve the efficiency of the Brayton cycle by adding extra devices
 - Extra combustion chamber → reheating the air during expansion
 - Inter cooler → cooling the air during compression
 - Regenerator / recuperator → relative hot turbine exhaust gases pre heat air before combustion

- Effectiveness regenerator (ε): $\varepsilon = \frac{q_{reg-actual}}{q_{reg-max}} = \frac{h_5 - h_4}{h_9 - h_4}$

- Thermal efficiency:

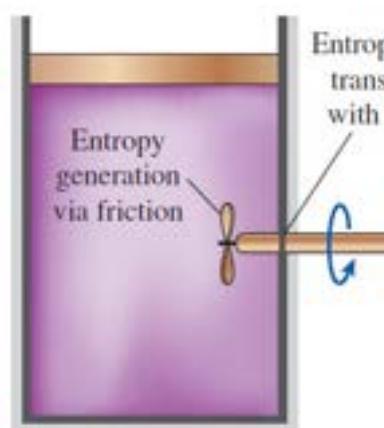
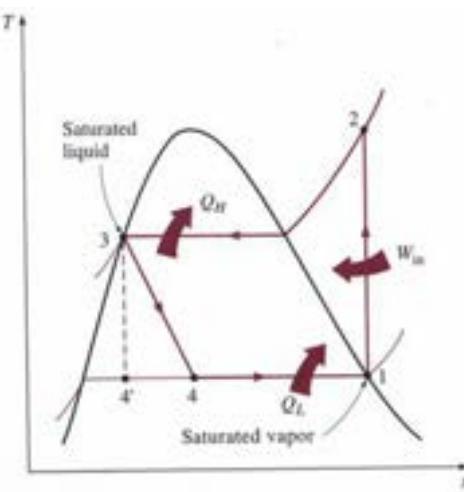
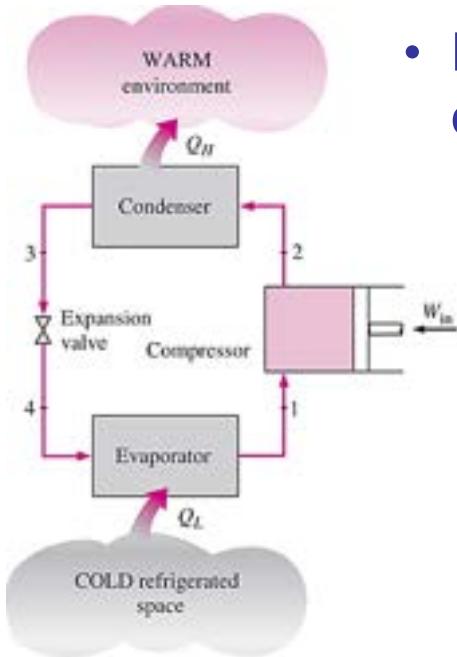
$$\eta_{th} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_{out-HPT} + \dot{W}_{out-LPT} - \dot{W}_{in-c1} - \dot{W}_{in-c2}}{\dot{Q}_{in-combuster-1} + \dot{Q}_{in-combuster-2}}$$

- Aircraft gas turbine engines, just enough work is produced to power the compressor and the rest of the energy of the gases that exit the turbine at a relative high pressure are accelerated in a nozzle to provide thrust ($F = ma$)
- Combined gas – vapor power cycles



Next Module: Engineering Thermodynamics 2

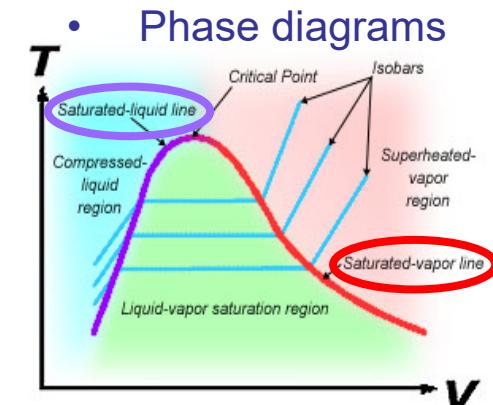
- Engineering thermodynamics 2 (1.5 ec) in module 3 is a follow up of engineering thermodynamics 1 (3 ec)
 - Class 12: Refrigerating / heat pump cycles
 - Class 13: Internal combustion engines
 - Class 14: More about entropy, calculation of entropy generation
 - Class 15, 16 & 17: Mathematical background Thermodynamics
 - How are tables and diagrams composed?
 - How can unknown properties that can not be measured be determined from a set of limited available data?



Entropy may be generated within the system as work is dissipated into a less useful form of energy

Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal efficiency $\eta_{thermal} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Mixture fraction $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
- Ideal gas law $Pv = RT$, $c_p - c_v = R$
- For an ideal gas $du = c_v dT$ and $dh = c_p dT$
- Conservation of mass $m_{in} = m_{out}$, mass flow rate $\dot{m} = \rho v A$
- Conservation of energy, first law of thermodynamics
 - Closed system $du = \delta w - \delta q \rightarrow \Delta u = w - q$
 - 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 $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)
- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdP$
- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Isentropic processes ideal gas $Pv^k = \text{constant}$, $Tv^{k-1} = \text{constant}$, $P^{(k-1)/k}/T = \text{constant}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$ Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$



Preparation Exam

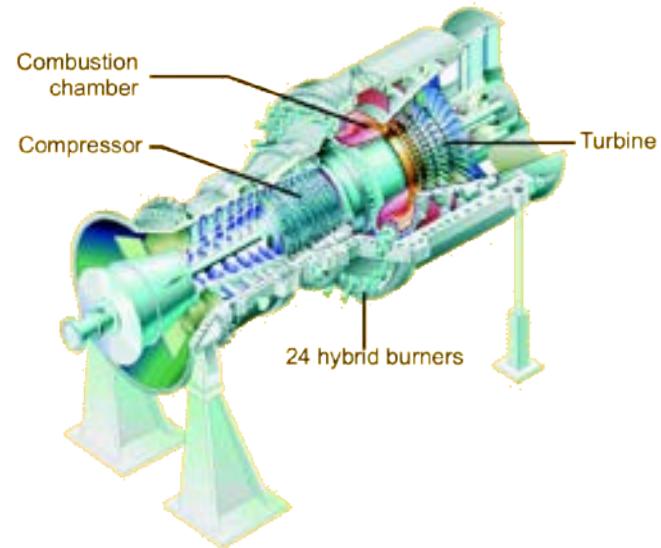
Engineering Thermodynamics 1



F 16 jet engine, former air base Twente

Objectives Engineering Thermodynamics

1. Conversion of heat into work / electricity → heat engine



2. Transportation of heat using work / electricity
→ refrigerator / heat pump

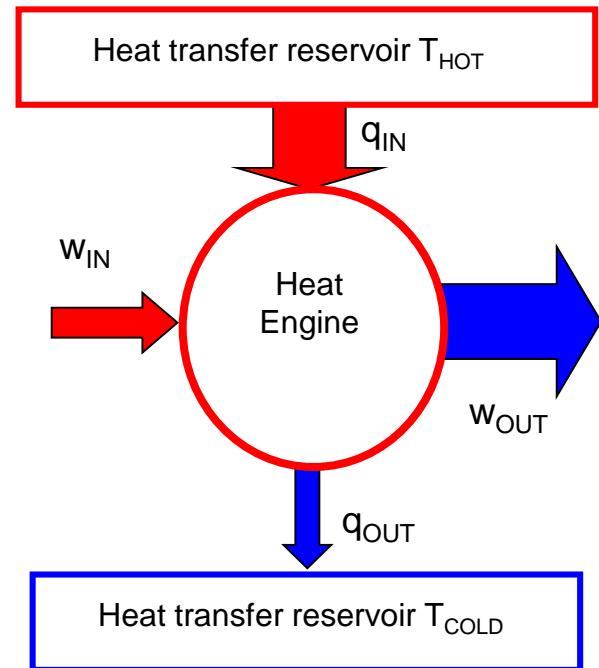


Objectives Engineering Thermodynamics

1. Heat engine → installation to convert heat from a hot temperature source into work

Examples:

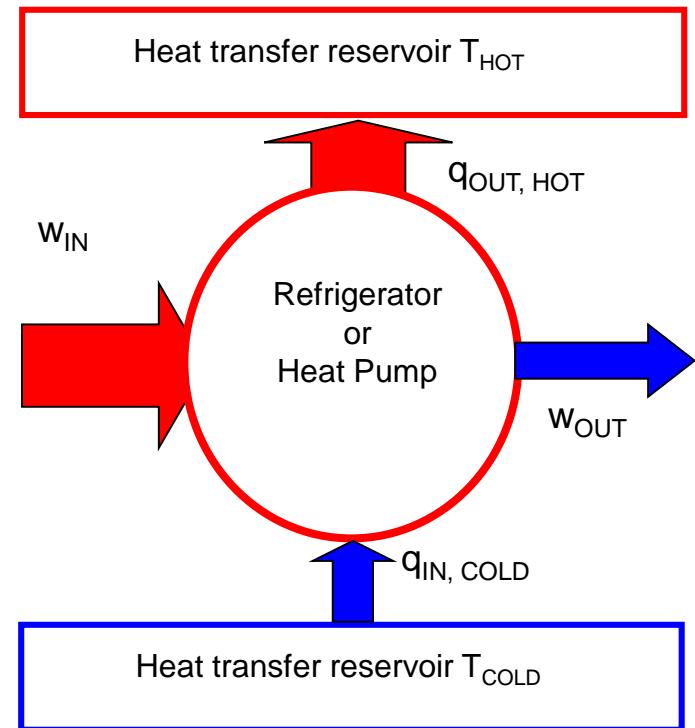
- Vapor power cycle using a steam turbine / Rankine cycle
- Gas power cycle using a gas turbine / Brayton cycle
- Efficiency can never be 100% (due to second law always some of the input heat has to be rejected)
- Maximum efficiency for ideal cycle: $\eta_{Carnot} = 1 - \frac{T_L}{T_H}$



Objectives Engineering Thermodynamics

2. Refrigerator / heat pump → installations that use power to transport heat from a cold environment to a hot environment (the non-natural way)

- Goals:
 - Refrigerator: cooling, $q_{in,cold}$
 - Heat pump: heating, $q_{out,hot}$
- COP instead of efficiency, mostly higher than 1
- Maximum COP for ideal cycle: COP_{Carnot}



Notify the reversed direction of the flows

Outline Engineering Thermodynamics (ET)

- Basic knowledge and tools
 - Thermodynamic concepts and definitions (class 1)
 - Thermodynamic states and processes (class 1)
 - Classification of energy into various forms (class 2)
 - Thermodynamic properties of substances (class 3 & 9)
 - First law energy conservation / transformation (class 4)
 - Entropy and the second law (class 5)
 - Building thermodynamic power cycles (class 6)
- Engineering applications
 - Vapor power cycles (class 7 & 8)
 - Gas power cycles (class 10 & 11)

Exam Engineering Thermodynamics

- How will the exam look like?
- The exam consists of some MC questions and 3 or 4 open questions
 - One or two exercises are about a single device with gas and/or fluid
 - One exercise about a Brayton cycle (Class 10 -11)
 - One exercise about a Rankine cycle (Class 7 - 8)
- **100.00% an exercise with a Mollier diagram (water and / or air)**
- Content: Everything that was treated in the lectures, look at the slides (exceptions are clearly mentioned in the slides)
- Subjects can be found in the book, the book provides more information

Exam Engineering Thermodynamics

- Open book exam
 - You are allowed to bring your Thermodynamic book, text can be highlighted, **small** notes inside the book can be made but complete solutions are not accepted. Also post it's can be used as bookmarks. Prints from the slides or others papers are not allowed. You need the book for the Thermodynamic tables (there is no time during the exam to study the material)
 - You can also bring a printed version of the book or the tables
- A calculator is useful
- A3 Mollier diagram for water and air will be provided out as well
(If you need a new one during the exam you can ask us during the exam)

Exam Engineering Thermodynamics

- **Some remarks for the exam (in random order) :**
- **Read the instructions on the first page (see also sample exam)**
- **Work clean**, make tables and figures easy to read
- Use the space at the question sheets to make the figures and fill out the tables at the questions sheet when asked for
- Don't write down to little, this prevents calculation/rewriting mistakes
- Don't forget **the units**, no units are mistakes and are punished
- Be careful while converting units from kilo/mega, Bar/Pascal, Kelvin/Celsius and others
- Give your **solutions first as a formula** and after the numerical value. The correct value is less important/ gives less points

Exam Engineering Thermodynamics

- Remarks continued:
- Work smart :
 - Calculating intermediate answers is not necessary and costs a lot of time
 - Look for variables that cancel out
 - Sometimes you can combine formulas which can lead to the answer even though you do not have the value of all variables, e.g:
 - $T_1 = T_2$ then $v_1/v_2 = (T_1R/P_1) (P_2/T_1R) = P_2/P_1$ and the value of v is not necessary if you know the pressure
 - Don't waste your time to calculate things that you don't need! You will need the time for the rest of the exam!

Exam Engineering Thermodynamics

- Important theory / formulas / concepts for the exam that often go wrong, “pitfalls” in a random order :
- First law of thermodynamics → conservation of energy
- For a **closed system** $\Delta u = q_{\text{net}} - w_{\text{net}}$
- For a **stationary system** $\Delta h = q_{\text{net}} - w_{\text{net}}$
(neglecting kinetic and potential energy)
- For a cycle is $\Delta h = \Delta u = 0$ hence $q_{\text{net}} = w_{\text{net}}$ and $w_{\text{out}} - w_{\text{in}} = q_{\text{in}} - q_{\text{out}}$
- In several sub-parts q or w is absent and it reduces to $q = \Delta h$ of $w = \Delta h$
- For a pump in a Rankine cycle: $\Delta h = v\Delta P$ (for sure needed at the exam)

Exam Engineering Thermodynamics

- “pitfalls” continued:
 - Energy conservation is not sufficient to describe the direction of a process
 - **Second law of thermodynamics** → entropy increases in the total world
 - Entropy, needed to predict the direction of a process
 - Higher temperature → more entropy
 - Higher pressure → less entropy
 - Mixture → more entropy than a liquid
 - Mixture → less entropy than a vapor
 - Remember in a spontaneous process entropy always increases, e.g. a throttle valve, turbines, nozzle, diffuser
 - Entropy of a system can decrease but then the entropy of the environment should increase, more than the decrease of the entropy of the system

Exam Engineering Thermodynamics

- “pitfalls” continued:
- For ideal gas holds $dh = c_p dT$ and $du = c_v dT$ and $Pv = RT$ and for isentropic ($ds = 0$) processes $Pv^k = \text{constant}$
- Volume work is $\delta w = Pdv$ and if you integrate you can not just write P outside of the integral! That is only allowed if P is constant during the change in volume and that is often not the case for gas $\rightarrow w = \int Pdv = \int (TR/v)dv = TR\ln(v_1/v_2) = TR\ln(P_2/P_1)$ if T is constant. If P is constant it would be $\rightarrow w = \int Pdv = P(v_2 - v_1)$
- For compressed liquid at low pressures, there is no table, the h value is taken from saturated water at the same temperature (the ICL approximation); for example water at 20 degree C and 1 Bar, $h = 83,915 \text{ kJ/kg}$

Exam Engineering Thermodynamics

- “pitfalls” continued:
- While analyzing the cycle you will be asked to mention the 2 unique values which you need to calculate all other data, mark them **clearly**.
- Remember that you need **two values per point**, to calculate all other values
- These values can be, pressure, temperature, isentropic efficiency or $s_a = s_b$, but also saturated water/vapor (Pay attention, **superheated vapor is no unique** value, together with the pressure you still can not calculate other values like enthalpy), energy and mass balance can also be one of those.

Exam Engineering Thermodynamics

- “pitfalls” continued:
- The pressure at the outlet of a gas turbine is the pressure of the surrounding which is equal to the inlet pressure (around 1 Bar)
- The phase at the end of a condenser and the outlet of a mixing chamber is saturated water (if nothing else is mentioned)
- If there are **different mass flows in one cycle**, then you need extra conditions, that can be **mass balance or energy balance** at the point where the flow splits or meet again or for example the power that is delivered by the turbines or the power that is needed in the heating chamber

Exam Engineering Thermodynamics

- “pitfalls” continued:
 - Remember the difference between **power and work**
 - Power is in J/s = W , specific work is in J/kg, work times mass flow (kg/s) results in power → $\dot{W} = \dot{m}w$
 - The **net work** of a cycle is the work that is delivered by the turbines minus the work that is needed by the pump/compressor (do **not** neglect those !!!)
→ $W_{\text{net}} = W_{\text{out}} - W_{\text{in}}$
 - Heat enters the cycle at the heating chamber/ boiler (with reheating this happens more than ones)
 - Keep in mind that if the mass flow is different through sub-parts of the cycle that the power is also different! (important for the Rankine cycle)

Exam Engineering Thermodynamics

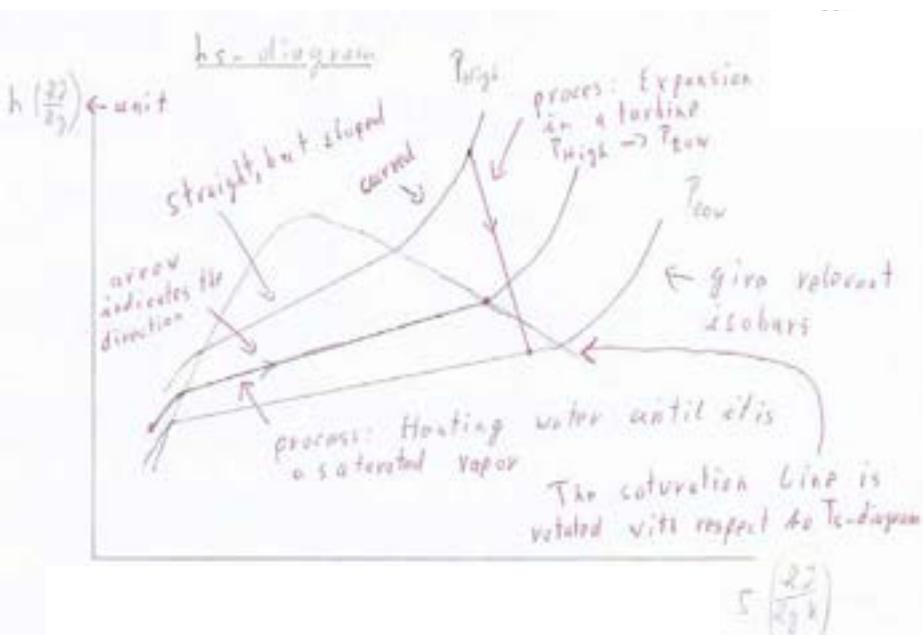
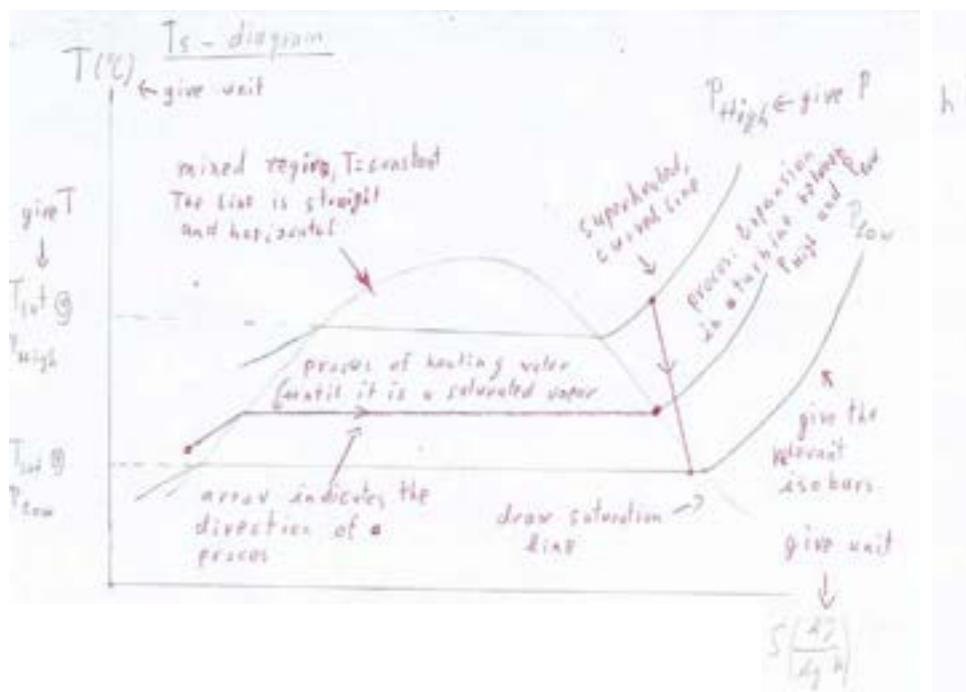
- “pitfalls” continued:
- The **thermal efficiency** is : $\eta_{TH_HE} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} = \frac{\dot{W}_{out} - \dot{W}_{in}}{\dot{Q}_{in}} = \frac{\dot{Q}_{in} - \dot{Q}_{out}}{\dot{Q}_{in}}$
- Keep in mind that with several turbines, compressor or pumps you also get several terms for w_{OUT} , w_{IN} and for reheating several terms of q_{IN} ; be aware of different mass flows through these parts
- If there are several mass flows, then while mixing, the energy and mass balances are needed to solve the system !
- Energy balance: $\dot{m}_1 h_1 + \dot{m}_2 h_2 = \dot{m}_3 h_3$ and mass balance: $\dot{m}_1 + \dot{m}_2 = \dot{m}_3$
- In a mixing chamber all in and outgoing pressures need to be the same
- An efficiency is **always smaller than 100%**

Exam Engineering Thermodynamics

- “pitfalls” continued:
- **Co-generation power plant:** Plant that produces (process) heat, $\dot{Q}_{Process\ heat}$ and power \dot{W}_{net}
- More of the total input energy is used in a useful way
- The **utilization factor** is : $\varepsilon_\mu = \frac{\dot{W}_{net} + \dot{Q}_{Process\ heat}}{\dot{Q}_{in}} = \frac{\dot{W}_{out} - \dot{W}_{in} + \dot{Q}_{Process\ heat}}{\dot{Q}_{in}}$
- Meaning how much of the total energy is use in a useful way
- The **utilization factor may be 100%**, but mostly it is lower but it should be higher than the thermal efficiency

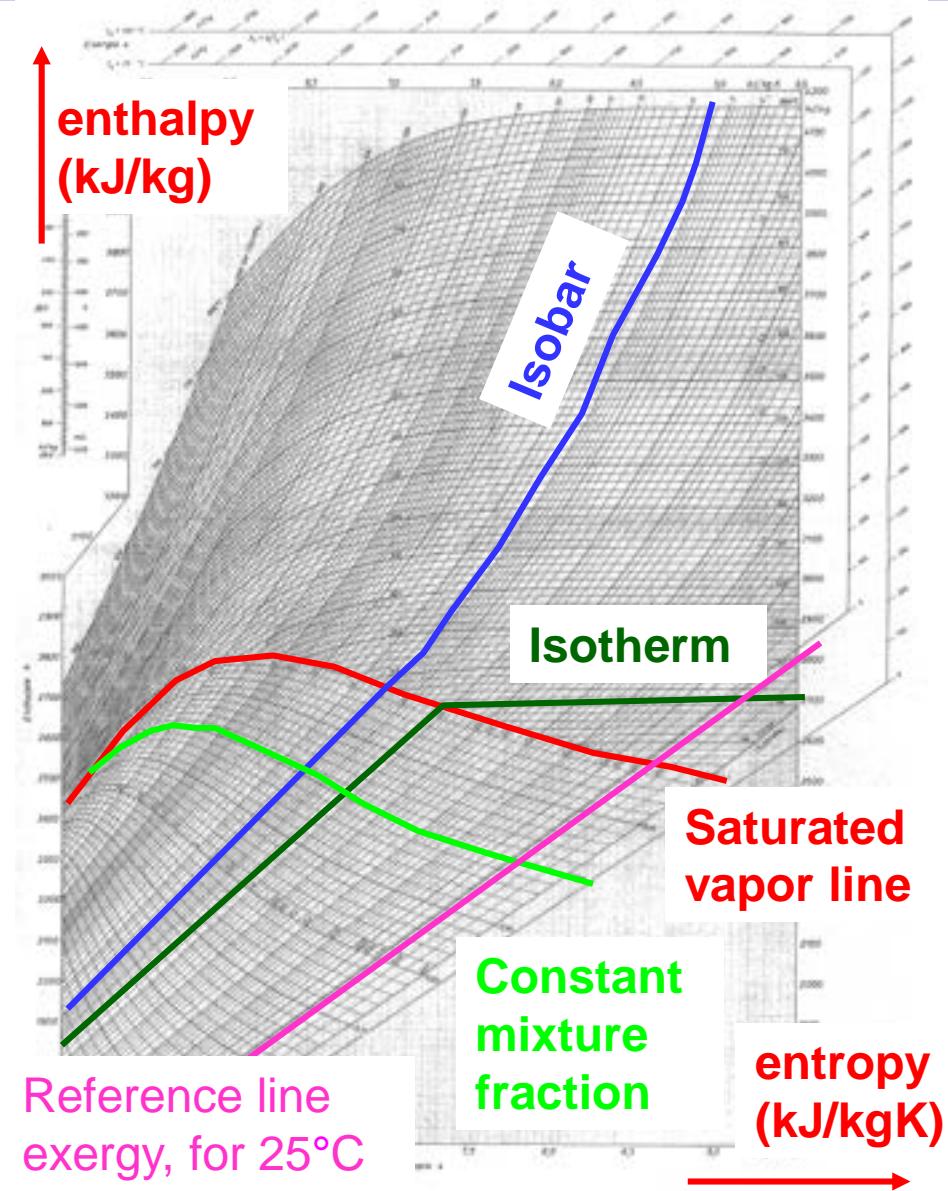
Exam Engineering Thermodynamics

- ...“pitfalls” continued:
- Be certain that you can draw Ts - diagrams and hs - diagrams
- Remember the difference between the Ts - diagrams and hs diagram
 - Remember that water has a saturation line, but not air/gas
 - See also the document on BB



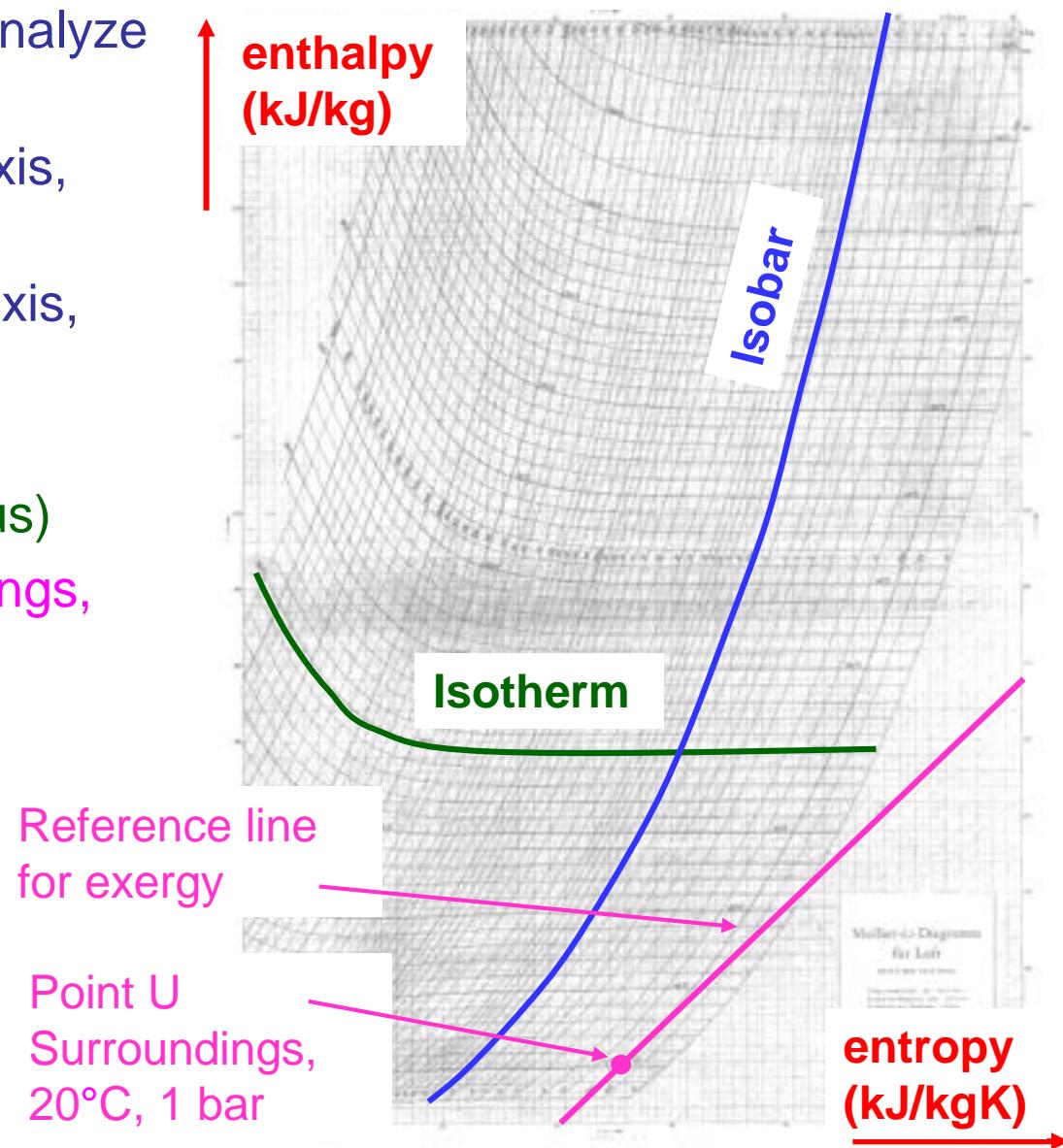
Mollier Diagram Water for Rankine Cycle

- Use the Mollier diagram for water 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
 - Reference line for exergy, tangent at T_0 (25°C here)
- Compressed liquid area is not shown \rightarrow diagram not usable, use tables



Mollier Diagram Air for Brayton Cycle

- The Mollier diagram for air to analyze the Brayton cycle
 - Enthalpy (kJ/kg) on the y-axis, horizontal line $\rightarrow dh = 0$
 - Entropy (kJ/kgK) on the x-axis, vertical line $\rightarrow ds = 0$
 - Isobars (in Bar !!)
 - Isotherms (in degree Celsius)
 - Conditions of the surroundings, $T = 20^\circ\text{C}$, $P = 1 \text{ bar}$
 - Reference line for exergy, tangent at T_0
- In contrast to the diagram for water also the point at low temperatures and pressures can be found in the diagram



Exam Engineering Thermodynamics

- “pitfalls” continued:
- **Mollier diagrams** → pressure in BAR and temperature in °C and remember $1 \text{ bar} = 100 \text{ kPa} = 0.1 \text{ MPa}$ and $0^\circ\text{C} = 273 \text{ K}$
 - Be sure that you understand how the diagrams work and what the difference between the A3 water and air diagram is
 - The **air diagram** consists **all data for the cycle**
 - The **water diagram**, consists **only the superheated vapor** and a **part of the saturated mixture region**, hence the compressed liquid part is not present (the saturation line ($x=1$) is present, the saturated liquid line ($x=0$) not)
 - You cannot draw the full cycle on the A3 Mollier diagram
 - Uses tables for values outside the diagram
 - **100.000% certainty** you need to draw cycles on the A3 diagram

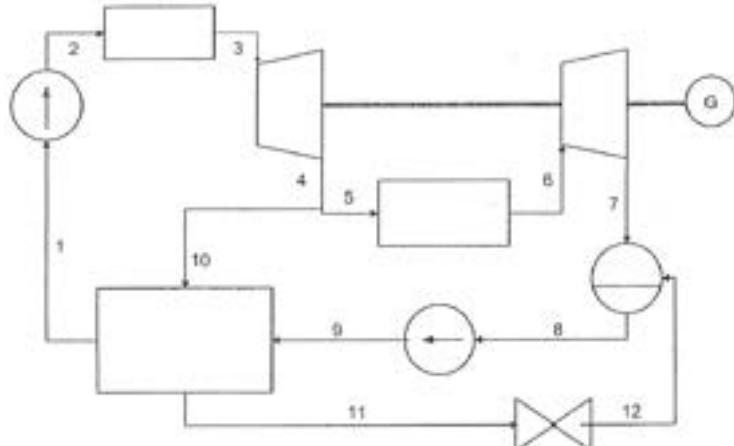
Exam Engineering Thermodynamics

- “pitfalls” continued:
- **Mollier diagrams** → Use it for the analysis of water and gas cycles
 - Using the diagram is quicker than using the tables
 - Reading off the diagram doesn’t need to be super precise (per ‘20’ is more than accurate)
 - Draw the cycle in the diagram, trace all important lines. Draw “help” lines thin or dotted. A pencil is useful, because you can erase the lines.
 - Also show the processes which leave the diagram, example: slide 24.
 - Open gas turbine cycle: do not connect the inlet and the outlet
 - Caution! Entropy has to increase for turbines, compressor and pumps , $ds > 0$, if not something is wrong
 - Try not to scribble!

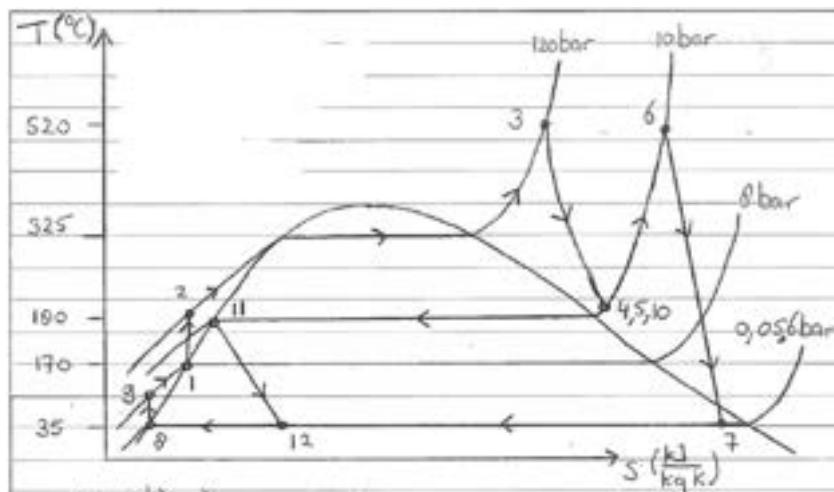
Exam Engineering Thermodynamics

- “pitfalls” continued: (as promised in the lecture, some examples of strange diagrams, that I saw on exams)

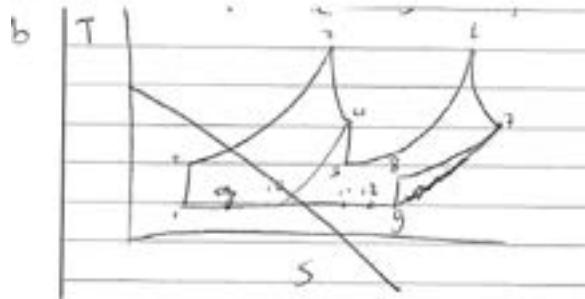
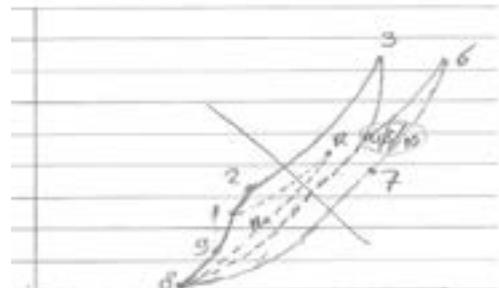
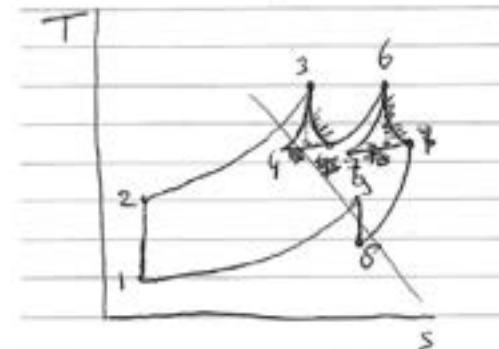
The Rankine cycle with closed feedwater preheating



A correct Ts-diagram for the Cycle



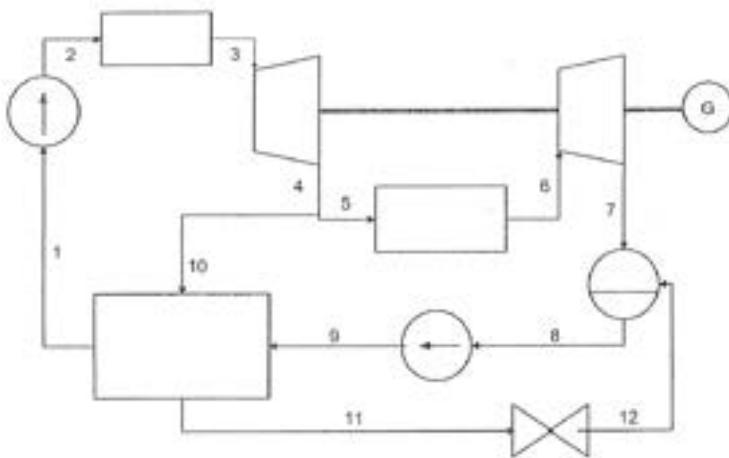
Below some wrong answers from an exam: Vapor dome is missing, in the vapor dome horizontal isobars. Points 1, 8 and 11 should be on the saturated liquid line.



Exam Engineering Thermodynamics

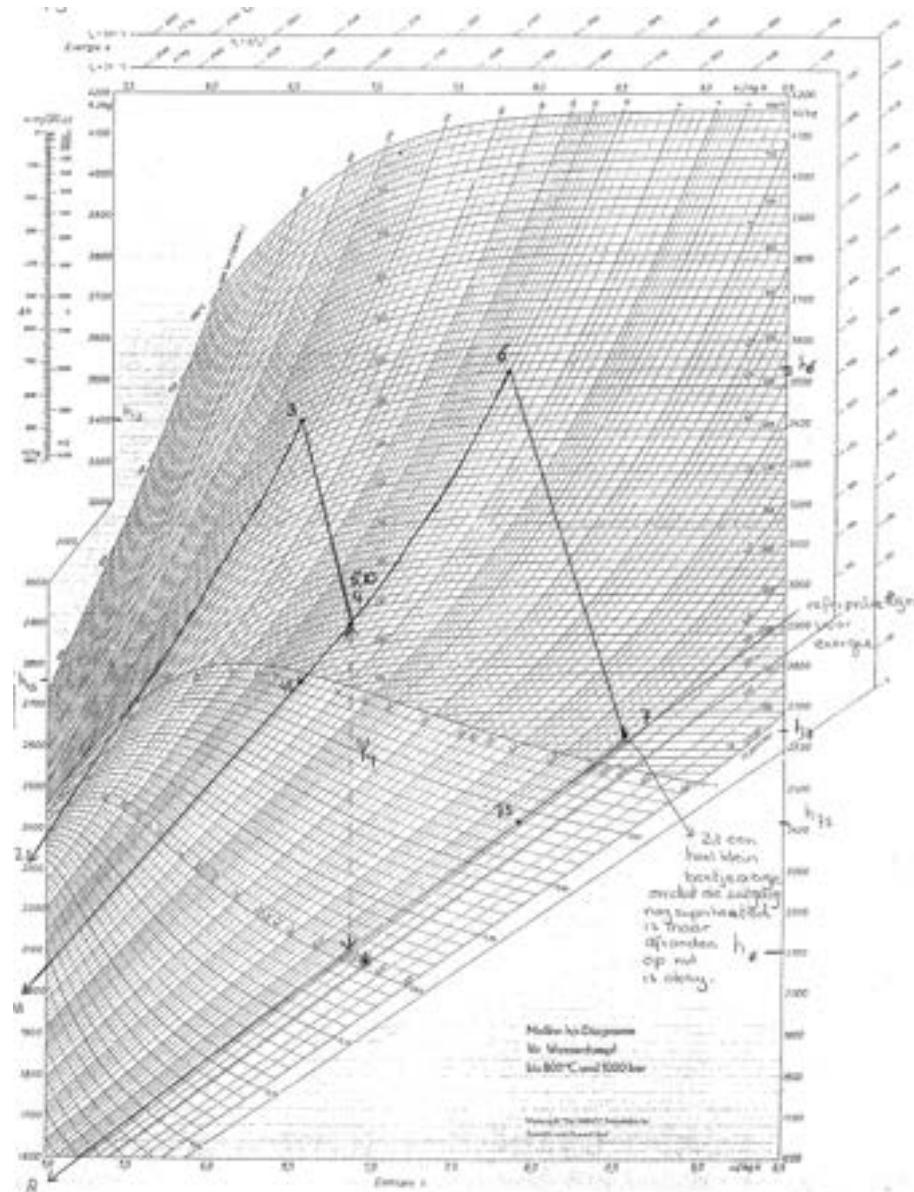
- “pitfalls” continued: (as promised in the lecture, some examples of strange diagrams, that I saw on exams)

The cycle, Rankine with closed feedwater preheating



This is the correct A3 Mollier diagram. Notice that you also need to draw the lines from point 3 and from point (4, 5, 10) and point 7 towards 1 and 11 (leaving the diagram).

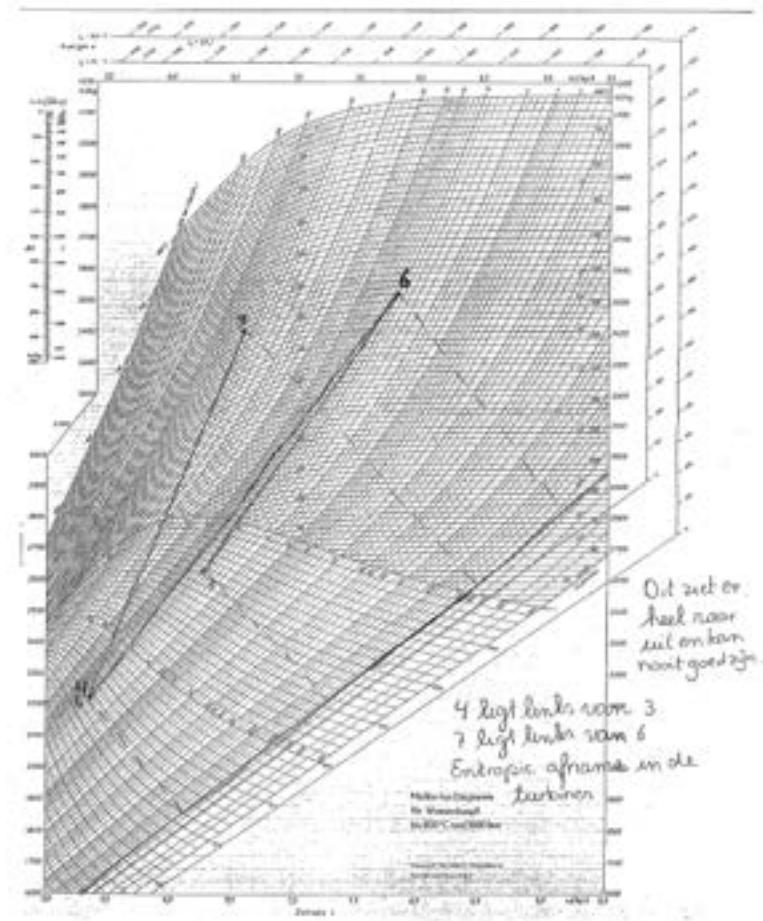
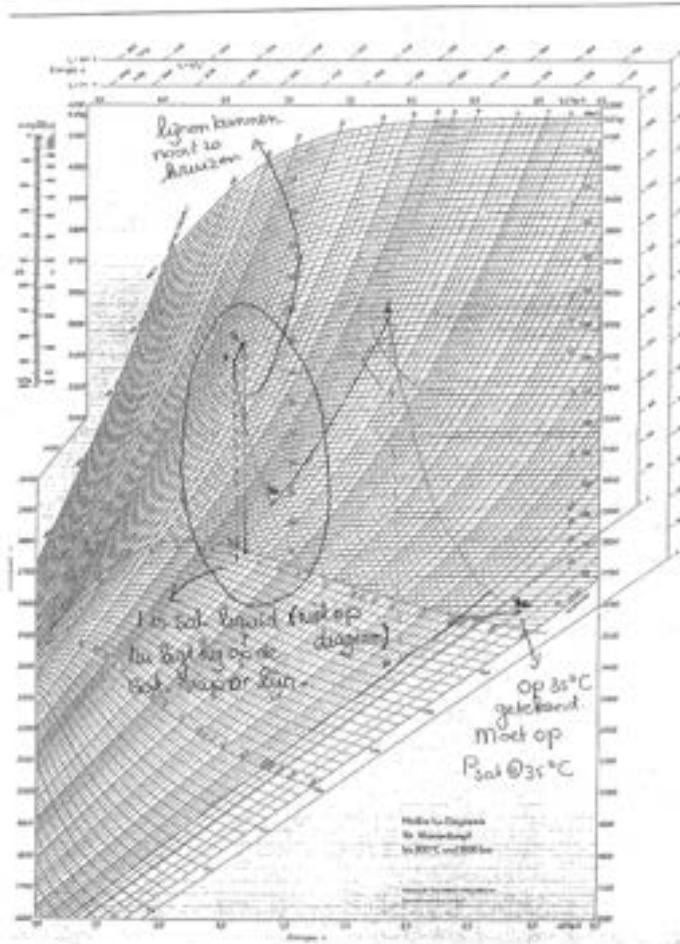
On the next 2 slides are examples what I saw on the exam. Notice that you can not draw the full cycle on this diagram and how some people still tried it.



Exam Engineering Thermodynamics

- “pitfalls” continued: (some examples of strange diagrams, that I saw on exams, sorry for the Dutch I don not have English ones yet, try to avoid that yours are here next year.....)

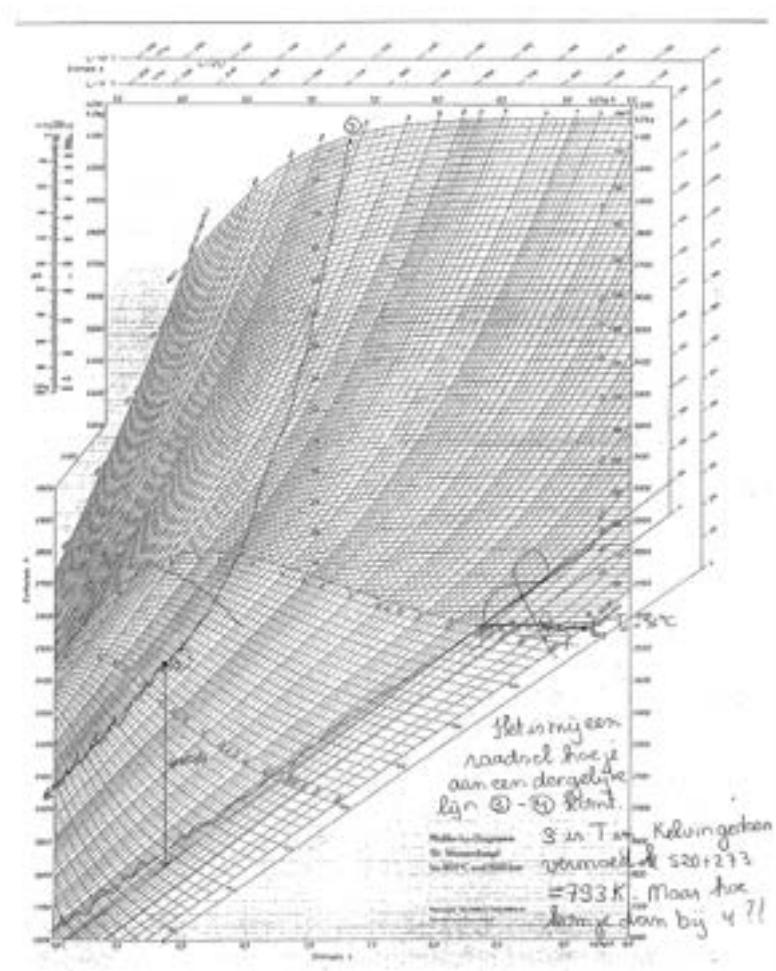
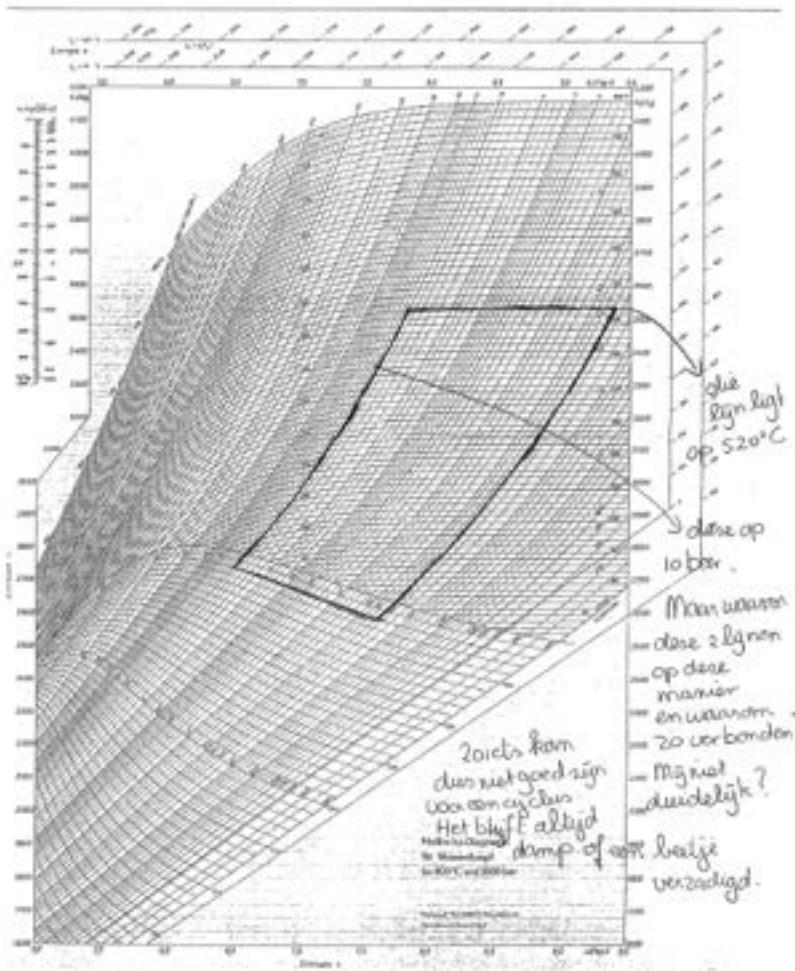
Rankine cycle with closed feedwater preheating, **wrong diagram !!**



Exam Engineering Thermodynamics

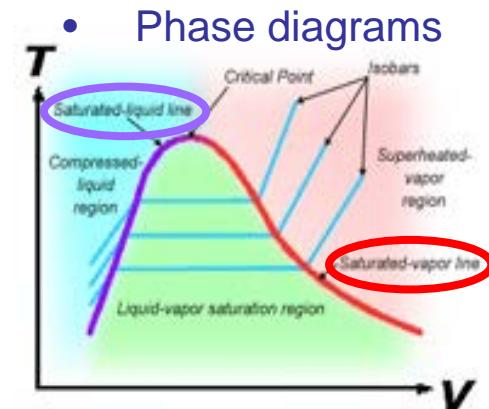
- “pitfalls”continued: (some examples of strange diagrams, that I saw on exams, sorry for the Dutch I don not have English ones yet, try to avoid that yours are here next year.....)

Rankine cycle with closed feedwater preheating, **wrong diagram !!**



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- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal efficiency $\eta_{thermal} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Mixture fraction $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
- Ideal gas law $Pv = RT$, $R = c_p - c_v$
- For an ideal gas $du = c_v dT$ and $dh = c_p dT$
- Conservation of mass $m_{in} = m_{out}$, mass flow rate $\dot{m} = \rho v A$
- Conservation of energy, first law of thermodynamics
 - Closed system $du = \delta q - \delta w \rightarrow \Delta u = q - w$
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- S increases, second law $ds_{total} = ds_{system} + ds_{surroundings} = \delta s_{gen} \geq 0$
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- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Isentropic processes ideal gas $Pv^k = \text{constant}$, $Tv^{k-1} = \text{constant}$, $P^{(k-1)/k}/T = \text{constant}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$ Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$



Class 13

Refrigeration and Heat Pumps

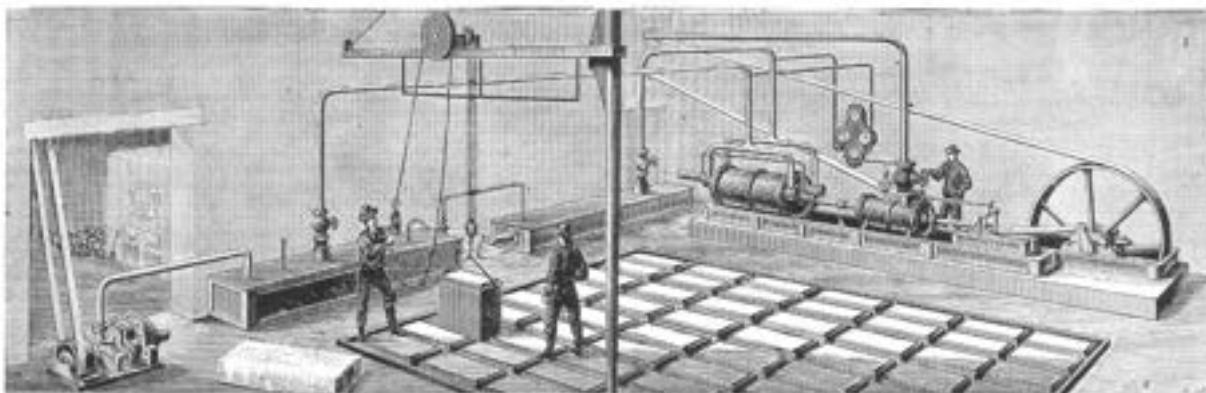
The New York Ice Machine Company

Room 54, No. 21 Cortlandt Street, New York.

Patents of C. M. Tessie du Motay and Leonard F. Beckwith, and of C. M. Tessie du Motay and A. J. Rossi.

LOW PRESSURE BINARY ABSORPTION SYSTEM. NON-INFLAMMABLE.

Ice and Refrigerating Machines 1 ton to 50 tons per day. Cost of Ice, everything included, less than \$1.00 per ton.



ADVANTAGES OVER ALL OTHER MACHINES.

SELF LUBRICATING. NO LEAKS. BINARY LIQUID MIXED WITH WATER HAS NO ACTION ON METALS EVEN IF MIXED WITH WATER. Makes 25 to 30 per cent, more ice or cold air. Uses only 5¢ of water of condensation. Pressure at rest @ instead of 20 to 100 lbs. Pressure when running, 17 lbs. instead of 15 to 300 lbs. Machines as easy of attendance as Low-Pressure Steam Engines. Send for descriptive Circulars and Pamphlet.

AUTOMATIC FAMILY MACHINES making 5 lbs. and 10 lbs. per hour. These Machines can be run by any boy or servant. No danger whatever of any kind in raising them. A 6-ton Ice Machine can be seen at work at C. H. Delamater & Co., Foot of West 14th St., New York.

All the Machines are Guaranteed. E. GILLET, Sec'y. Reference, C. H. DELAMATER & CO., New York City

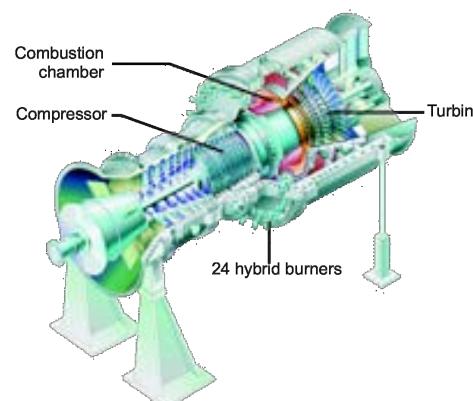
While heating is an ancient technology, the widespread application of cooling technologies occurred only after a firm understanding of thermodynamic cycles was established.

Recap: What is Eng. Thermodynamics?

- **Engineering Thermodynamics:** application of thermodynamics to solve technological problems that engineers face
- Analysis of transport and conversion of various forms of energy:
work \leftrightarrow electricity \leftrightarrow heat \leftrightarrow cold
- **The objectives are:**
 1. Conversion of heat (fuel) into work / electricity (heat engine)
 2. Transportation of heat using work / electricity (cooling / heat pump)



Heat converted into work (electricity) [1]



Heat converted into work to generate power [1]



Work (electricity) converted into cold [2]

Recap: Eng. Thermodynamics – Heat engine

1. Convert fuel / heat in work (heat engine)

- What do you want to know?
 - How much net work / electricity (power) is produced
 - How much heat (energy / fuel) do you have to put in
 - What is the efficiency



Recap: Examples – Heat engine

- Installations or machines that convert fuel or heat to work or electricity (power) using water / steam as working fluid

How does a thermal power plant work?

<https://www.youtube.com/watch?v=IdPTuwKEfmA>



Recap: Examples – Heat engine

- Installations or machines that convert fuel or heat to work or electricity (power) using hot and compressed air as working fluid

How do jet engines work?

<https://www.youtube.com/watch?v=eA699AKxT7s>



Recap: Eng. Thermodynamics - Cooling

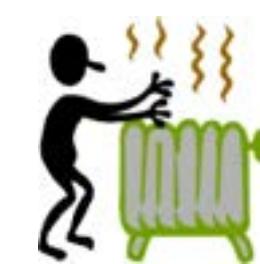
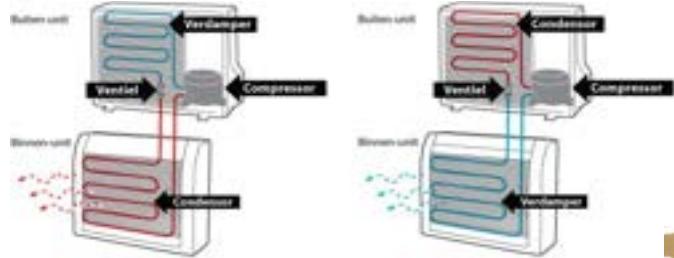
2. Transportation of heat using work / electricity (cooling / heat pump)

- What do you want to know?
 - What is the cooling capacity
 - How much electricity is required
 - What is the coefficient of performance (COP)



Recap: Examples – Cooling / Heat-pump

- Installations or machines that transport heat in the non-spontaneous direction (cold to hot) using work / electricity



Recapitulate Thermo 1 (class 1 – 11)

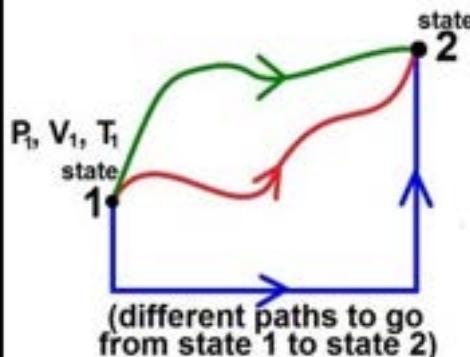
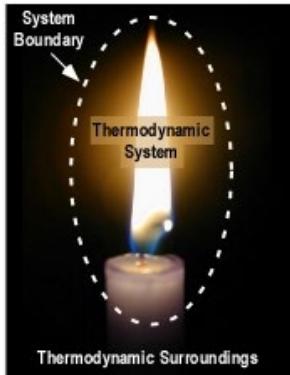
- Class 1 - 5 → Concepts, definitions, open – and closed systems energies, properties of water, 1 and 2 law of thermodynamics (energy conservation and entropy increase)
 - **all tools to make and analyze thermodynamic systems**
- Class 6 → A **thermodynamic cycle** is composed of a series of processes which return to the initial state
 - **Heat power cycles** produce power from heat
 - **Refrigeration / heat pump cycles** transport heat using power
- Class 7, 8 → Vapor cycles, cycles using a working medium that undergoes a phase change during the cycle to produce power
 - Steam engine, Rankine cycle (steam turbine cycle)
 - Combined heat and power (CHP) cycle (co-generation)
- Class 9 → Properties of gas (a missing tool)
- Class 10, 11 → Gas cycles, cycles using gas as working medium to produce power
 - Brayton cycle (gas turbine cycle, jet engine), combined cycles

Content Engineering Thermodynamics 2

- Engineering Thermodynamics 2 is a follow – up of Thermo 1
- Class 13 → Refrigeration and heat pumps cycles, cycles that transport heat in the non-spontaneous direction using work (instead of using heat to produce power as in heat engines like gas- and steam turbines) **This one**
- Class 14 → Internal combustion engines like, Stirling, Otto and Diesel engines, another type of cycle using gas as working fluid
These cycles don't use a gas turbine, as we studied before, to convert heat into work, but they use a piston cylinder device
- Class 15, 16, 17 → Theory behind thermodynamic diagrams, formulas,
 - This is the Mathematical background of Engineering Thermodynamics (in Dutch: Wiskunde achtergrond Technische Thermodynamica, abbreviated to WaTT, which is so nice that I kept the abbreviation to denote this part of the course)
 - There is a separate reader, that also contains the assignments for this WaTT part

Refresh: Roadmap Engineering Thermodynamics 1

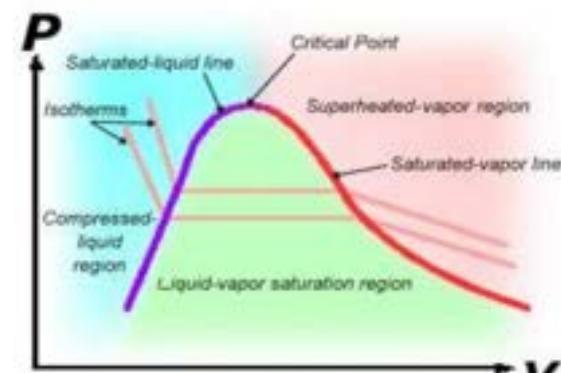
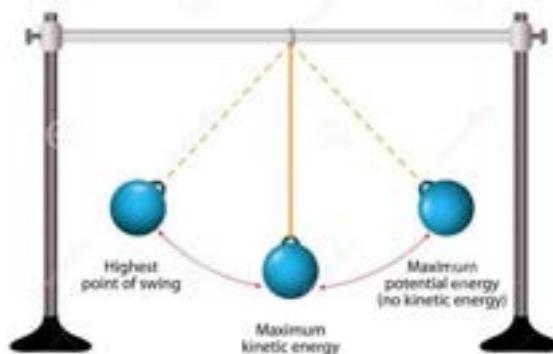
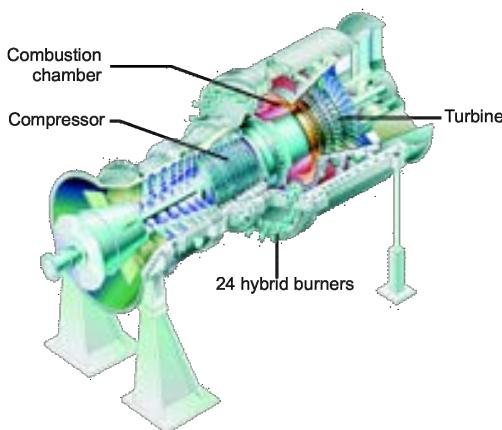
- Using thermodynamics for practical applications requires knowledge of:
Concepts and definitions (Class 1) → Various forms of energy (Class 2)



- Power cycles
(Class 6 – 11)

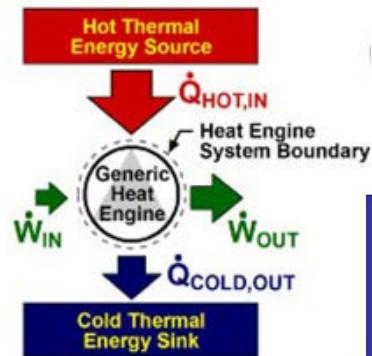
- Laws of Thermo
(Class 4 and 5)

- Properties of Substances
(Class 3, 9)

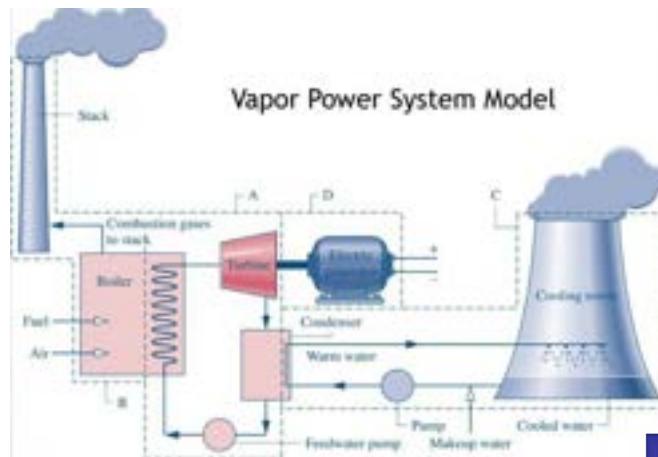


Refresh: Roadmap Engineering Thermodynamics 1

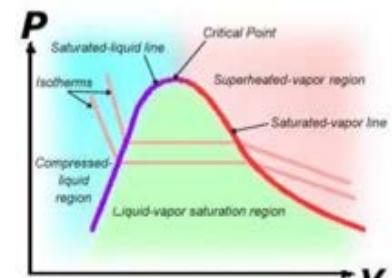
Thermodynamic cycles (Class 6)



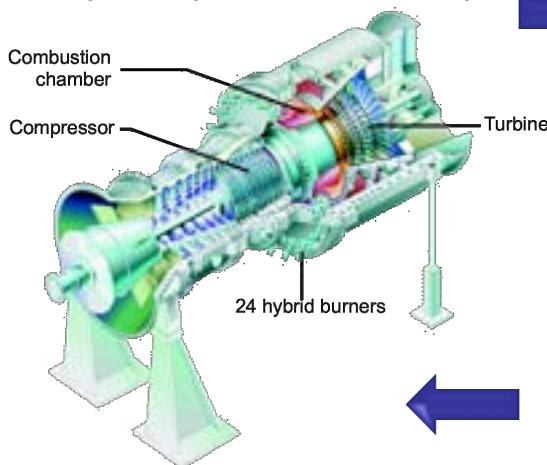
Vapor power cycles – Rankine cycle (Class 7, 8)



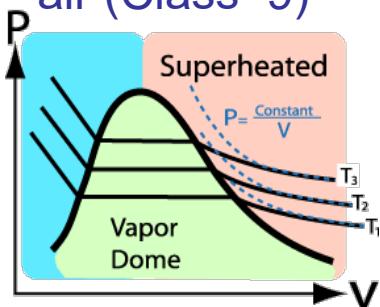
Properties of water (Class 3)



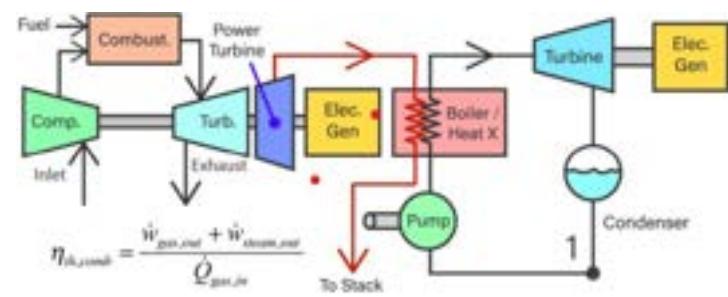
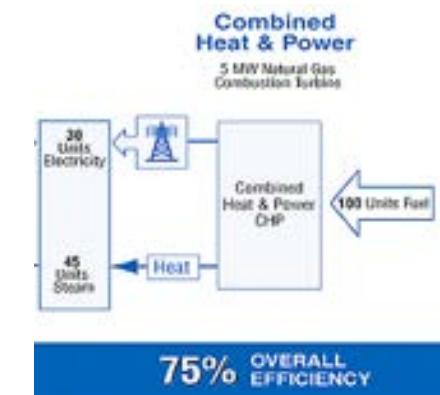
Gas power cycles – Brayton cycle (Class 10, 11)



Properties of air (Class 9)

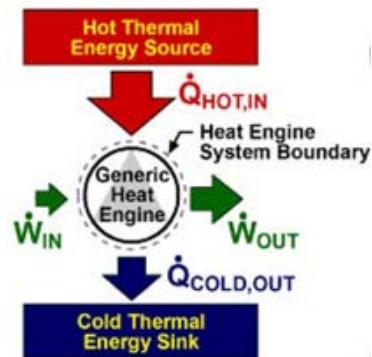


Combined cycles
Combined heat & power (Class 8, 11)

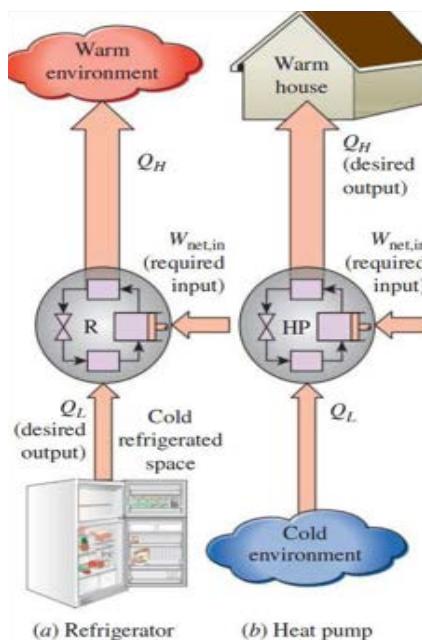


Roadmap Engineering Thermodynamics 2

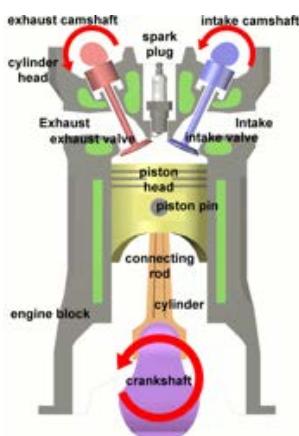
Thermodynamic cycles (Class 6)



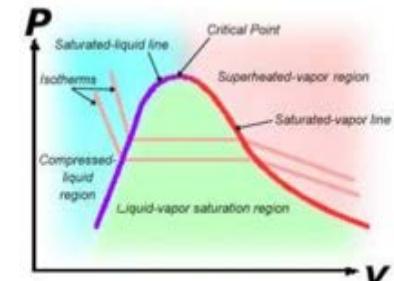
Vapor – compression cycles – refrigeration & heat pumps (Class 13)



Gas power cycles – Otto & Diesel cycle (Class 14)



Properties of R-134a (Class 3)



Math for Thermo
(Class 15, 16, 17)

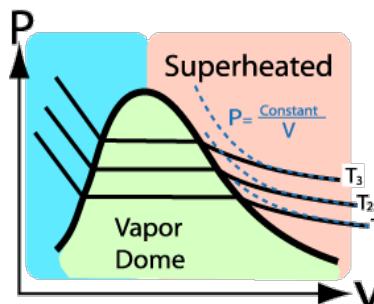
$$\left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P$$

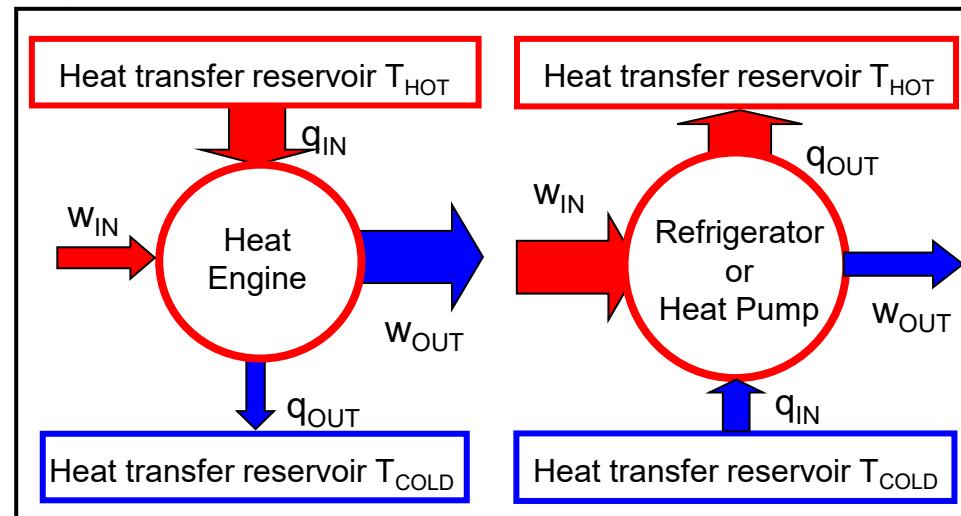
Properties of air (Class 9)



Recapitulate cooling class 6

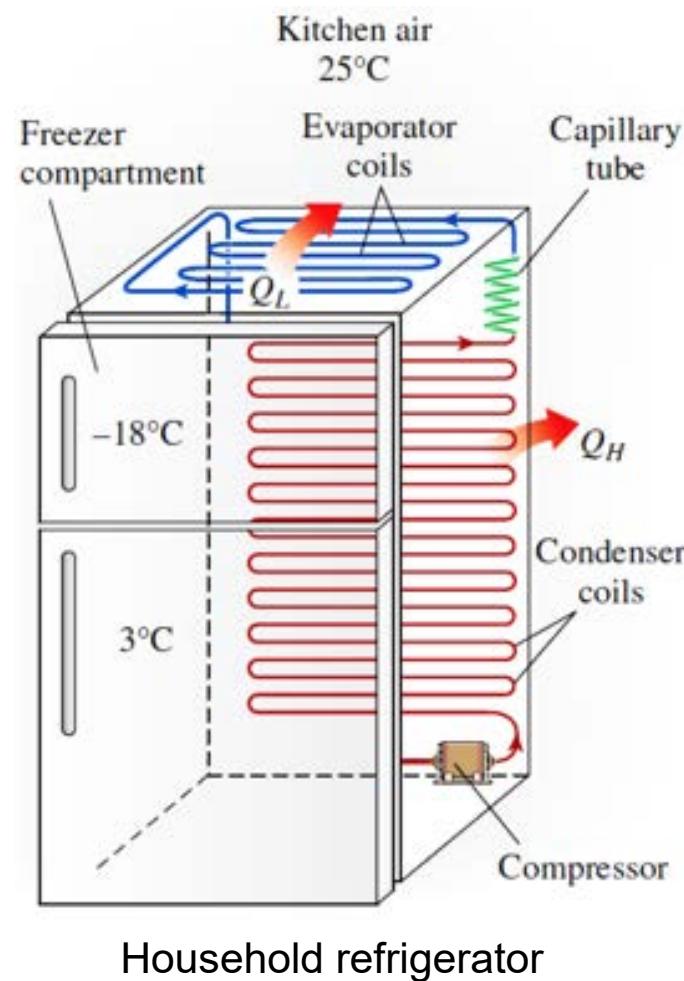
- A **thermodynamic cycle** is composed of a series of processes which return to the initial state, it works between a hot and a cold thermal reservoir
 - 1. **Heat power cycles** produce power from heat
 - 2. **Refrigeration / heat pump cycles** transport heat using power
- First law for a cycle: $w_{net} = q_{net}$
- Second law for a cycle: $\sum_{i=1}^n \frac{q_{net,i}}{T_i} \leq 0$ or $\oint \frac{\delta q_{net,i}}{T_i} \leq 0$
- Thermal efficiency for heat / power cycles: $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$
- COP for refrigeration and heat pump cycles
 - $COP_{ref} = \frac{q_{in,cold}}{w_{in}}$
 - $COP_{heat\ pump} = \frac{q_{out,hot}}{w_{in}}$
- Carnot (ideal) cycle has maximum COP

Energy flows in a heat engine (left) and in a refrigeration or heat pump cycle (right)



Content Class 13

- **Refrigeration & heat pump cycles – cycles transporting heat in the non-spontaneous direction using power**
 - Basics of cooling and heating / COP
 - Ideal and non-ideal vapor compression cycle
 - Comparison to Rankine cycle
 - Special cooling cycles
 - Heat pumps and air conditioners
 - Gas refrigeration cycle
- **Learning goal:** recognize a thermodynamic system to produce cold/heat, explain the configuration, analyse the thermodynamic aspects from the view-point of the first law of thermodynamics, interpret and evaluate the results and suggest improvements



Early days: Icehouses for cooling

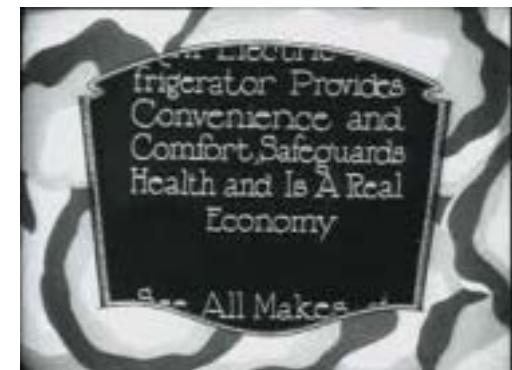
- Underground chambers, usually man made, but also buildings with various types of insulation, often straw or sawdust
- Store ice cut from lakes or rivers throughout the year (ice), prior to the invention of the refrigerator
- The ice remains frozen for many months, often until the following winter, and could be used as a source of ice during summer months.
- Main application was the storage of foods, but it could also be used simply to cool drinks or allow ice cream to be prepared



Left: On the estate of Twickel Castle in Delden is a double ice cellar, the only one in the Netherlands. The left-hand ice cellar was built in 1906, the right-hand is probably of an older date. <http://www.cultuurwijzer.nl/oud/i000227.html>

Nowadays: Refrigerators for cooling

- Nowadays ice cellars are no longer used
- The refrigerator is not that old yet!
- It was only after that it was well understood how thermodynamics worked that the technology for cooling could be further developed and the refrigerator was born
- First cooling systems were developed around 1900
- In the Netherlands in the first half of the 20th century
- Nowadays everyone has a refrigerator but at the time there was still a lot of advertising to convince people that it was a handy device
- See the American advertising video, Buy an electrical refrigerator, Electric League of Pittsburgh, 1926

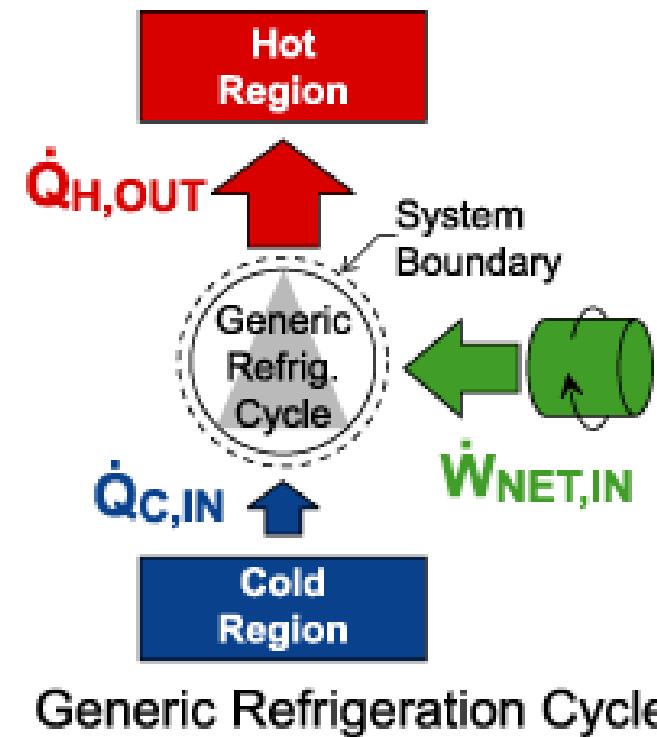
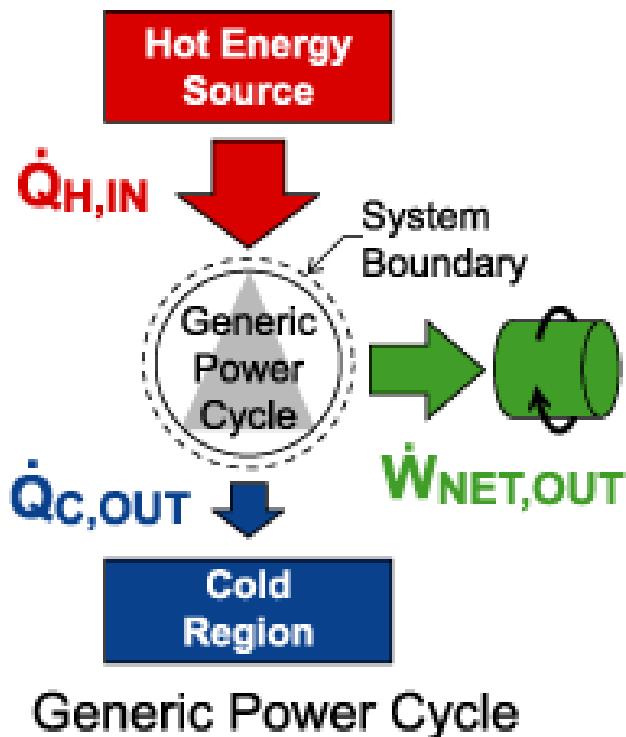


1926 silent film commercial for electric refrigerators

http://commons.wikimedia.org/wiki/File:Theater_commercial,_electric_refrigerator,_1926.ogg

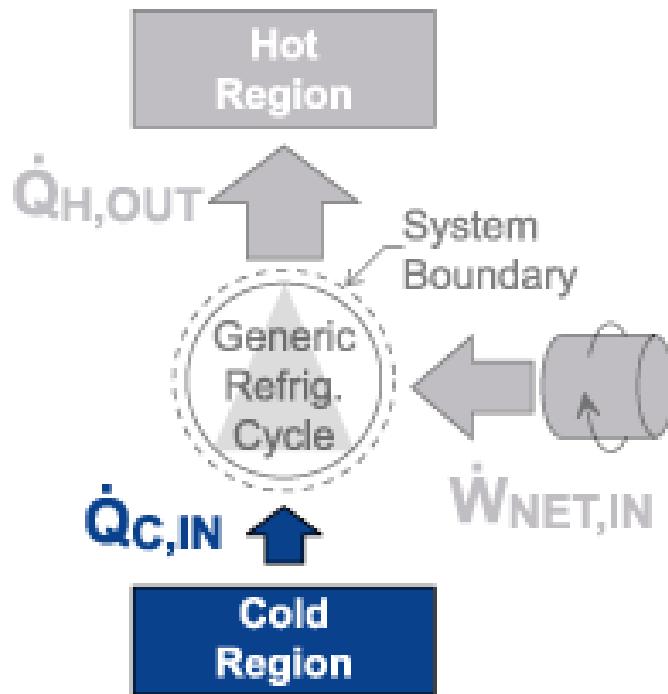
Refrigeration Basics

- For refrigeration or heat pump cycles the first law of thermodynamics, the basic energy balance is still full filled
- The first law for **all** cycles (power as well as refrigeration cycles) is
$$W_{IN} - W_{OUT} = q_{IN} - q_{OUT} \rightarrow W_{NET} = q_{NET}$$
- For refrigeration cycles, typically $w_{OUT} = 0 \rightarrow w_{IN} = q_{OUT} - q_{IN}$

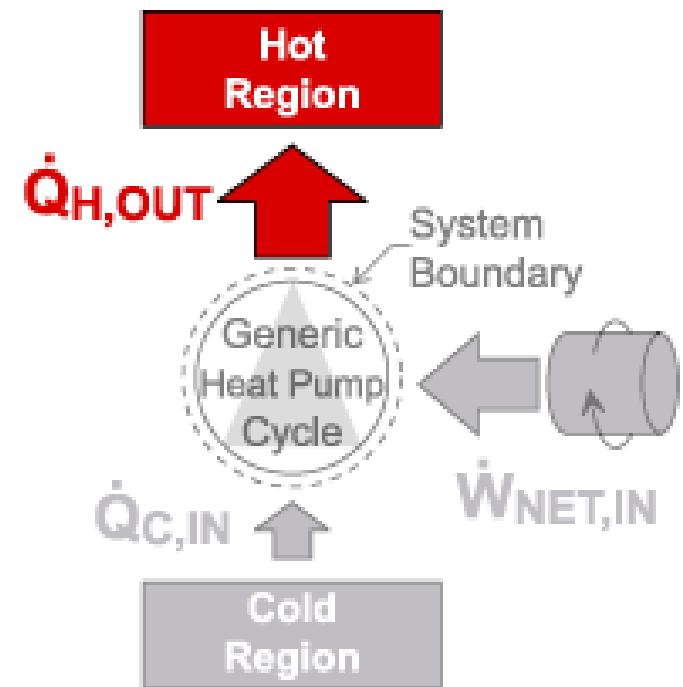


Refrigeration versus Heat Pump

- Refrigeration & heat pump cycles → It is the same cycle, but they have a different goal
 - Refrigeration, the goal is cooling → $q_{in,cold}$ ($= q_{evaporator}$)
 - Heat pump, the goal is heating → $q_{out,hot}$ ($= q_{condenser}$)



Generic Refrigeration Cycle



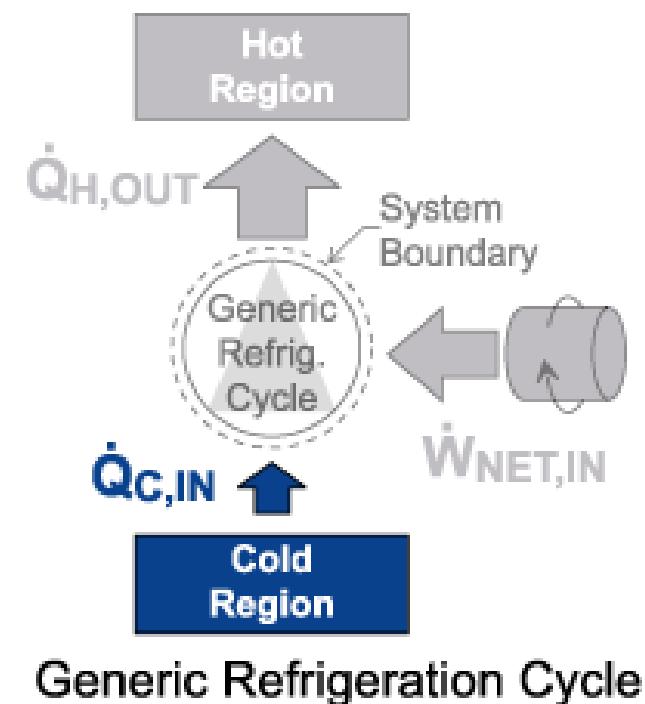
Generic Heat Pump Cycle

COP and desired output for Refrigeration

- For **refrigeration** cycles the goal is to cool a region and **the desired energy** is the energy subtracted from the cold region, $q_{in,cold}$ ($= q_{evaporator}$)
 - The energy that is used to achieve his goal is the electricity needed to drive the compressor, the work input, w_{in}
 - To quantify the performance of refrigeration the COP (Coefficient of Performance) is used and not an efficiency
 - For **refrigeration** cycles mostly $w_{OUT} = 0$
-
- $COP_{ref} = \frac{Energy\ desired}{Energy\ used} = \frac{q_{in,cold}}{w_{in}} = \frac{q_{evaporator}}{w_{in}}$
 - The maximum performance of a refrigerator is achieved for Carnot refrigeration

$$COP_{ref,Carnot} = \frac{1}{\frac{T_{hot}}{T_{cold}} - 1}$$

(see class 6)



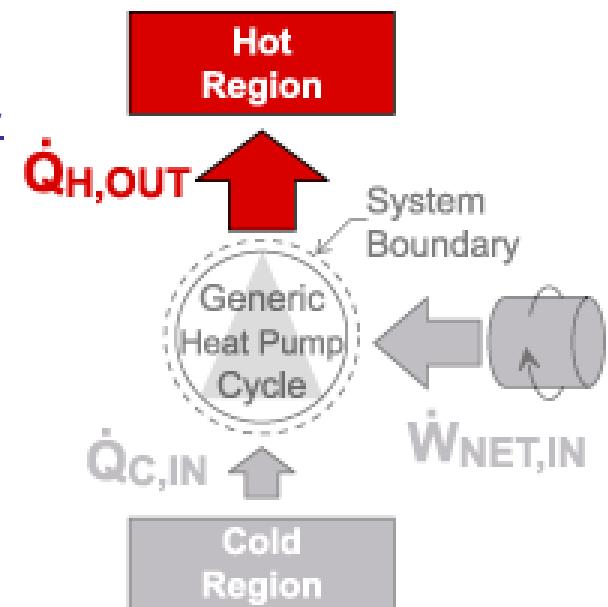
COP and desired output for Heat Pumps

- For heat pump cycles the goal is to heat a region and the desired energy is the energy rejected to the hot region, $q_{out,hot}$ ($= q_{condenser}$)
 - The energy that is used to achieve his goal is the electricity needed to drive the compressor, the work input, w_{in}
 - To quantify the performance of a heat pump the COP (Coefficient of Performance) is used and not the efficiency
 - For heat pump cycles mostly $w_{OUT} = 0$
- $COP_{heat\ pump} = \frac{Energy\ desired}{Energy\ used} = \frac{q_{out,hot}}{w_{in}} = \frac{q_{condenser}}{w_{in}}$
- The maximum performance of a heat pump is achieved for a Carnot heat pump

$$COP_{heat\ pump,Carnot} = \frac{1}{1 - \frac{T_{cold}}{T_{hot}}}$$

(see class 6)

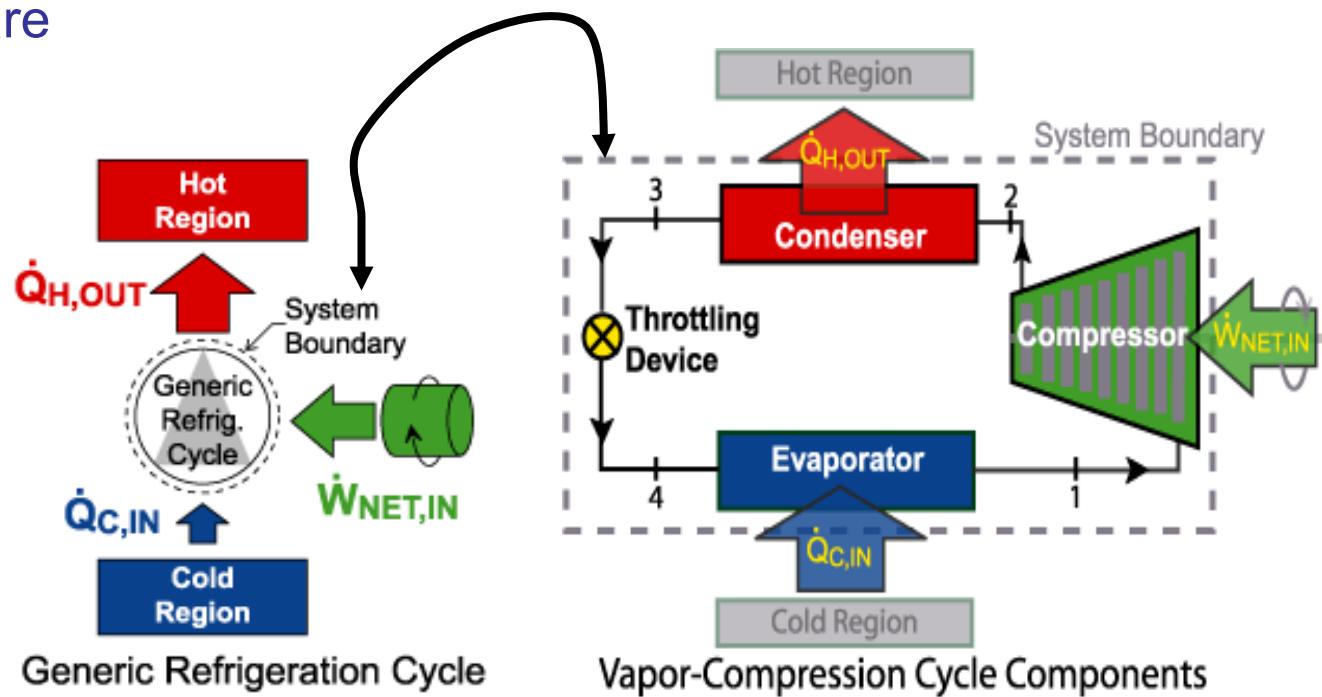
- In general, $COP_{heat\ pump} - COP_{ref} = 1$



Generic Heat Pump Cycle

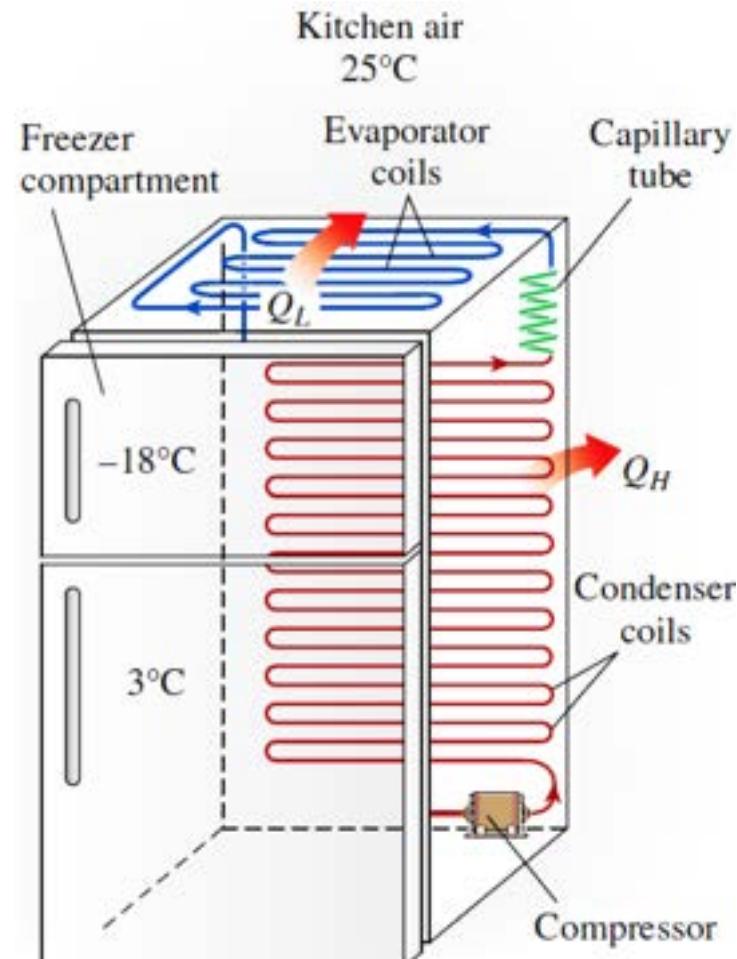
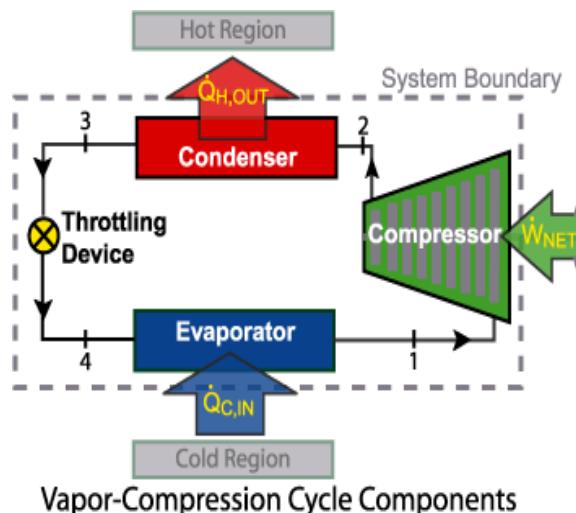
Components Basic Vapor-Compression Cycle

- The basic cooling cycle, called a vapor-compression, cycle consists of four components that are like the components of a Rankine cycle (vapor power)
- However, the fluid goes in **the reversed** direction and therefore, the cycle is also called a reversed Rankine cycle
- The components are
 - Throttle valve
 - Compressor
 - Condenser
 - Evaporator



Components Basic Vapor Compression Cycle

- Compare the cooling cycle with an ordinary household refrigerator (with freezer compartment)
- Components:
 - Throttle valve (= capillary tube)
 - Compressor
 - Condenser (coils)
 - Evaporator (coils)



Principle of Ideal Vapor Compression Cycle

- **1 → 2 Isentropic compression (w_{in})**

Saturated vapor at low pressure is compressed to high P and T (superheated vapor), the compressor is assumed to be adiabatic and ideal (reversible, isentropic)

- **2 → 3 Isobaric heat rejection ($q_{hot,out}$)**

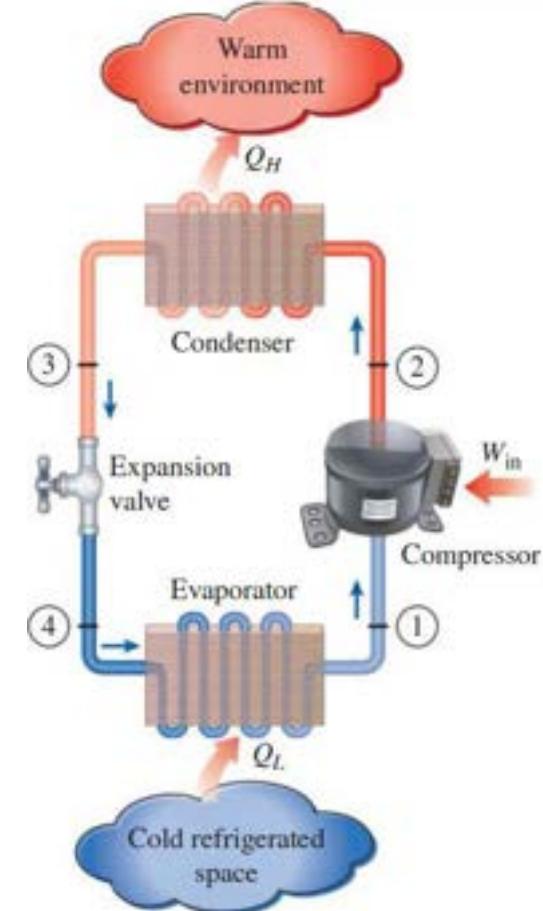
In the condenser, at high constant pressure heat rejection occurs from the high temperature working fluid to the high temperature reservoir, the superheated vapor changes phase to saturated liquid

- **3 → 4 Isenthalpic throttling ($w_{out}=0, q=0$)**

Reduction of the pressure by throttling, the saturated liquid is reduced in temperature and the outcome is a saturated mixture of low quality

- **4 → 1 Isobaric heat addition ($q_{cold,in}$)**

In the evaporator heat is added at constant low pressure from the low temperature reservoir to the lower temperature working fluid, the liquid phase evaporates, and a saturated vapor remains

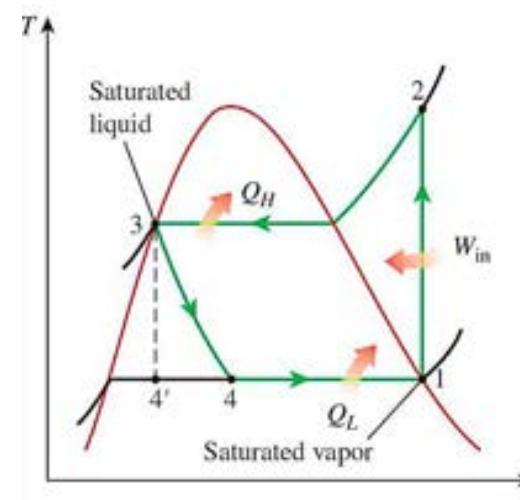
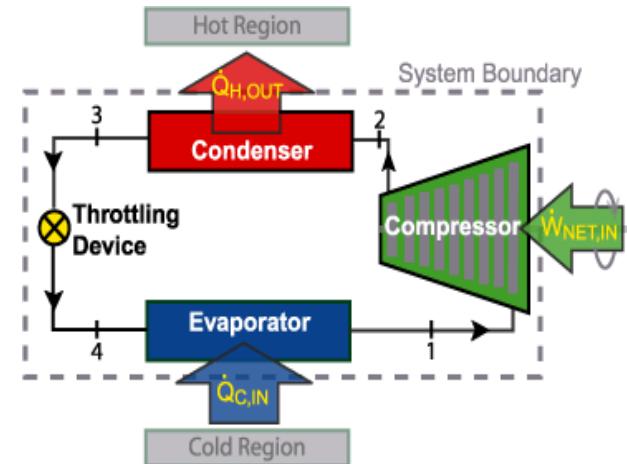


Vapor Compression Cycle Analysis

- Like the Rankine and Brayton cycle the vapor compression cycle consists of a series of processes occurring in open devices
- Analogue to the Rankine and Brayton cycle the devices should be analyzed separately
- Process $1 \rightarrow 2$, **isentropic pressure increase by ideal compressor:**

$$W_{\text{compressor,in}} = h_{\text{out}} - h_{\text{in}} = h_2 - h_1$$

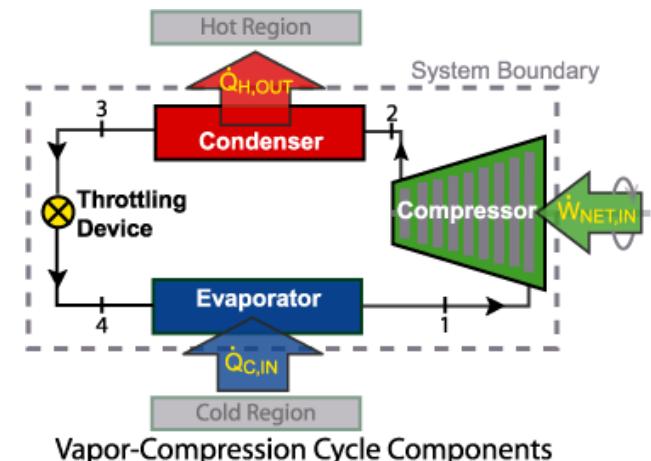
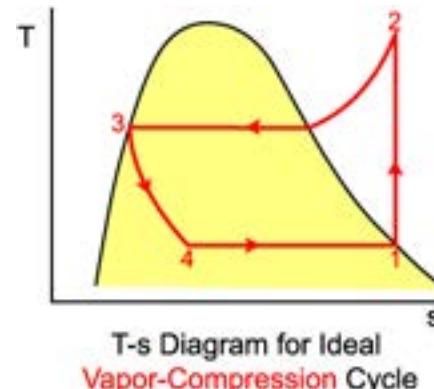
- Process $2 \rightarrow 3$, **isobaric heat rejection in the condenser:** $q_{\text{hot,out}} = h_2 - h_3$
- Process $3 \rightarrow 4$, **isenthalpic pressure reduction by throttling valve:** $h_3 = h_4$
- Process $4 \rightarrow 1$, **isobaric heat addition in the evaporator:** $q_{\text{cold,in}} = h_1 - h_4$



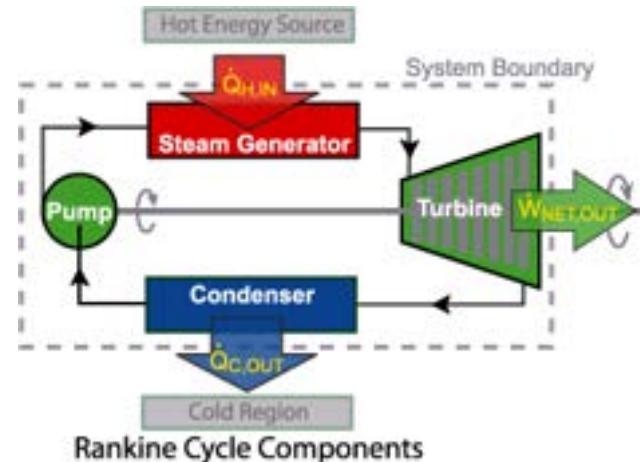
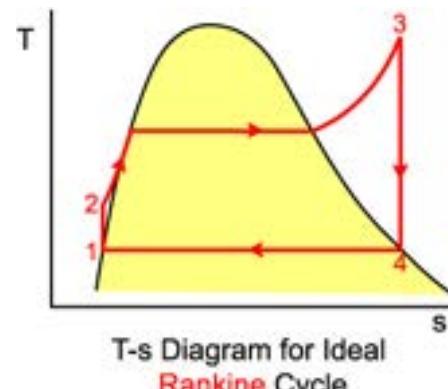
Comparison Vapor Compr. to Rankine Cycle

- A vapor-compression cycle acts like a reversed Rankine cycle, there are some differences:
- The pump is replaced by a compressor (why?)
- The turbine is replaced by a throttling valve
- Ideal Rankine $1 \rightarrow 2$: $s = \text{constant}$
- Ideal vapor compression $3 \rightarrow 4$: throttle valve $h = \text{constant}$ BUT s increases
- Different working fluid
- The working fluid goes in the reversed direction!**

Reversed Rankine cycle (vapor-compression cycle)

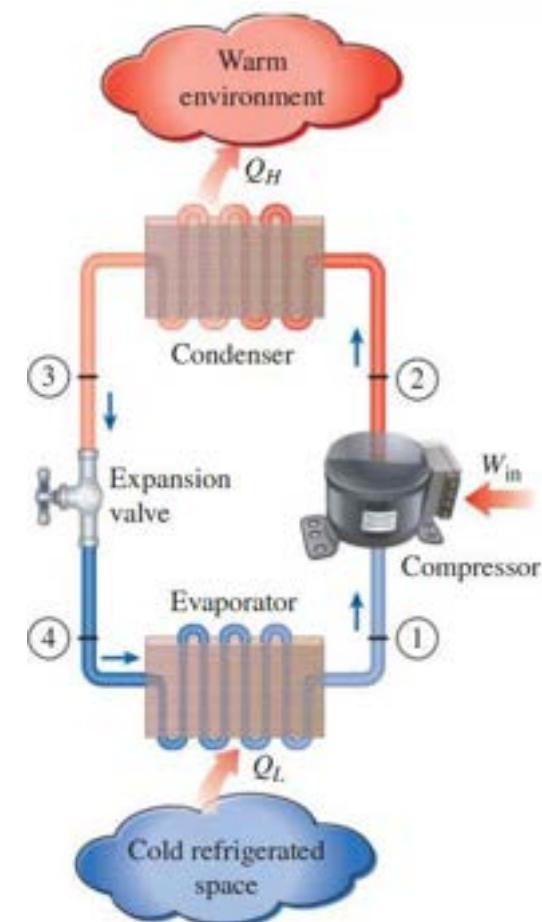
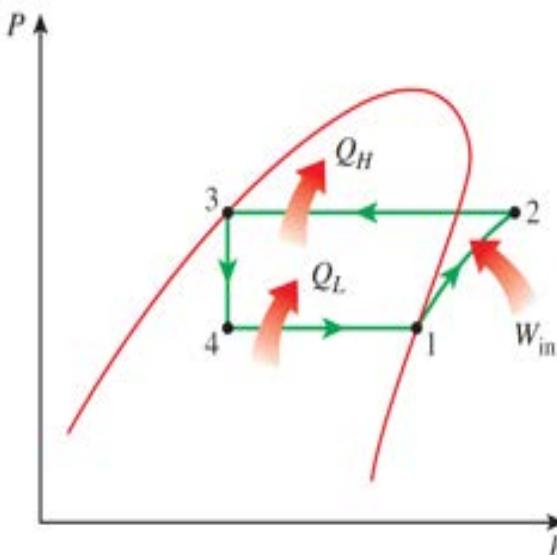
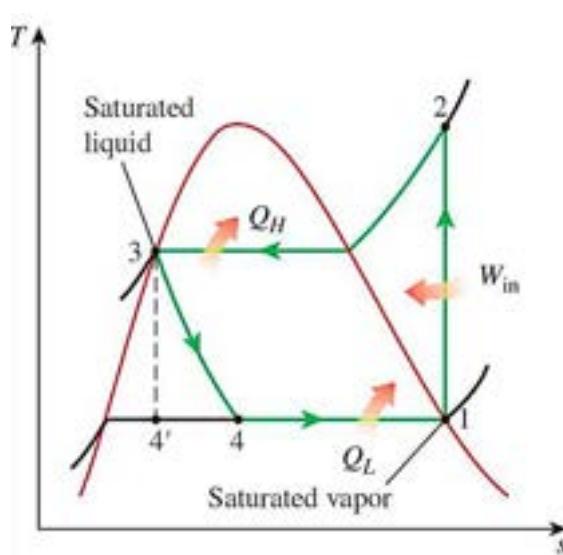


Rankine cycle



Ideal Vapor Compression Cycle Diagrams

- There are different ways to represent the vapor-compression cycle in a diagram
- For refrigeration cycle cycles often a Ph-diagram is used to illustrate the process (this clearly shows the constant enthalpy process in the throttle valve / expansion valve)



Processes Ideal Vapor Compression Cycle

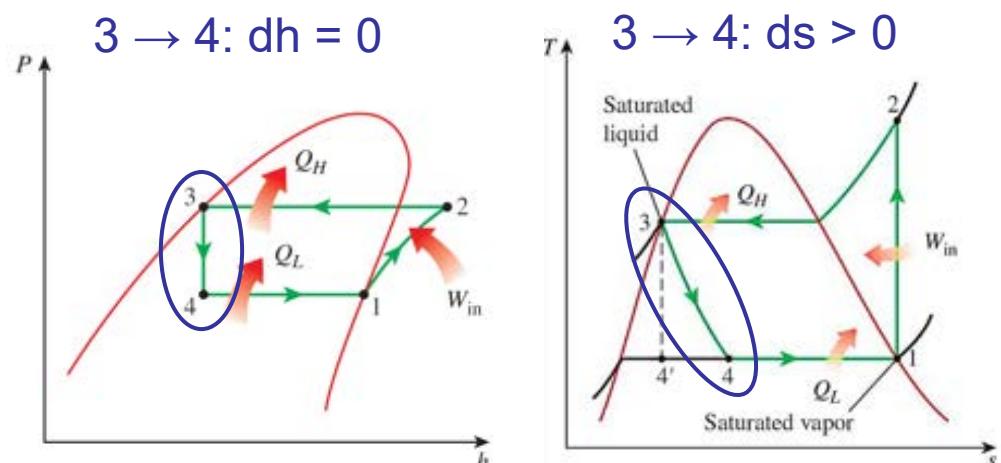
Process	Component	q	w	Constant Property
$1 \rightarrow 2$	Compressor	0	w_{IN}	Entropy, s
$2 \rightarrow 3$	Condenser	q_{OUT}	0	Pressure, P
$3 \rightarrow 4$	Throttling Device	0	0	Enthalpy, h
$4 \rightarrow 1$	Evaporator	q_{IN}	0	Pressure, P

- Process $3 \rightarrow 4$, throttling:

$dh = 0$ and $ds > 0$ because:

$$dh = Tds + vdp$$

$$dp < 0 \rightarrow ds > 0$$

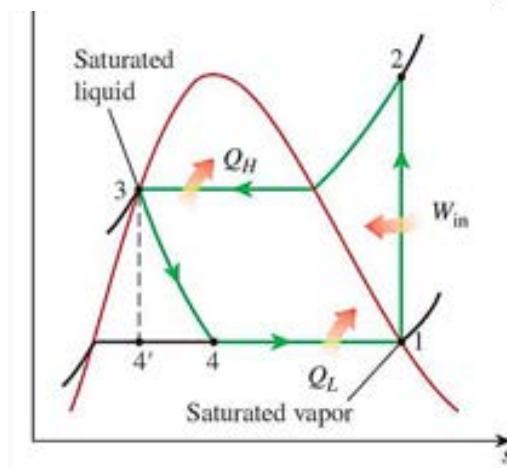
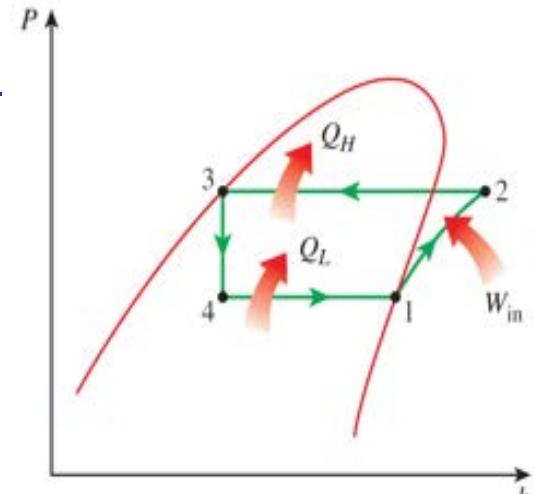
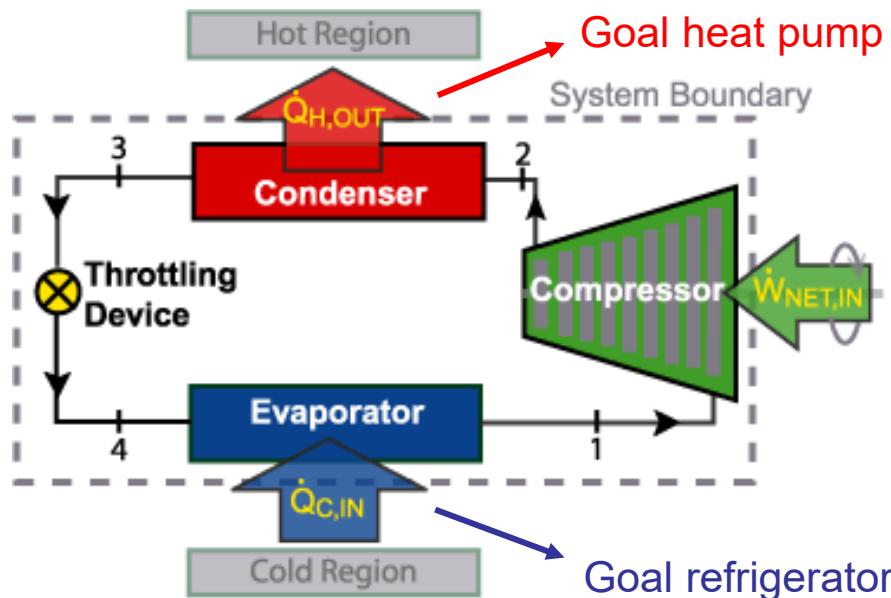


- Note: an ideal vapor compression cycle is not reversible, the process in the throttle valve cannot be reversed

COP Refrigerator or Heat Pump

- The Coefficient of Performance (COP) denotes how good the cycle is
- As the goal for refrigeration is different from the goal for a heat pump the COP is defined different

- Refrigerator: $COP_{refrigerator} = \frac{q_{in,cold}}{w_{in}} = \frac{h_1 - h_4}{h_2 - h_1}$
- Heat pump: $COP_{heat\ pump} = \frac{q_{out,hot}}{w_{in}} = \frac{h_2 - h_3}{h_2 - h_1}$



Refrigerator or Heat Pump Capacity

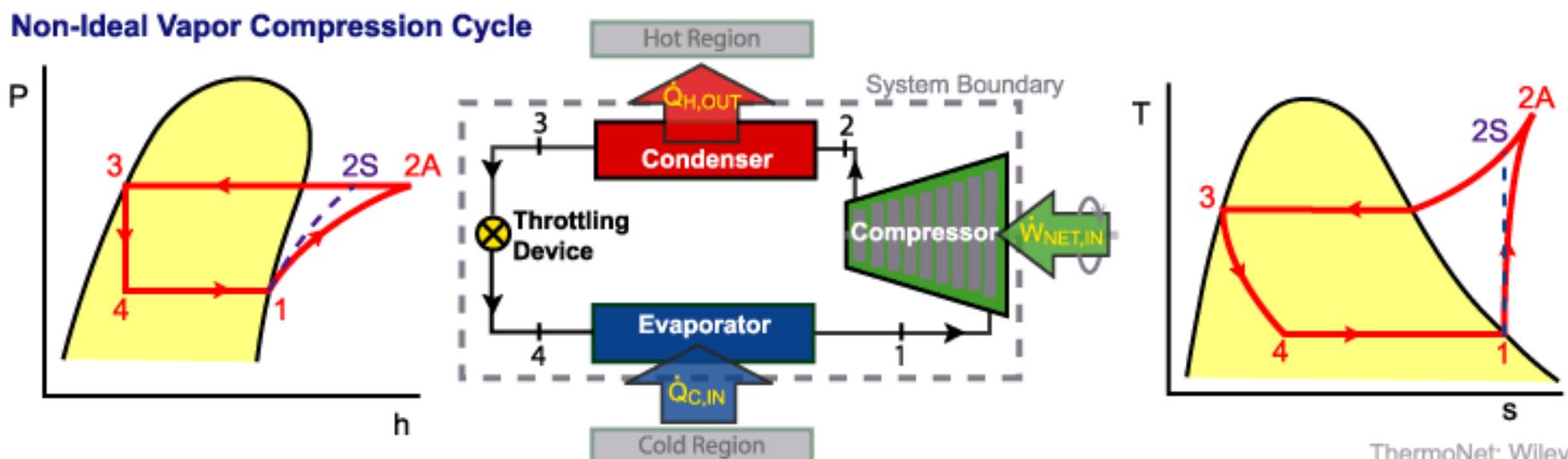
- The cooling or heating capacity, also called the load, denotes how much energy per second can be subtracted from the cold region to cool or can be rejected to the hot region to heat (like power in a heat engine)
 - Refrigeration/Air-Conditioning: $Load_{REF} = \dot{m}q_{in,evap} = \dot{Q}_{in,evap}$
 - Heat Pump: $Load_{HP} = \dot{m}q_{out,cond} = \dot{Q}_{out,cond}$
- The compressor power that is needed follows from required load:
 - Refrigeration/Air-Conditioning: $\dot{W}_{comp,in} = \frac{\dot{Q}_{in,evap}}{COP_{REF}}$
 - Heat Pump: $\dot{W}_{comp,in} = \frac{\dot{Q}_{out,cond}}{COP_{HP}}$
- By adjusting the mass flow of the refrigerant, the load of a system with certain parameters can be adjusted

Non-Ideal Vapor Compression Cycle

- Real vapor compression cycles have effects that deviate from the ideal cycle, the most important one of them is that the compressor between point 1 and 2 is not ideal, it is a non-isentropic compressor, and the isentropic efficiency of the compressor should be considered
- Calculate h_2 using the isentropic efficiency and $s_{2s} = s_1$

$$\eta_{COMP,S} = \frac{w_{IN,S}}{w_{IN,A}} = \frac{h_{2s} - h_1}{h_2 - h_1}$$

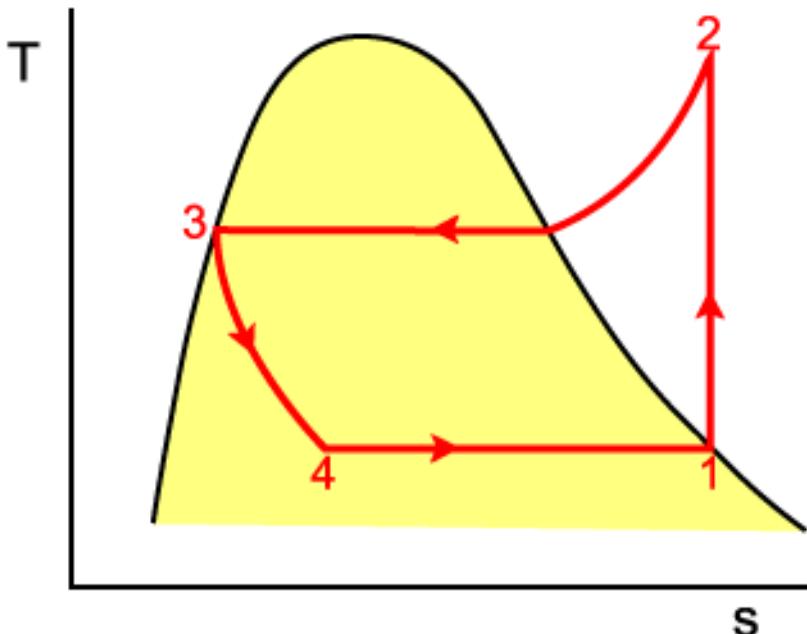
Non-Ideal Vapor Compression Cycle



ThermoNet: Wiley

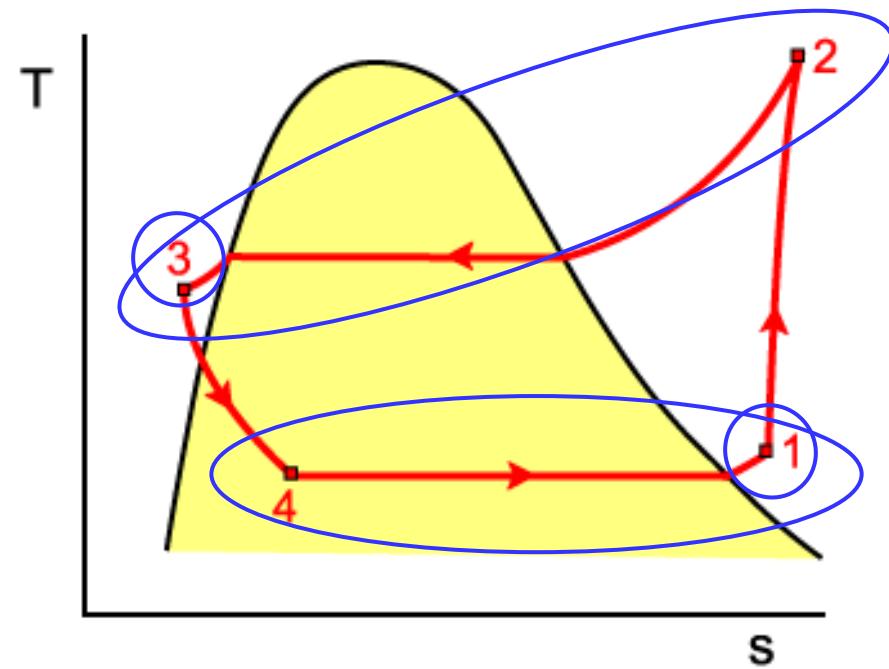
Non-Ideal Vapor Compression Cycle

- Other effects in real vapor compression cycles are
 - Sub - cooled liquid leaving condenser (at 3)
 - Superheated vapor leaving evaporator (at 1)
 - Pressure drops in condenser (2-3) and evaporator (4-1)



Ideal Vapor Compression Cycle

ThermoNet: Wiley

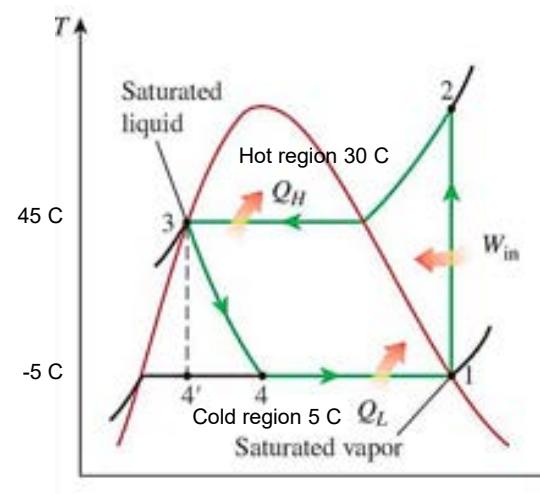


Non-Ideal Vapor Compression Cycle

ThermoNet: Wiley

Working Fluid Vapor Compression Cycle

- For the cooling cycle a different working fluid, with a different boiling point is required → these are refrigerants with pressure dependent saturation temperatures in the desired working range (the fluid undergoes a phase change like water!)
 - Fluorocarbons (e.g., R-134a)
 - Hydrocarbons
 - Ammonia
- To select the right refrigerant, it is important to consider
 - The temperature of the cold region, inside the refrigerator
 - The temperature of the hot region, the environment



The boiling point at the high pressure should be above the T of the hot region, the environment, to be able to transfer the heat

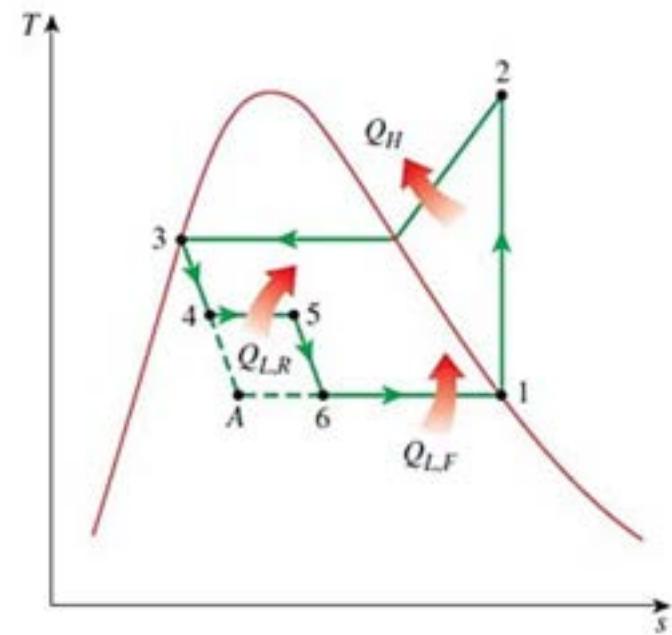
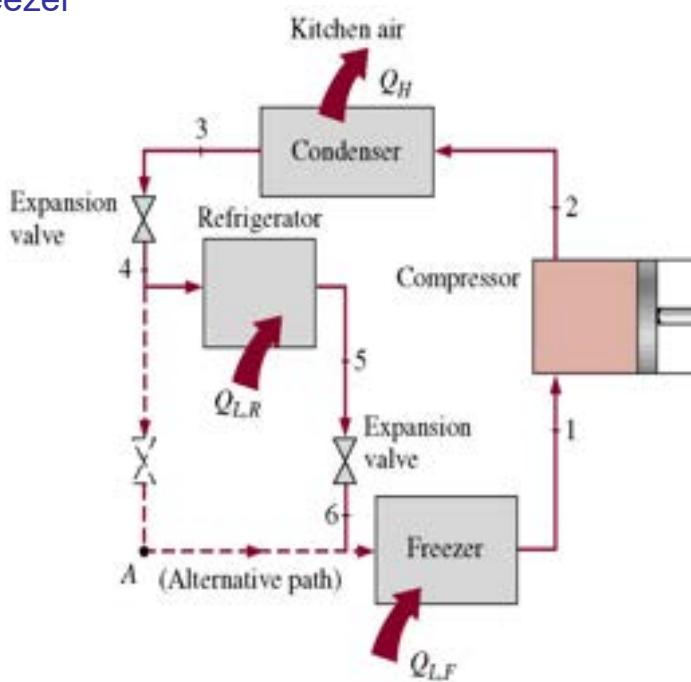
The boiling point at the low pressure should be a little below the desired T of the cold region to be able to transfer the heat

Working Fluid Vapor Compression Cycle

- Several refrigerants may be used in refrigeration systems such as chlorofluorocarbons (CFCs), ammonia, hydrocarbons (propane, ethane, ethylene, etc.), carbon dioxide, air (in the air-conditioning of aircraft), and even water (in applications above the freezing point).
- The industrial and heavy-commercial sectors use ammonia (it is toxic).
- R-11, R-12, R-22, R-134a, and R-502 account for over 90 percent of the market.
- R-11 is used in large-capacity water chillers serving A-C systems in buildings.
- R-134a (replaced R-12, which damages ozone layer) is used in domestic refrigerators and freezers, as well as automotive air conditioners.
- R-22 is used in window air conditioners, heat pumps, air conditioners of commercial buildings, and large industrial refrigeration systems, and offers strong competition to ammonia.
- R-502 (a blend of R-115 and R-22) is the dominant refrigerant used in commercial refrigeration systems such as those in supermarkets.
- CFCs allow more ultraviolet radiation into the earth's atmosphere by destroying the protective ozone layer and thus contributing to the greenhouse effect that causes global warming. Fully halogenated CFCs (such as R-11, R-12, and R-115) do the most damage to the ozone layer. Refrigerants that are friendly to the ozone layer have been developed.
- Two important parameters that need to be considered in the selection of a refrigerant are the temperatures of the two media (the refrigerated space and the environment) with which the refrigerant exchanges heat.

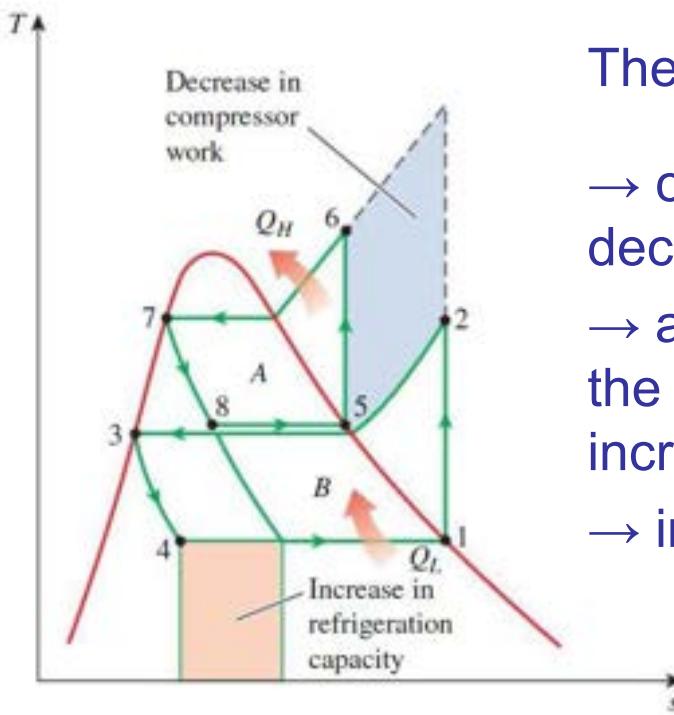
Freezer Compartment in Refrigeration Cycle

- In a refrigerator with a separate freezer compartment two regions with different temperatures are present
- This is achieved by adding an additional throttling valve to get three different pressure levels with the desired boiling temperatures
 1. Condenser T_{hot}
 2. Refrigerator $T_{\text{refrigerator}}$
 3. Freezer T_{freezer}



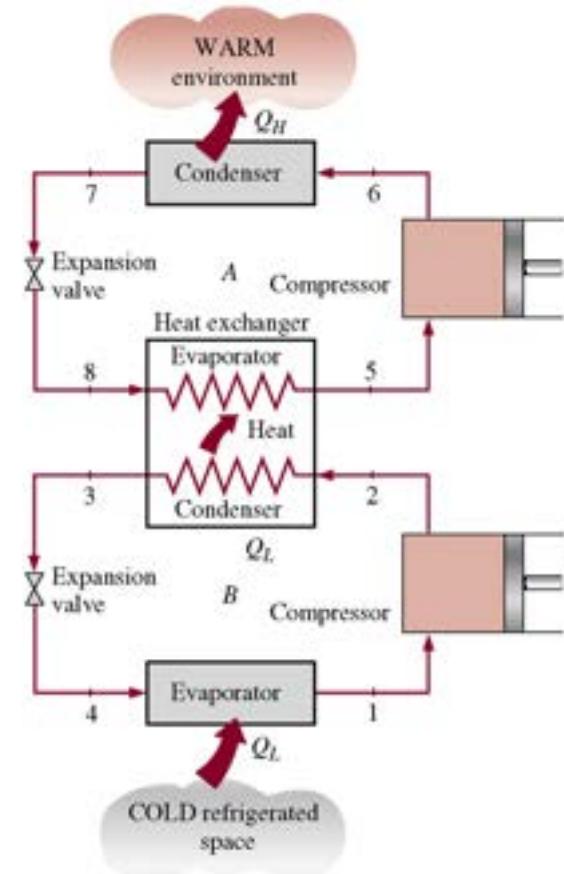
Cascade Refrigeration Systems

- Some industrial applications require moderately low temperatures, and the temperature range may be too large for a single refrigeration cycle
- A way to deal with this is to perform the refrigeration process in stages, two or more refrigerators operate in series at different pressures
- $\dot{Q}_{L\text{-upper}} = \dot{Q}_{H\text{-lower}}$



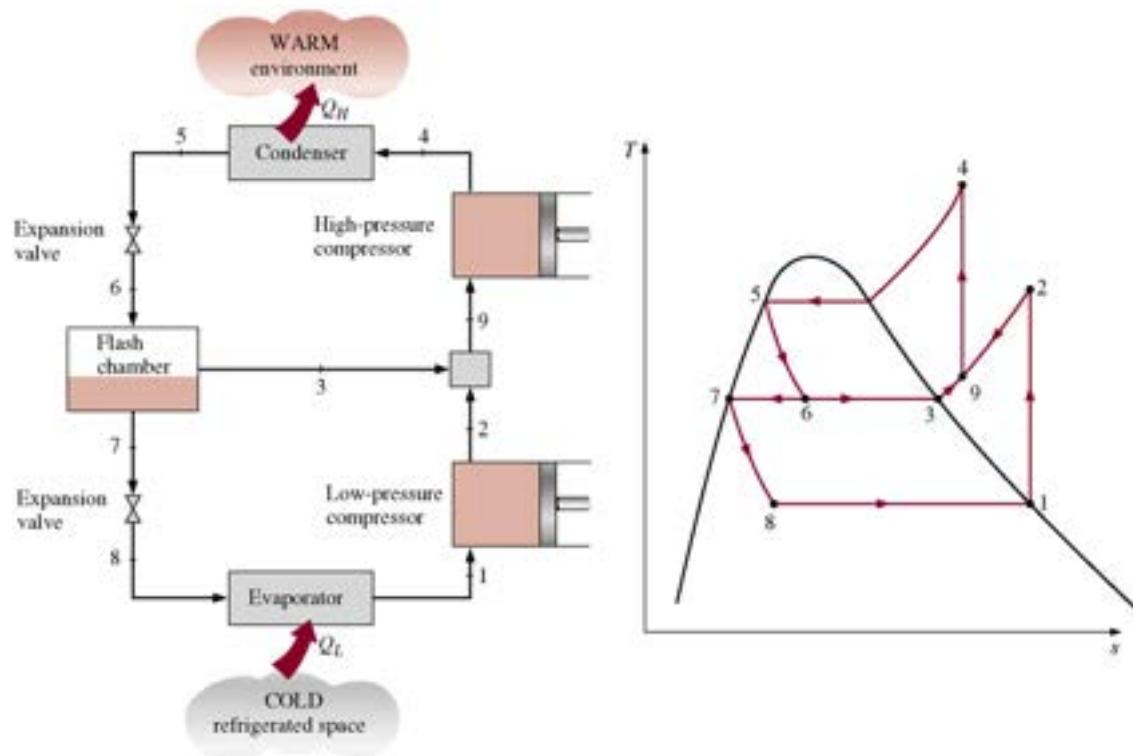
The Ts – diagram shows

- compressor work decreases
- amount of heat from the refrigerated space increases
- improves COP



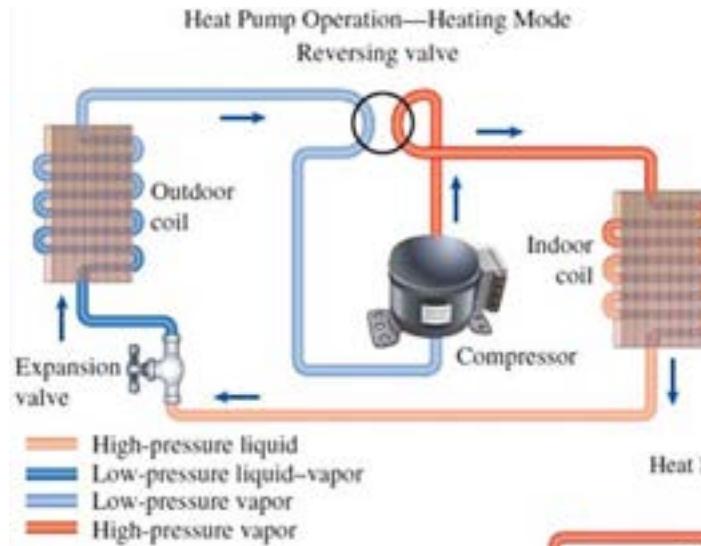
Multistage Compres. Refrigeration Systems

- When the fluid used throughout the refrigeration system is the same, the heat exchanger between the stages can be replaced by a mixing chamber since it has better heat transfer characteristics
- Liquid refrigerant condensed at high P expands in expansion valve (5 – 6)
- Part of the liquid vaporizes (saturated mixture in flash chamber)
- The saturated vapor (3) mixes with the superheated vapor (2) from comp.
- This is in essence a regeneration process
- This mixture enters the high P compressor (9)
- Sat. liquid (7) expands through a second valve into the evaporator and picks up heat from the refrigerated space
- Compressor work decreases

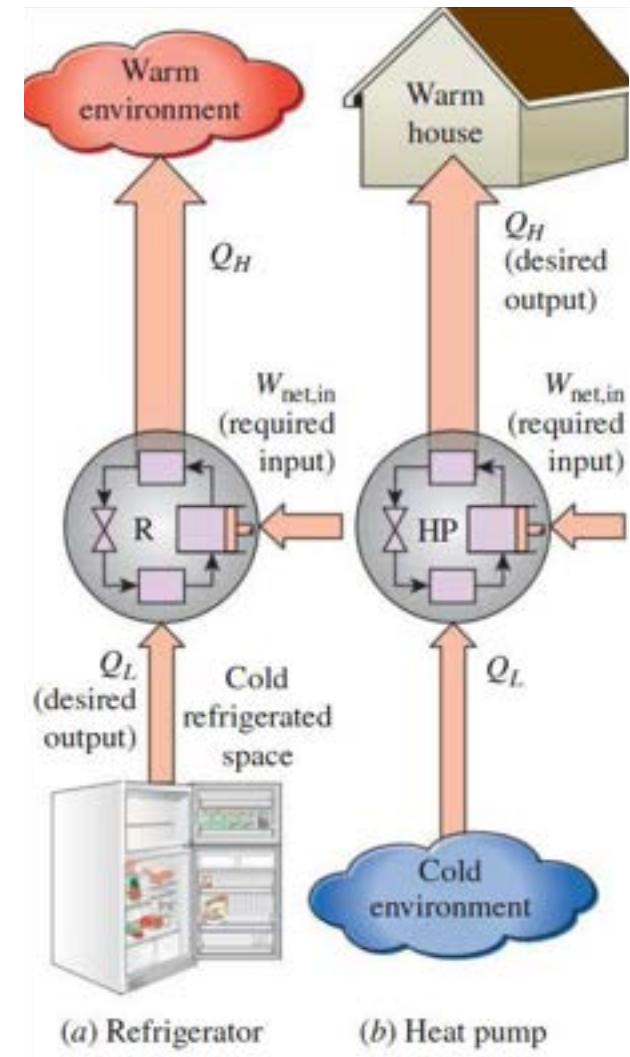
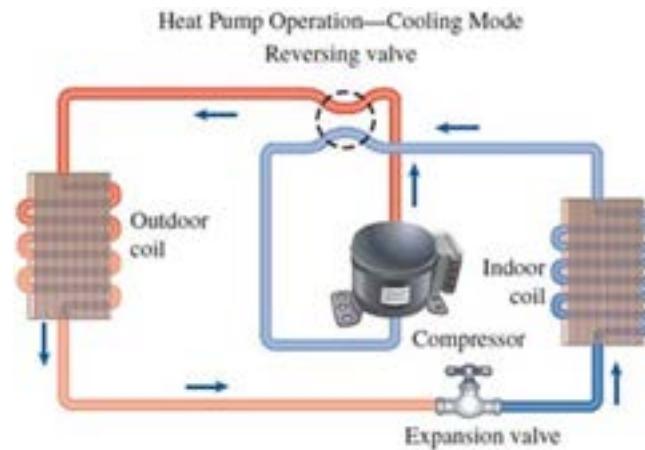


Air Conditioners and Heat Pumps

- The thermodynamic analysis of heat pumps and refrigeration systems is similar (except for the definition of the COP)
- Differences are in practical applications and different arrangement of the components

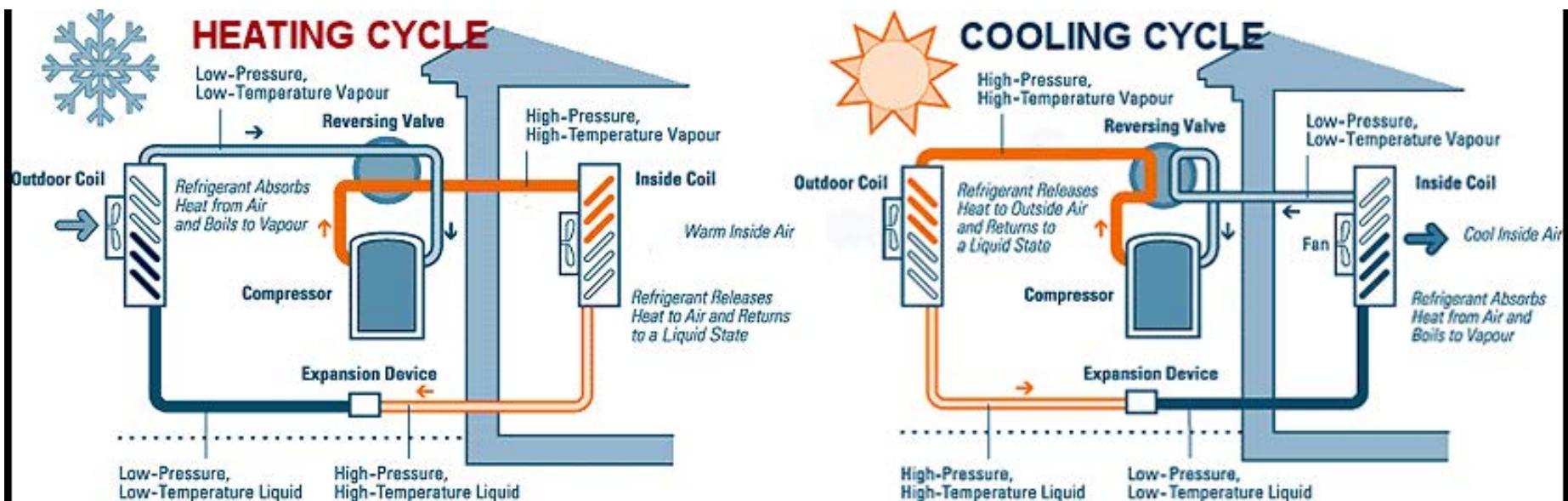


A heat pump can be used for heating in winter (top) and for cooling in summer (right)



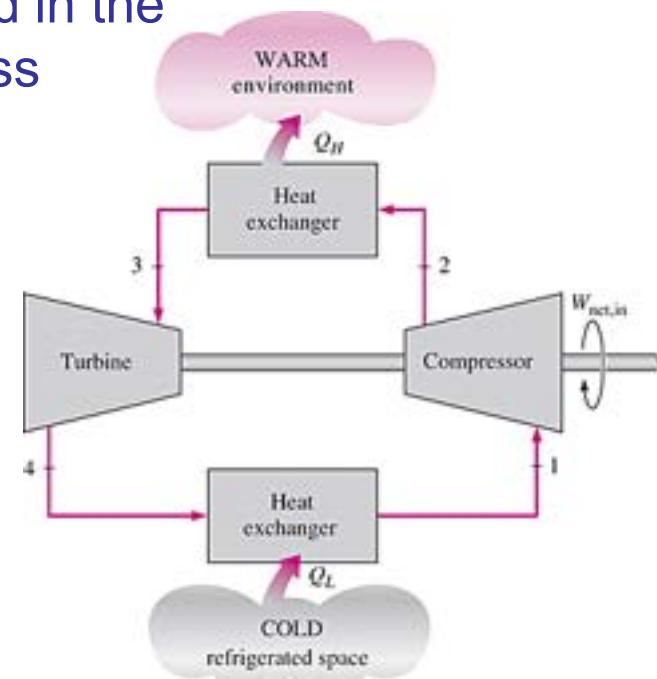
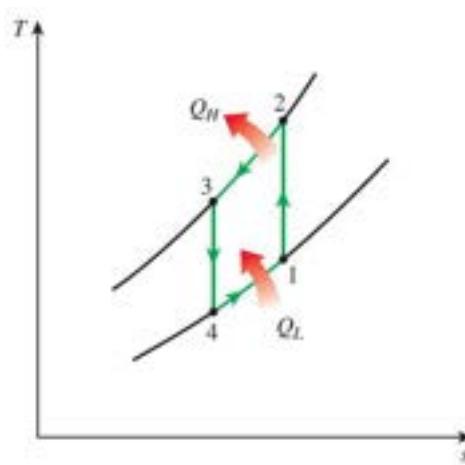
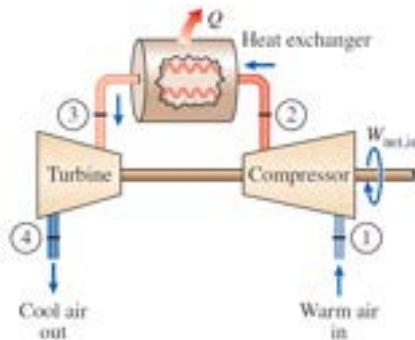
Air Conditioners and Heat Pumps

- Different arrangement of the components of the vapor – compression cycle for cooling and heating a house



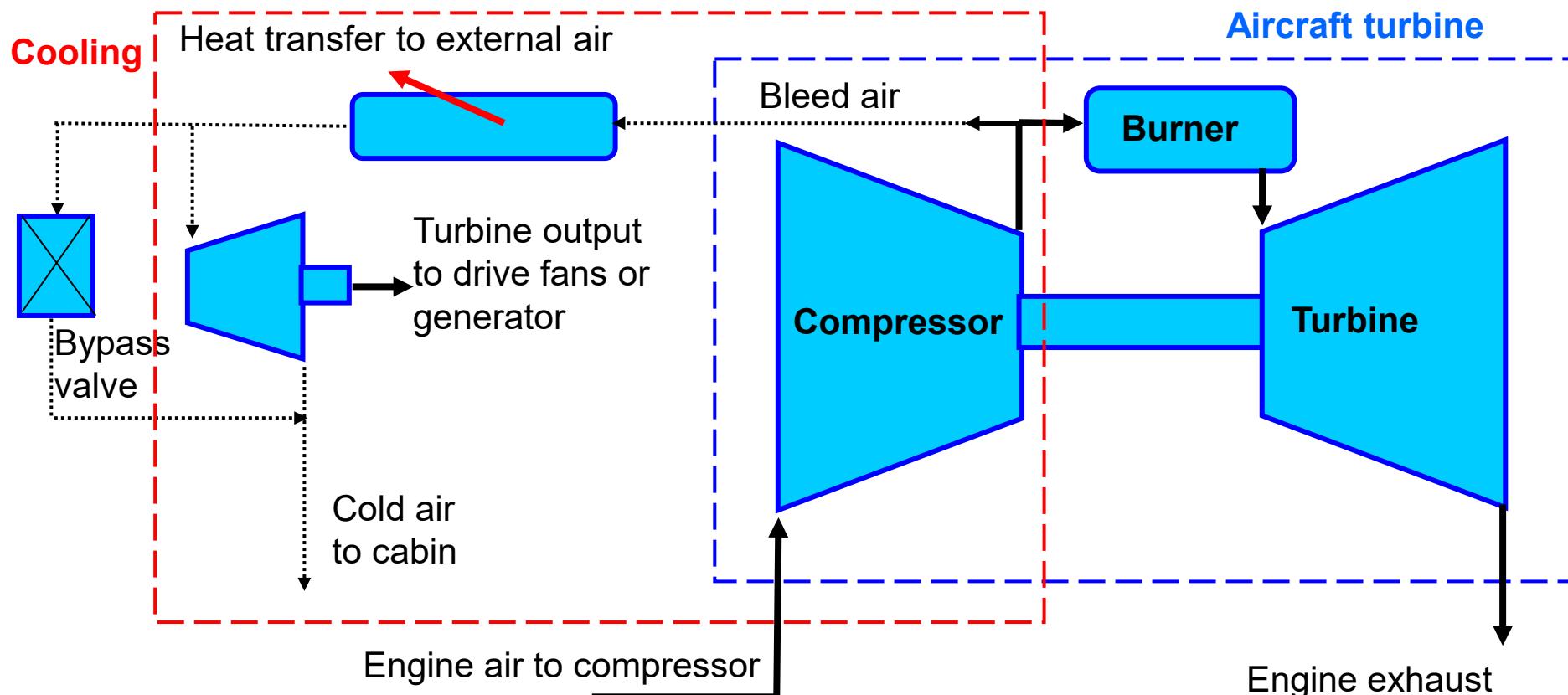
Gas Refrigeration Cycles

- The vapor - compression cycle is the most widely used however some other cooling cycles are used for special applications
 - Reverse Brayton cycle, the throttle valve is replaced by a turbine
 - In the ideal cycle it has isentropic expansion, $ds = 0$ instead of $dh = 0$
 - The turbine converts some work during the pressure decrease
 - Compressor requires more work than converted in the turbine → Still net work input is required, but less
- $$COP_{reverse\ Brayton} = \frac{q_{in,cold}}{w_{in,compressor} - w_{out,turbine}}$$
- $$= \frac{h_1 - h_4}{(h_2 - h_1) - (h_3 - h_4)}$$



Reverse Brayton Cycle for Aircraft Cooling

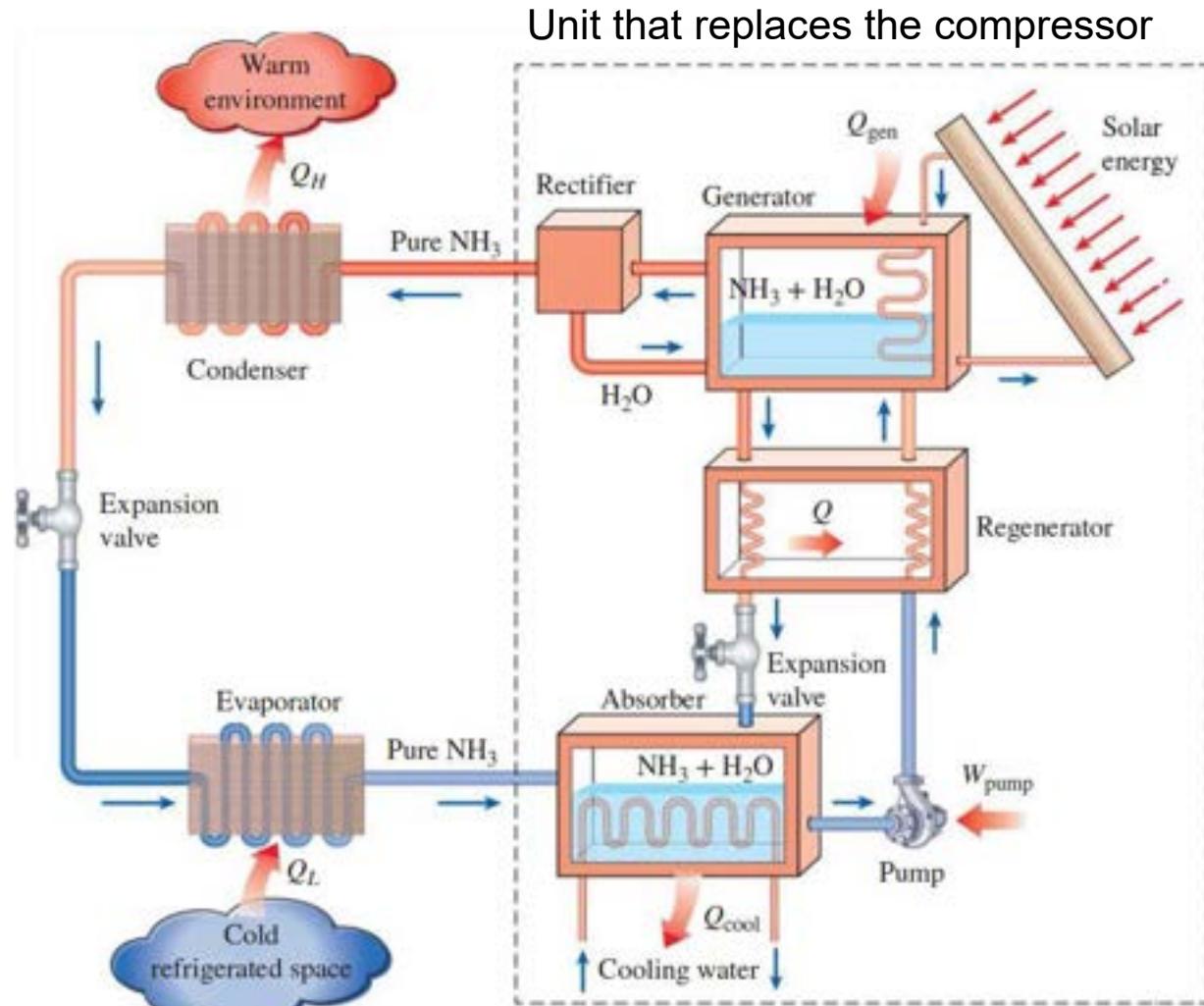
- Reverse Brayton cycle → Aircraft air-conditioning systems to cool aircraft cabins



- Compressor of Brayton cycle for the engine & the reversed Brayton cycle for cooling is the same

Absorption Refrigeration Cycle

- Absorption refrigeration cycle uses (waste) heat for cooling
- Absorption refrigeration can be used when there is a source of inexpensive thermal energy at a temperature of 100 to 200°C.
- Some examples include geothermal energy, solar energy, waste heat from co-generation or process steam plants.
- The compressor is replaced by a unit that uses heat to compress the refrigerant



Not part of the exam

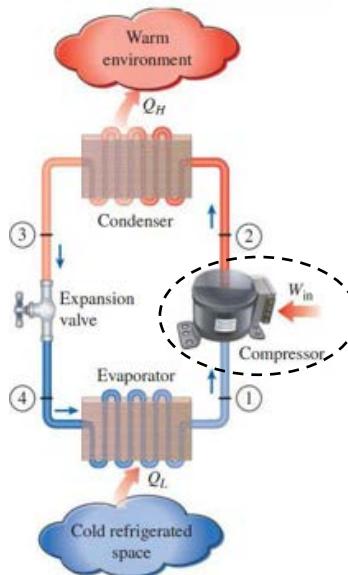
Absorption Refrigeration Cycle

- Absorption refrigeration systems (ARS) involve the absorption of a *refrigerant* by a *transport medium*, a two-component mixture.
- The most widely used system is the ammonia–water system, where ammonia (NH_3) serves as the refrigerant and water (H_2O) as the transport medium.
- Other systems include water–lithium bromide and water–lithium chloride systems, where water serves as the refrigerant. These systems are limited to applications such as A-C where the minimum temperature is above the freezing point of water.
- Compared with vapor-compression systems, ARS have one major advantage: A liquid is compressed instead of a vapor and as a result the work input is very small (on the order of one percent of the heat supplied to the generator) and often neglected in the cycle analysis.
- ARS are often classified as ***heat-driven systems***.
- ARS are much more expensive than the vapor-compression refrigeration systems. They are more complex and occupy more space, they are much less efficient thus requiring much larger cooling towers to reject the waste heat, and they are more difficult to service since they are less common.
- Therefore, ARS should be considered only when the unit cost of thermal energy is low and is projected to remain low relative to electricity.
- ARS are primarily used in large commercial and industrial installations.

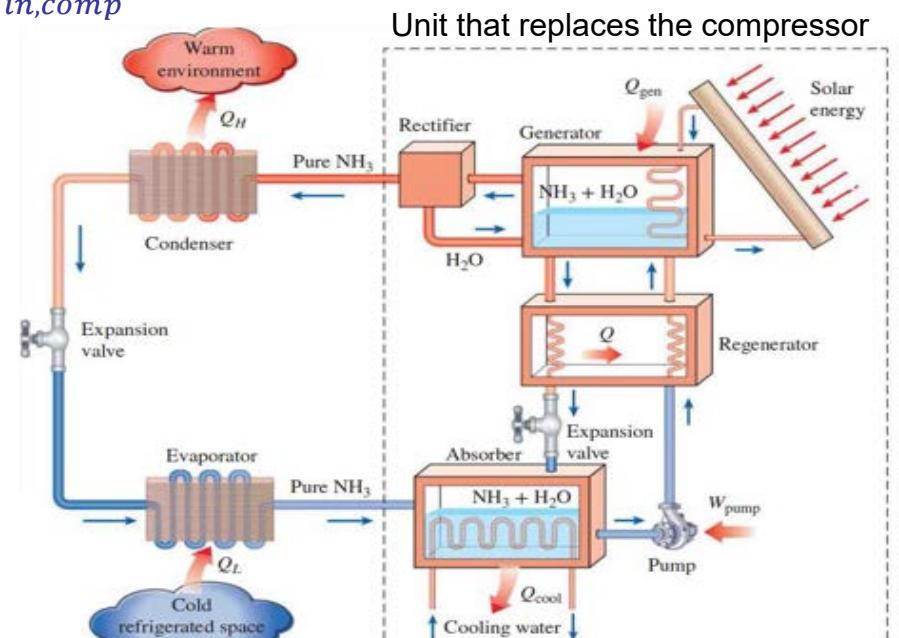
Not part of
the exam

Absorption Refrigeration Cycle

- Waste heat $q_{in,gen}$ heats the high pressure two component mixture
- The low boiling point refrigerant is vaporized and goes to the condenser from where it runs through the cooling cycle
- The high boiling point absorbent goes back to the absorber by the throttle valve
- After the cooling process the low boiling point refrigerant vapor is absorbed into the high boiling point absorbent in the absorber and the two-component mixture
- The liquid is pressurized by the pump and uses less power as a $W_{comp} \gg W_{pump}$
- COP defined as $COP_{absorption} = \frac{q_{in,evap}}{q_{in,gen} + w_{in,comp}}$
- $W_{in,pump}$ is small compared to $q_{in,gen}$



In an absorption cooling cycle the compressor of the vapor-compression cycle is replaced by a complicated unit using heat of low temperature to achieve the compression, this saves work input as a pump compresses a liquid, however the COP is lower, often $COP_{abs} < 1$ ((typically 0.7 – 0.8))



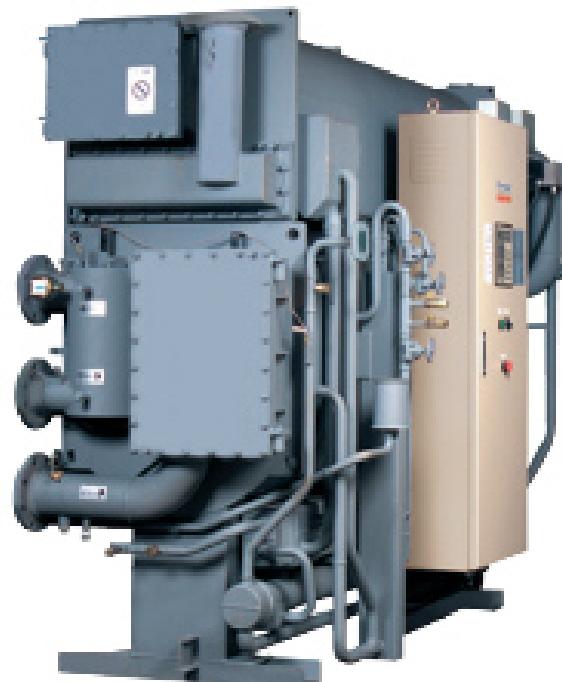
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Application Absorption Refrigeration System

- **Absorption refrigeration systems** can be applied where (waste) heat of sufficient temperature is available, heat of about 80 degree is needed
 - Waste heat from heat engine
 - Geothermal energy, solar energy, thermal sources
 - City heating delivering heat in winter can in summer be used for cooling via absorption cooling
 - Waste heat from production process in factories



<https://www.youtube.com/watch?v=nUW1OleNUrl>



Not part of the exam

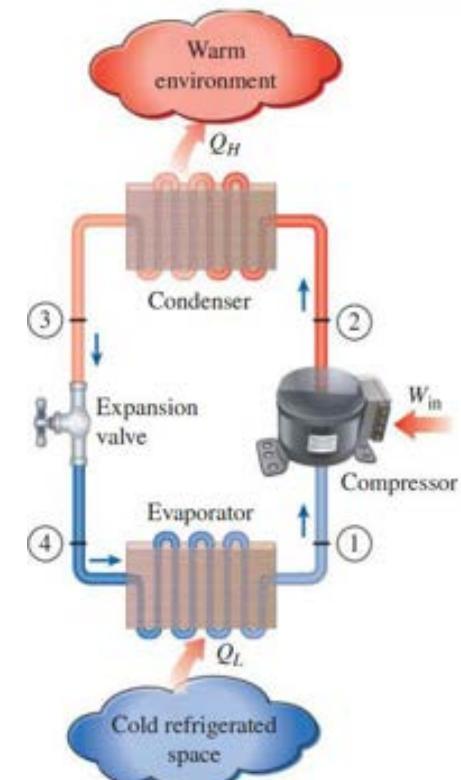
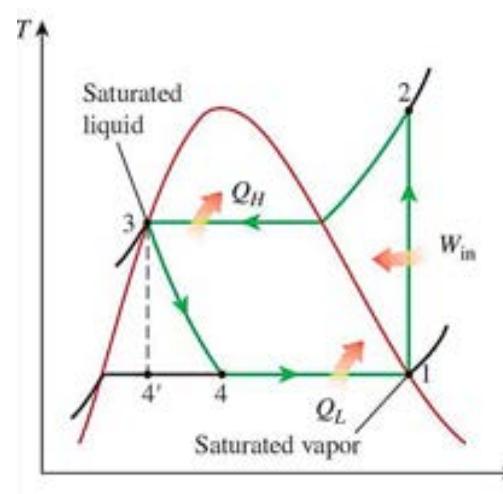
Bron: Carrier

Recapitulate Class 13

- Vapor – compression cycle, cycle that transports heat in the non – spontaneous direction using work
- Thermodynamically the cycle for cooling (refrigeration) is like the cycle for heating (heat pump)
- **Coefficient of performance, COP**

$$COP_{ref} = \frac{q_{in,cold}}{w_{in}} \quad \text{and} \quad COP_{heat\ pump} = \frac{q_{out,hot}}{w_{in}}$$

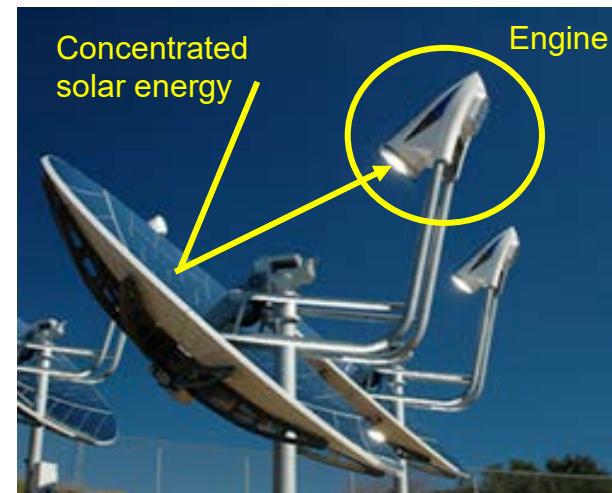
- Ideal and non - ideal vapor - compression cycle for cooling / heating
 - Reversed Rankine cycle with throttling valve in stead of turbine
(note: throttling $h_{in} = h_{uit}$)
- Reverse Brayton cycle
- Special cooling cycles



Vapor-compression cycle
and Ts -diagram

Next Class 14: Stirling, Otto & Diesel Engine

- The gas turbine cycle (Brayton cycle) uses gas as working fluid through the whole cycle (Class 10 & 11)
- Internal combustion engines, like Otto & Diesel engines also use gas as working fluid but these cycles are executed in a piston – cylinder device
- Stirling cycle
- Otto cycle
- Diesel cycle



Solar powered Stirling engine



Cutaway view of 4-Cylinder Gasoline Engine (Image Courtesy BMW)

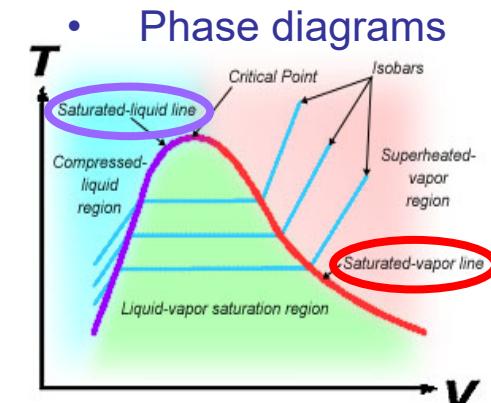
ThermoNet: Wiley



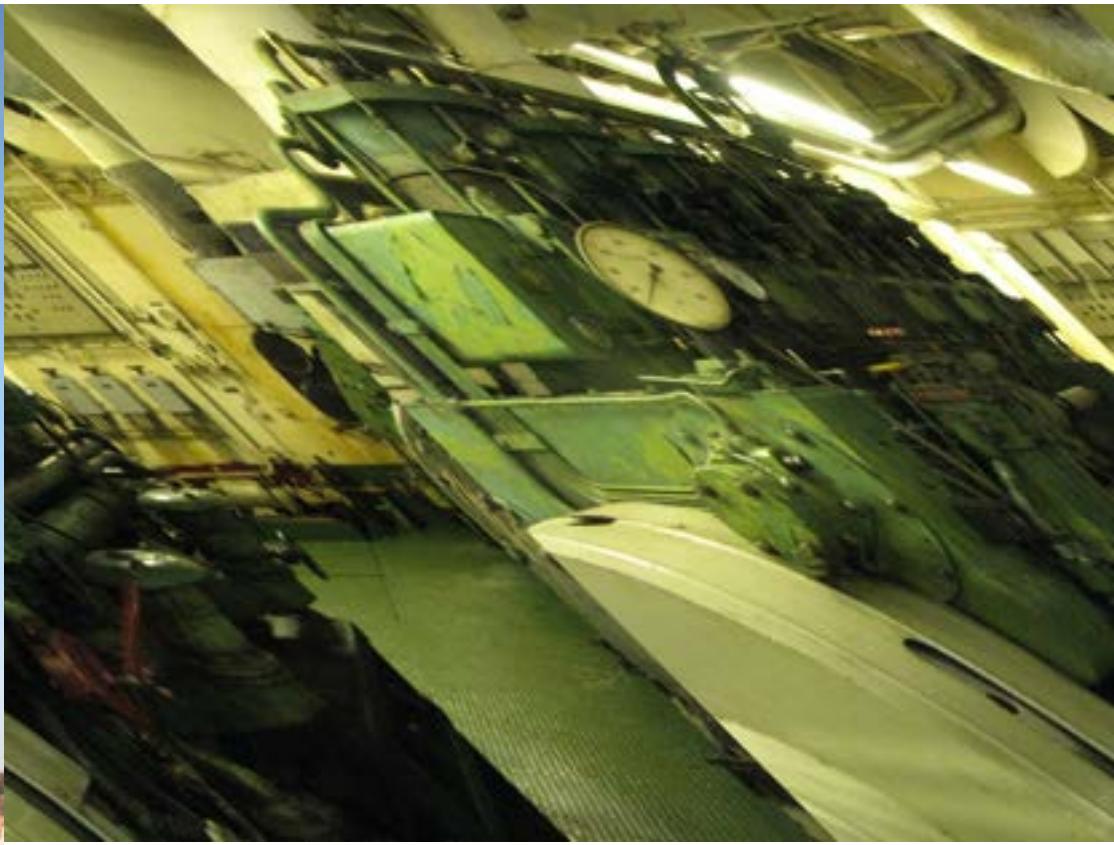
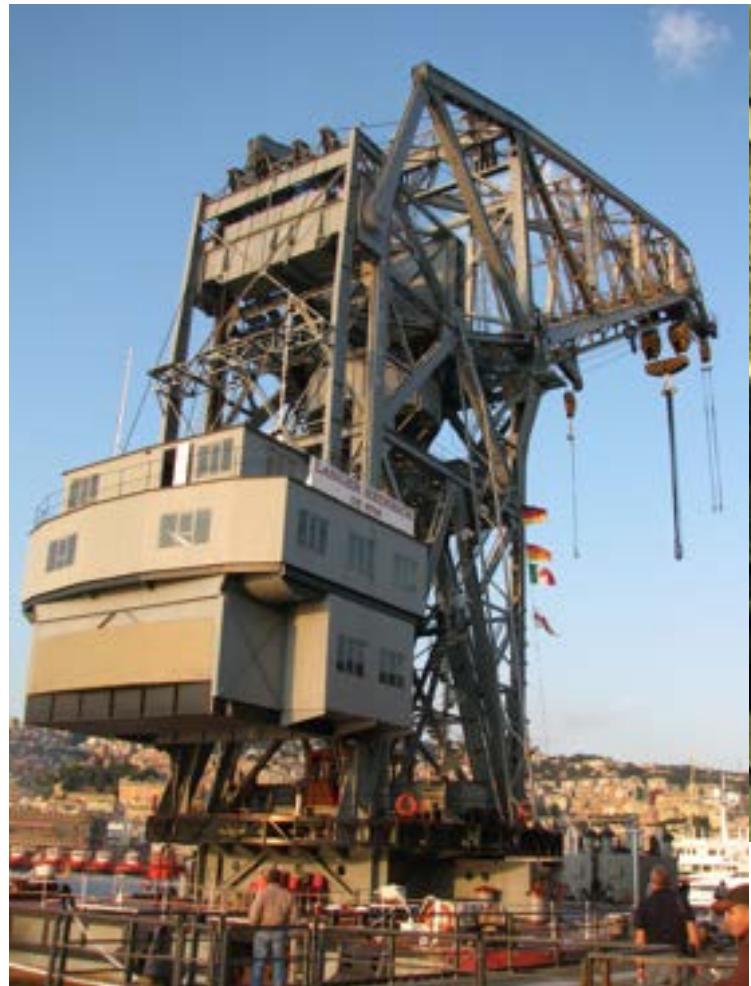
Diesel engine

Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal efficiency $\eta_{thermal} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Mixture fraction $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
- Ideal gas law $Pv = RT$, $c_p - c_v = R$
- For an ideal gas $du = c_v dT$ and $dh = c_p dT$
- Conservation of mass $m_{in} = m_{out}$, mass flow rate $\dot{m} = \rho v A$
- Conservation of energy, first law of thermodynamics
 - Closed system $du = \delta w - \delta q \rightarrow \Delta u = w - q$
 - 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 $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)
- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdP$
- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Isentropic processes ideal gas $Pv^k = \text{constant}$, $Tv^{k-1} = \text{constant}$, $P^{(k-1)/k}/T = \text{constant}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$ Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$



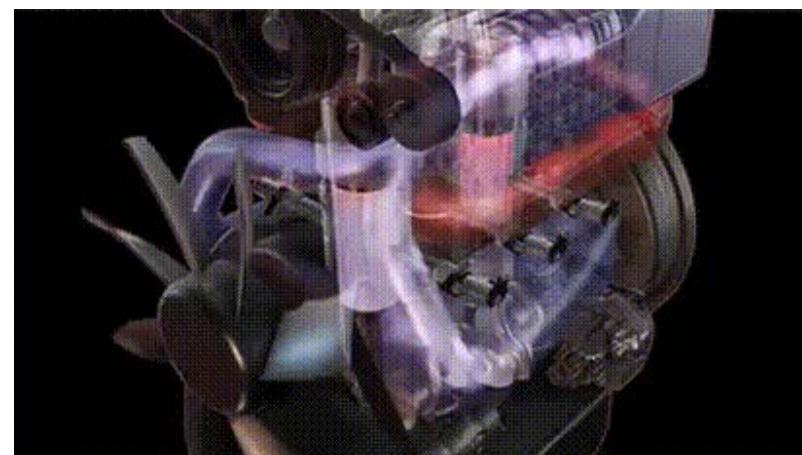
Class 14: Gas Power Cycles Reciprocating Combustion Engines



Diesel engine to power a crane (Langer Heinrich) on a platform for work on the sea

Content Class 14

- In Thermo 1 in module 2 we have introduced theory and tools to study thermodynamic systems that produce power or cold (class 1 – 6)
- We have seen vapor power cycles (Rankine cycle) that produce work using a working fluid that changes phase during the cycle (class 7, 8)
- We have seen gas turbine cycles (Brayton cycle) that produce power using gas through the whole cycle as the working fluid (class 10, 11)
- We have seen refrigeration cycles that use power to transport heat from cold to hot (class 13)
- Class 14 is about gas cycles pertaining to reciprocating engines
 - Open & closed cycles
 - Air standard cycle
 - Stirling cycle (video 18a)
 - Otto cycle (video 18a)
 - Diesel cycle (video 18b)



Open and Closed Gas Power Cycles

- **Gas power cycles** use gas as working fluid (WF) throughout the cycle
- **Closed cycle**
 - Working fluid completely sealed (not exchanged with environment)
 - External “Combustion” (EC), nuclear, geothermal, solar energy possible
 - Helium common working fluid
 - Light atoms → fast motion
→ efficient heat transfer
 - Non-flammable (unlike H₂)
 - Low C_P → added heat efficiently converted into higher pressure
 - Example: **Stirling cycle**



A solar powered Stirling engine is an example of a closed gas power cycle

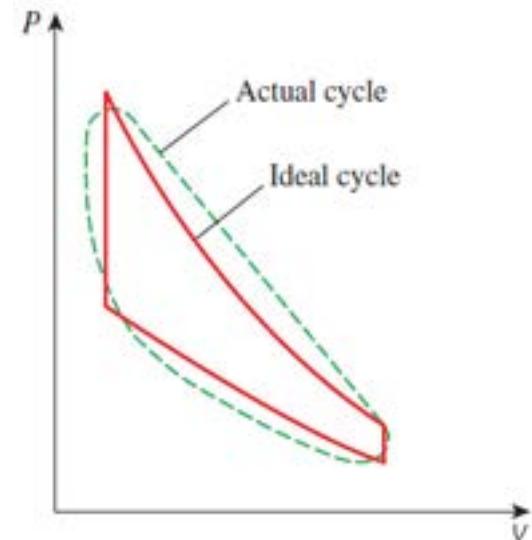
Open and Closed Gas Power Cycles

- **Gas power cycles** use gas as working fluid (WF) throughout the cycle
- **Open cycle**
 - Working fluid exchanged with environment (intake & exhaust)
 - Internal Combustion (IC) inside the system
 - Working fluid: Air + Fuel → Air + Combustion Products
 - Examples:
 - Otto
 - Diesel
 - Brayton (Gas Turbine)



The Air Standard Cycle

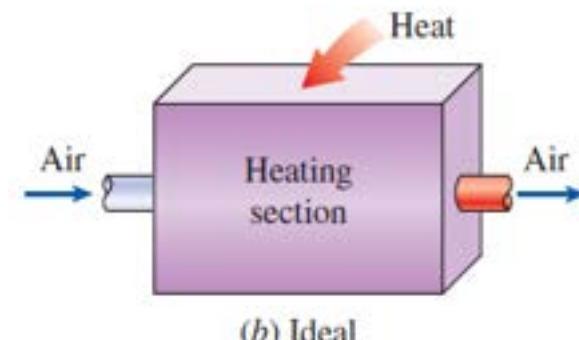
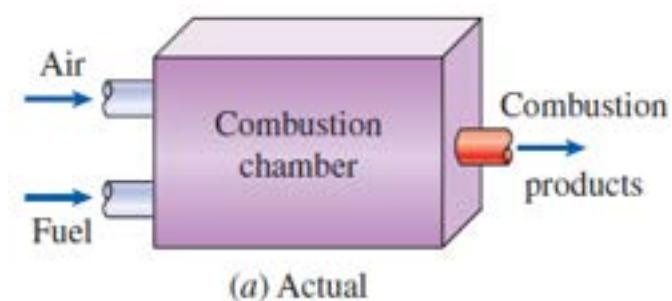
- The **air standard cycle** is a simplifying approximation of the real gas cycles
- This approximation is
 - Good for comparing trends
 - Good for comparing systems
 - Not good for detailed analyses
- Another assumption
 - Constant specific heats: **Ideal air standard cycle**
 - Constant specific heats at room temperature 25°C: **Cold ideal air standard cycle**



The analysis of many complex processes can be reduced to a manageable level by utilizing some idealizations

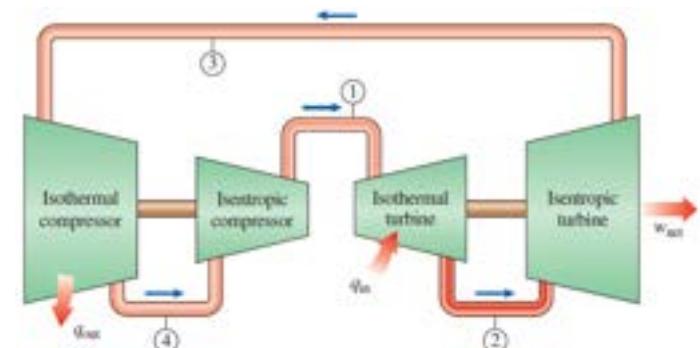
The Air Standard Cycle

- Assumptions for the air standard cycle
- The working fluid is dry air, which continuously circulates in a closed loop and always behaves as an ideal gas ($Pv=RT$) (consequently fuel and combustion products are neglected)
- All the processes that make up the cycle are internally reversible
- The combustion process is replaced by a heat-addition process from an external source
- The intake and exhaust processes are replaced by a heat transfer processes to the surroundings

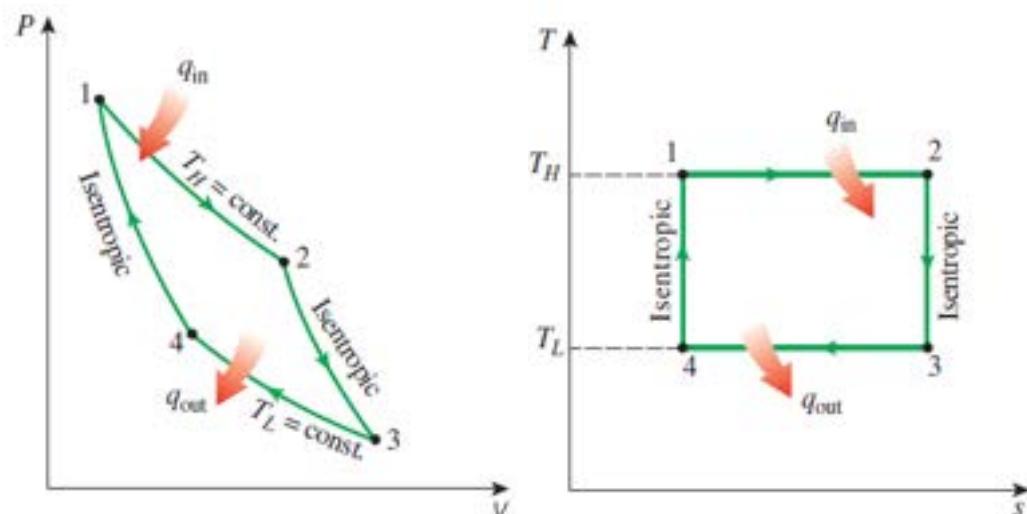


Recap Carnot Cycle

- The **Carnot cycle** is composed of four totally reversible processes:
 - isothermal heat addition
 - isentropic expansion
 - isothermal heat rejection
 - isentropic compression
- Thermal efficiency: $\eta_{CarnotT} = 1 - \frac{T_{COLD}}{T_{HOT}}$
- For both ideal and actual cycles, the thermal efficiency increases with an increase in the average temperature at which heat is supplied to the system or with a decrease in the average temperature at which heat is rejected from the system

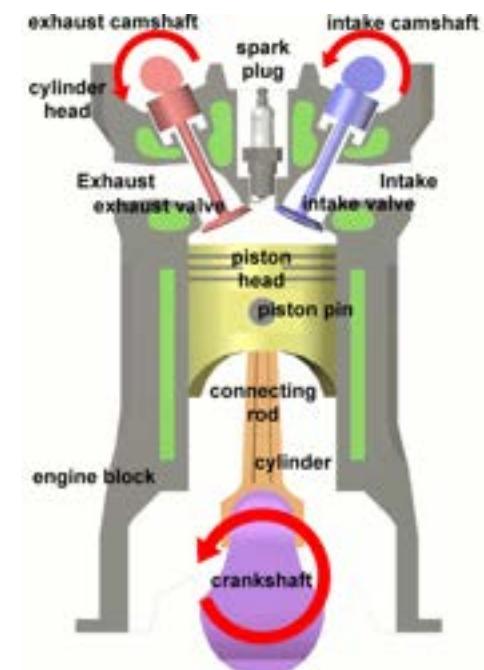


A steady-flow Carnot engine



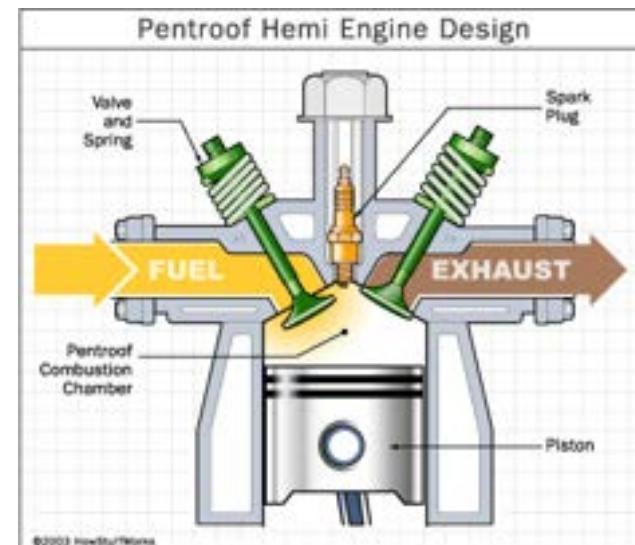
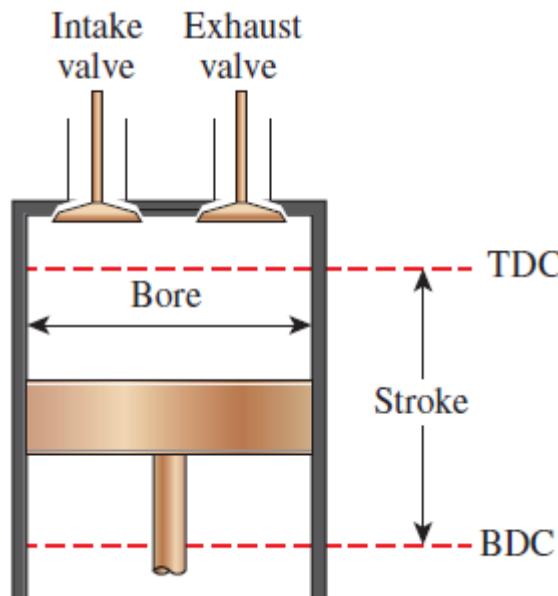
Reciprocating Engines

- A reciprocating engine, also known as a piston engine, is typically a heat engine that uses one or more reciprocating pistons to convert pressure into a rotating motion, the main types are:
 - the internal combustion engine, used extensively in motor vehicles
 - the steam engine, the mainstay of the industrial revolution
 - the Stirling engine, a niche application
- The last two are external combustion engines, heat is added from an external heat sources
- Internal combustion engines are classified in
 - spark-ignition (SI) engines, where the spark plug initiates the combustion (gasoline or petrol engines working on an Otto cycle)
 - compression-ignition (CI) engine, where the air within the cylinder is compressed, thus heating it, so that the heated air ignites fuel that is injected then or earlier (Diesel engines)
- The process can be executed in 2 or 4 strokes



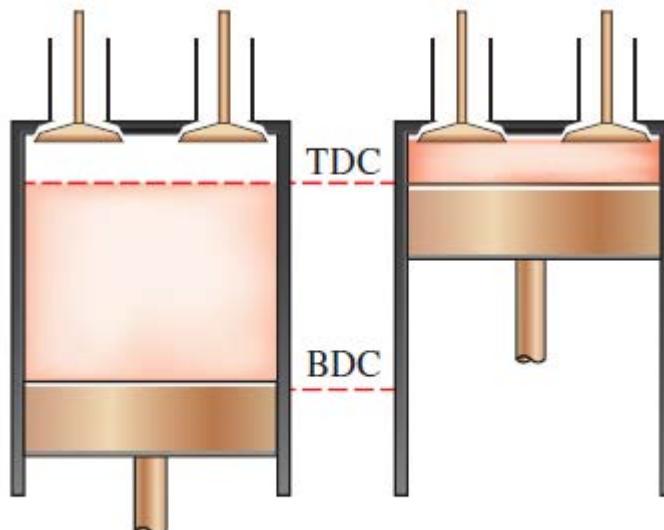
Nomenclature Reciprocating Cycles

- Bore = cylinder diameter
- BDC = Bottom Dead Center, lowest position cylinder
- TDC = Top Dead Center, highest position cylinder
- Stroke = distance between TDC and BDC



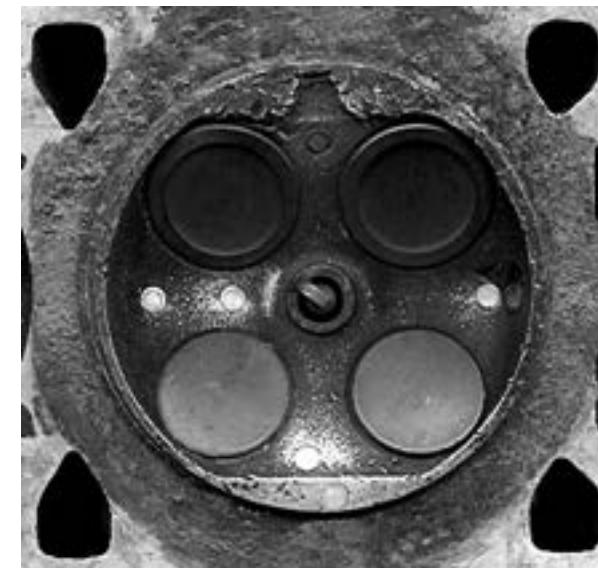
Nomenclature Reciprocating Cycles

- Swept or displacement volume = volume refreshed during a stroke
- Clearance volume = volume TDC position = minimum volume
- Maximum volume = clearance volume + swept volume



(a) Displacement
volume

(b) Clearance
volume



Cylinder Head Rover Twin Cam 1.6l

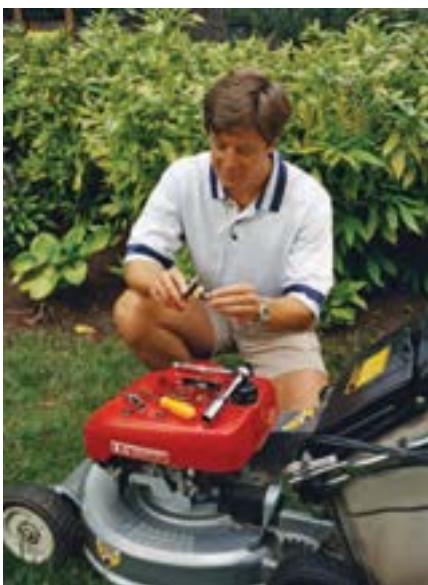
4 stroke internal combustion engines

- A four-stroke engine is an internal combustion engine in which the piston completes four separate strokes while turning the crankshaft. A stroke refers to the full travel of the piston along the cylinder, in either direction. The four separate strokes are:
- **Intake:** This stroke of the piston begins at TDC and ends at BDC, the intake valve must be in the open position while the piston pulls an air-fuel mixture into the cylinder by producing vacuum pressure into the cylinder through its downward motion. The piston is moving down as air is being sucked in by the downward motion against the piston.
- **Compression:** This stroke begins at BDC, or just at the end of the intake stroke, and ends at TDC, the piston compresses the air-fuel mixture in preparation for ignition. Both the intake and exhaust valves are closed during this stage.
- **Combustion:** This is the start of the second revolution of the four stroke cycle. At this point the crankshaft has completed a full 360 degree revolution. While the piston is at TDC, the compressed air-fuel mixture is ignited, forcefully returning the piston to BDC. This stroke produces mechanical work from the engine to turn the crankshaft.
- **Exhaust:** During the exhaust stroke, the piston, once again, returns from BDC to TDC while the exhaust valve is open. This action expels the spent air-fuel mixture through the exhaust valve.

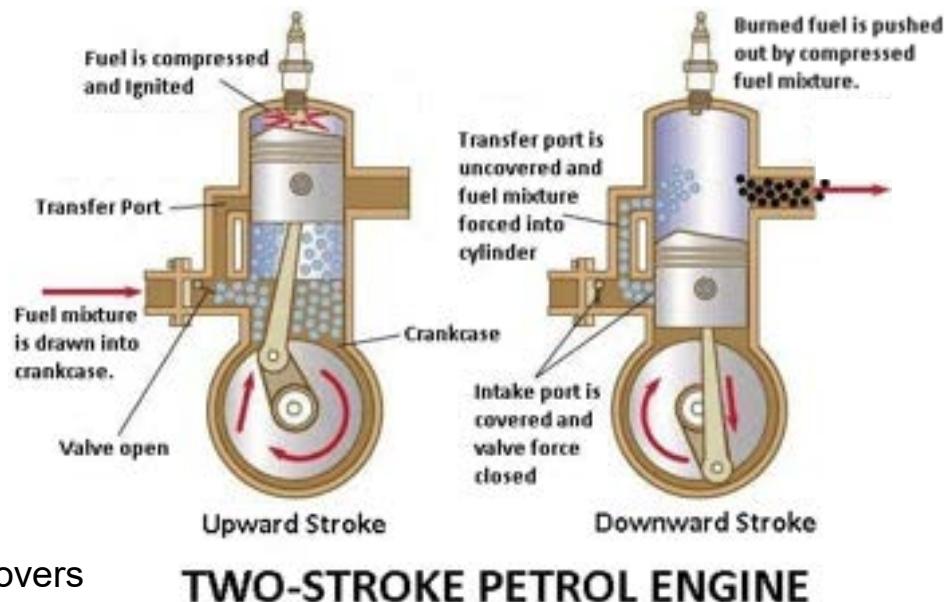


2 stroke internal combustion engines

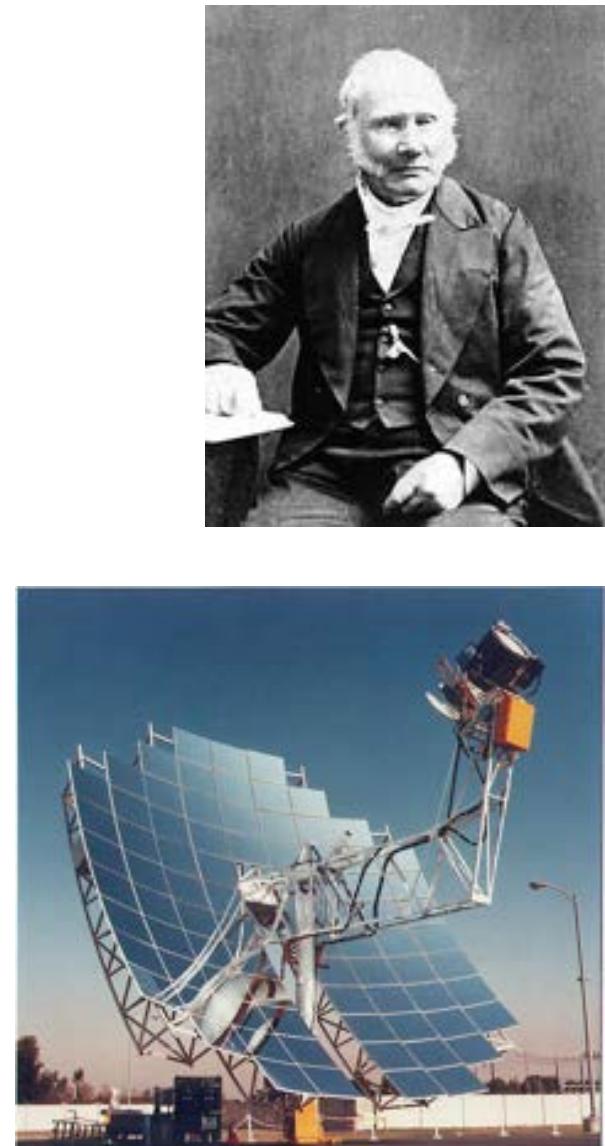
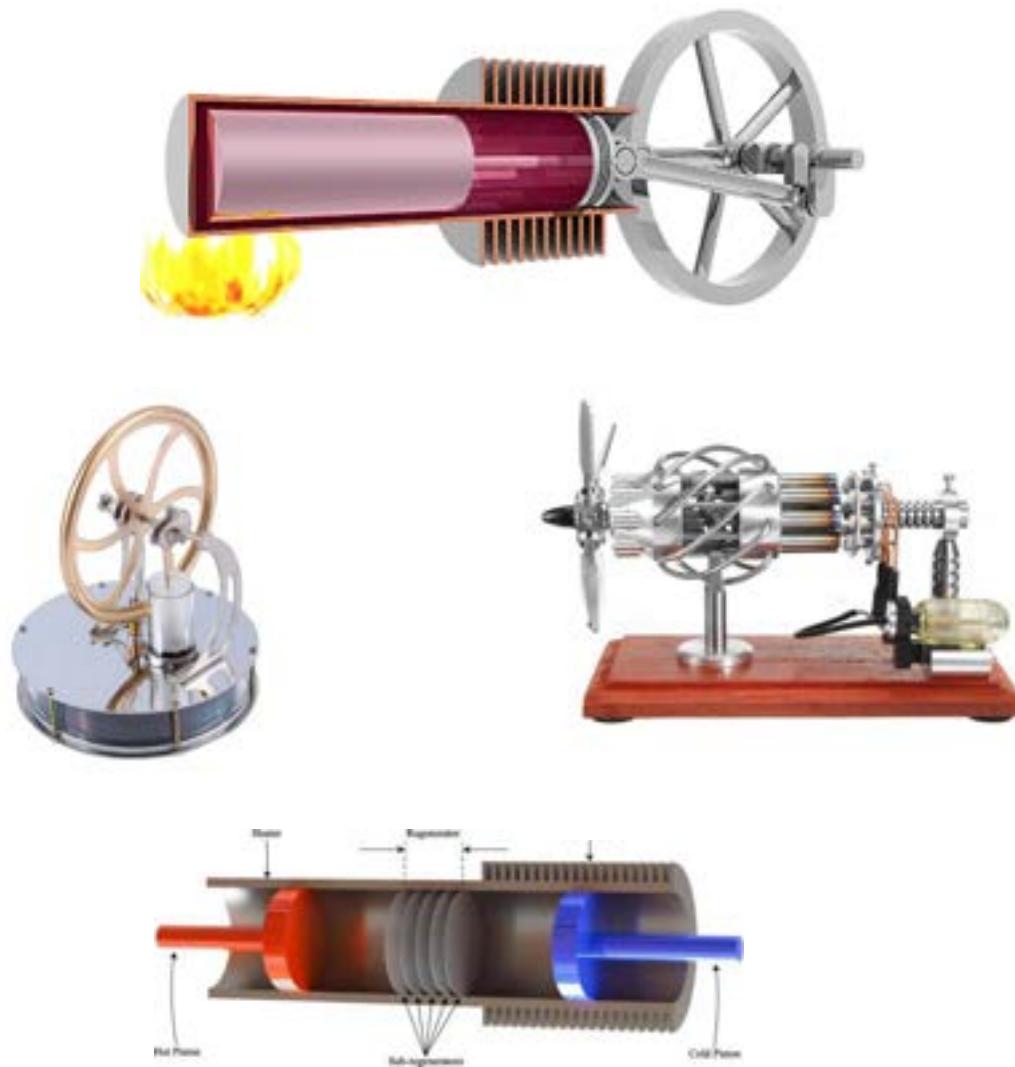
- A two-stroke engine is a type of internal combustion engine that completes a power cycle with two strokes (up and down movements) of the piston during only one crankshaft revolution
- This is in contrast to a "four-stroke engine", which requires four strokes of the piston to complete a power cycle during two crankshaft revolutions. In a two-stroke engine, the end of the combustion stroke and the beginning of the compression stroke happen simultaneously, with the intake and exhaust (or scavenging) functions occurring at the same time
- The two-stroke engines are generally less efficient than their four-stroke counterparts but they are relatively simple and inexpensive, and they have high power-to-weight and power-to-volume ratios



Two stroke engines
are commonly used in
motorcycles and lawn movers



The Stirling Cycle

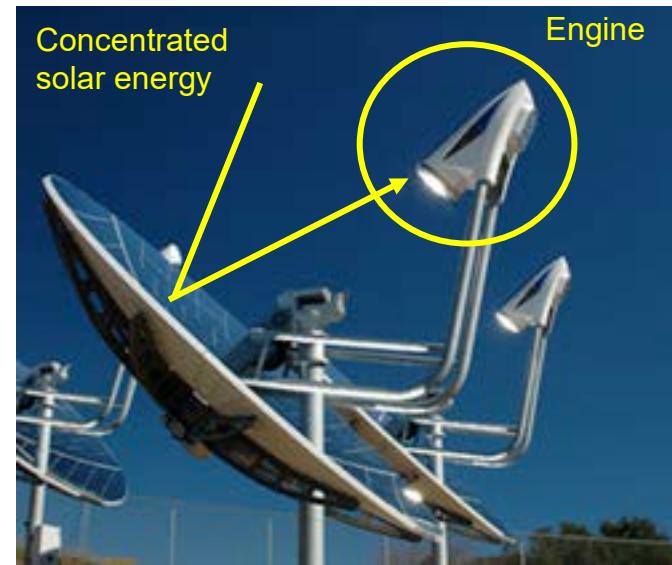


The Stirling Cycle

- The Stirling cycle is the oldest gas cycle
- It is developed by Robert Stirling in 1816
- It is a closed cycle → external heating
- It consists of 2 isochoric processes and 2 isothermal processes
- It uses a regenerator to recover heat from the exhaust gasses
- It is very efficiency, as the processes are reversible, in the ideal case its efficiency is the Carnot efficiency

$$\eta_{Stirling,rev} = \eta_{CarnotT} = 1 - \frac{T_{COLD}}{T_{HOT}}$$

- However, it is difficult to manufacture in practice
- There are different configurations, for example one or two cylinders



Solar powered Stirling engine



Robert Stirling

Principle of the Stirling Cycle

1 → 2 Isothermal expansion

2 → 3 Isochoric heat rejection

3 → 4 Isothermal compression

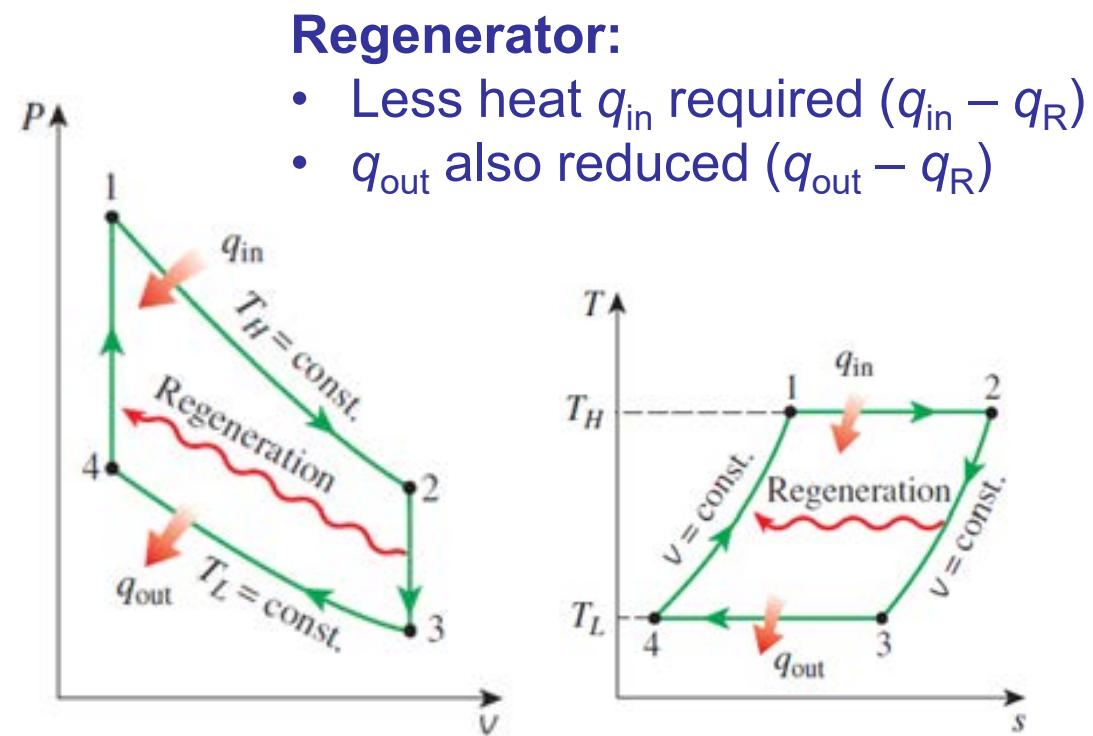
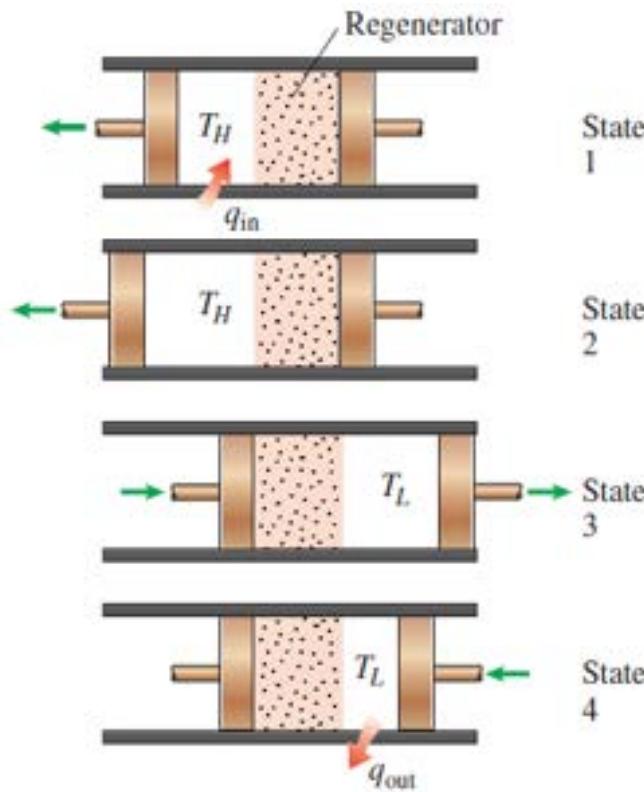
4 → 1 Isochoric heat addition

(heat addition from external source)

(internal heat transfer from the working fluid to the regenerator)

(heat rejection to the external sink)

(internal heat transfer from the regenerator back to the working fluid)

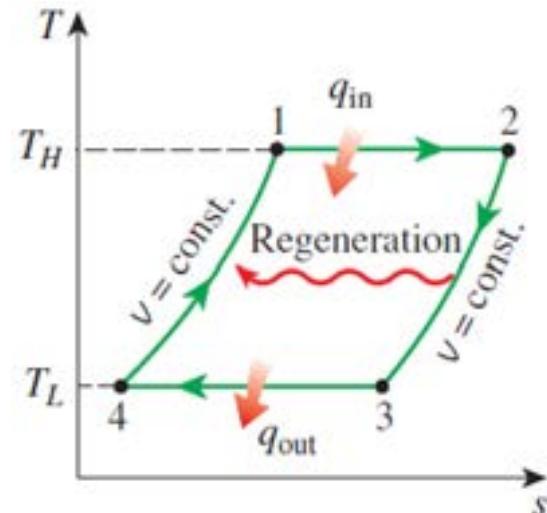


Regenerator:

- Less heat q_{in} required ($q_{in} - q_R$)
- q_{out} also reduced ($q_{out} - q_R$)

Stirling Cycle Analysis

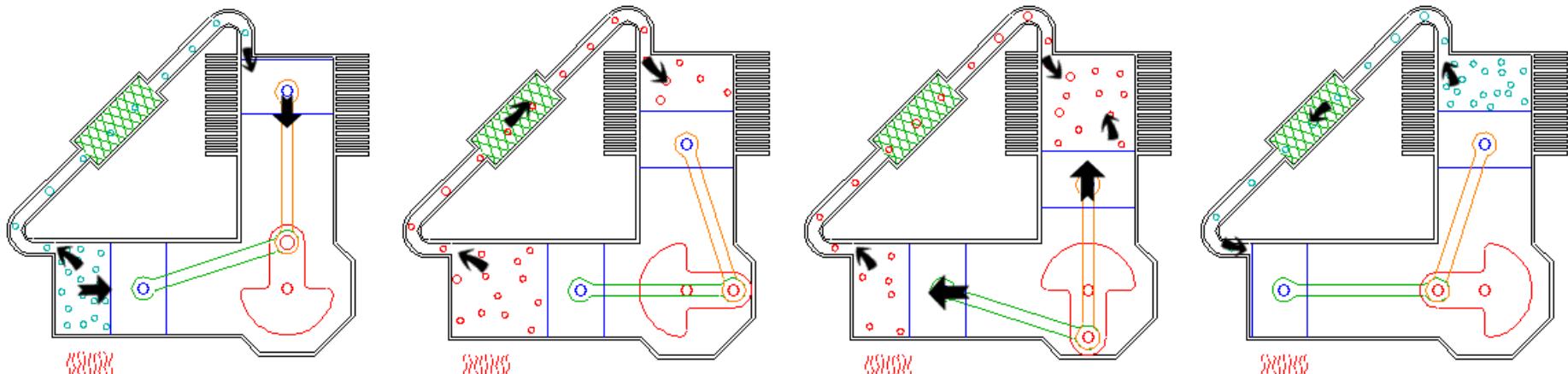
- Compression ratio: $r_V = v_{max}/v_{min} = v_2/v_1$
- Ideal gas: $Pv = RT$
- Regeneration
 - Use waste heat from $2 \rightarrow 3$ as input for $4 \rightarrow 1$
 - Reduces q_{IN} and q_{OUT} by same amount q_R
 - Increases the efficiency: $1 - \frac{q_{out}-q_R}{q_{in}-q_R} = \frac{q_{in}-q_{out}}{q_{in}-q_R}$



Process	q	w	Const Prop	Other Relations
$1 \rightarrow 2$	q_{IN}	w_{OUT}	T ($T_1 = T_2$)	$q_{IN} = w_{OUT}$ and $\delta w_{OUT} = Pdv$
$2 \rightarrow 3$	$q_{REGEN,OUT}$	0	v ($v_2 = v_3$)	$q_{REGEN,OUT} = q_{REGEN,IN}$
$3 \rightarrow 4$	q_{OUT}	w_{IN}	T ($T_3 = T_4$)	$q_{OUT} = w_{IN}$ and $\delta w_{IN} = - Pdv$
$4 \rightarrow 1$	$q_{REGEN,IN}$	0	v ($v_4 = v_1$)	-

Two Cylinder Stirling Engine

- The Stirling is a very simple engine, and was often billed as a safe alternative to steam, since there's no risk of a boiler explosion.
- It enjoyed some success in industrial applications, and also in small appliances like fans and water pumps, but it was eclipsed by the advent of inexpensive electric motors
- However, because it can run on any source of heat, it now holds promise for alternative fuel engines, solar power, geothermal power, etcetera
- Stirling engines feature a completely closed system in which the working gas (usually air but sometimes helium or hydrogen) is alternately heated and cooled by shifting the gas to different temperature locations within the system
- In the two-cylinder (or *alpha configured*) Stirling, one cylinder is kept hot while the other is kept cool. In this illustration, the lower-left cylinder is heated by burning fuel. The other cylinder is kept cool by air circulating through a heat sink (a.k.a. cooling fins). The Stirling cycle can be thought of as four different phases: expansion, transfer, contraction, and transfer



1: Expansion

Most of the gas in the system has just been driven into the hot cylinder. The gas heats and expands driving both pistons inward.

Not for the exam

2: Transfer

The gas has expanded (about 3 times in this example). Most of the gas (about 2/3) is still located in the hot cylinder. Flywheel momentum carries the crankshaft the next 90 degrees, transferring the bulk of the gas to the cool cylinder.

3: Contraction

The majority of the expanded gas has shifted to the cool cylinder. It cools and contracts, drawing both pistons outward.

4: Transfer

The contracted gas is still located in the cool cylinder. Flywheel momentum carries the crank another 90 degrees, transferring the gas to back to the hot cylinder to complete the cycle.

An animation can be found on: <http://www.animatedengines.com/vstirling.html>

Single Cylinder Stirling Engine

- This type of Stirling engine, known as the beta configuration, features just one cylinder with a hot end and a cool end.
- The working gas is transferred from one end of the cylinder to the other by a device called a displacer (illustrated in blue).
- The displacer resembles a large piston, except that it has a smaller diameter than the cylinder, thus its motion does not change the volume of gas in the cylinder—it merely transfers the gas around within the cylinder.
- The same four phases of the Stirling cycle are at work in this engine

1: Expansion

Most of the gas in the system has just been driven to the hot end of the cylinder. The gas heats and expands, driving the piston outward.

2: Transfer

The gas has expanded. Most of the gas is still located in the hot end of the cylinder. Flywheel momentum carries the crankshaft the next quarter turn. The bulk of the gas is transferred around the displacer to the cool end of the cylinder.

3: Contraction

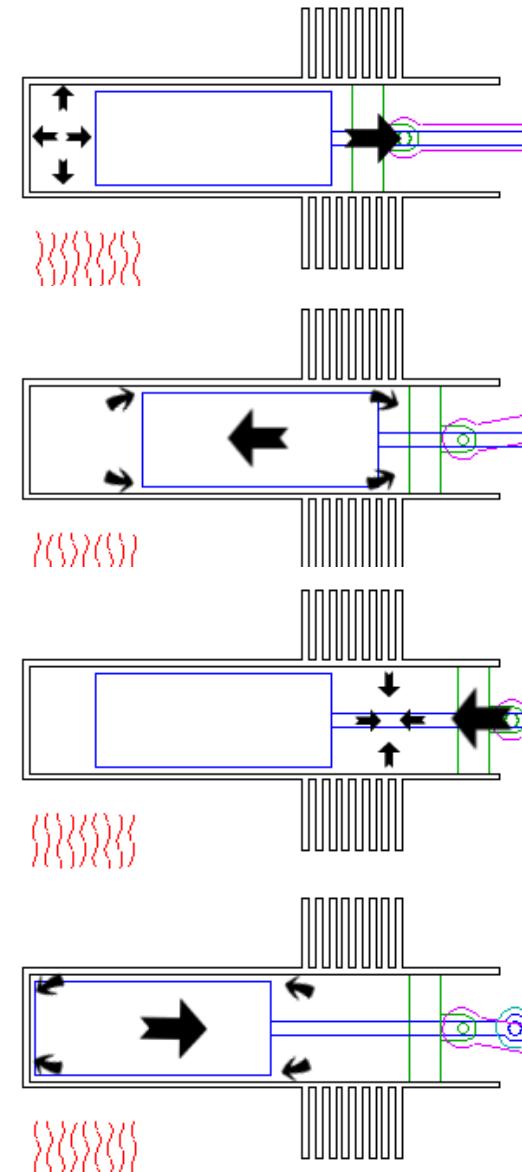
The majority of the expanded gas has shifted to the cool end. The gas cools and contracts, drawing the piston inward.

4: Transfer

The contracted gas is still located near the cool end of the cylinder. Flywheel momentum carries the crank another quarter turn, moving the displacer and transferring the bulk of the gas back to the hot end of the cylinder

An animation can be found on: <http://www.animatedengines.com/stirling.html>

Not for the exam



The Otto Cycle



Nicolaus Otto & his 1876 four cycle engine



The Otto Cycle

- **The Otto cycle**

- It is an idealization of the internal combustion gasoline engine cycle developed by Nikolaus August Otto (around 1878)
- It is executed in a reciprocating piston-cylinder device
- In practice it is an open cycle gas powered internal combustion engine, however it is modeled as a closed cycle
- It consists of 2 constant volume and 2 constant entropy processes
- The combustion starts using spark ignition
- It can be a 2 or 4 stroke process

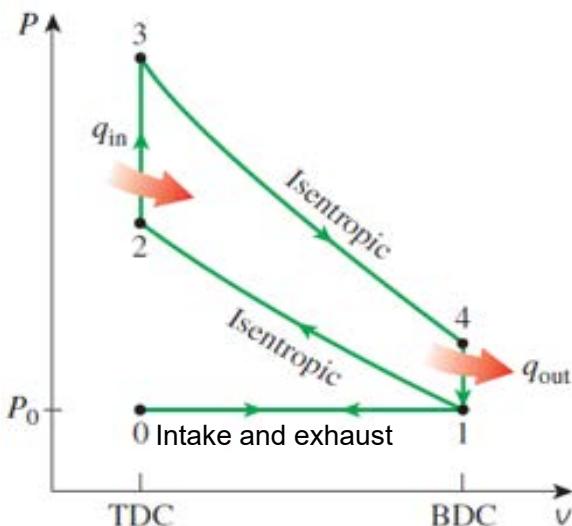


Cutaway view of 4-Cylinder Gasoline Engine (Image Courtesy BMW)

Thermopjet: Wiley

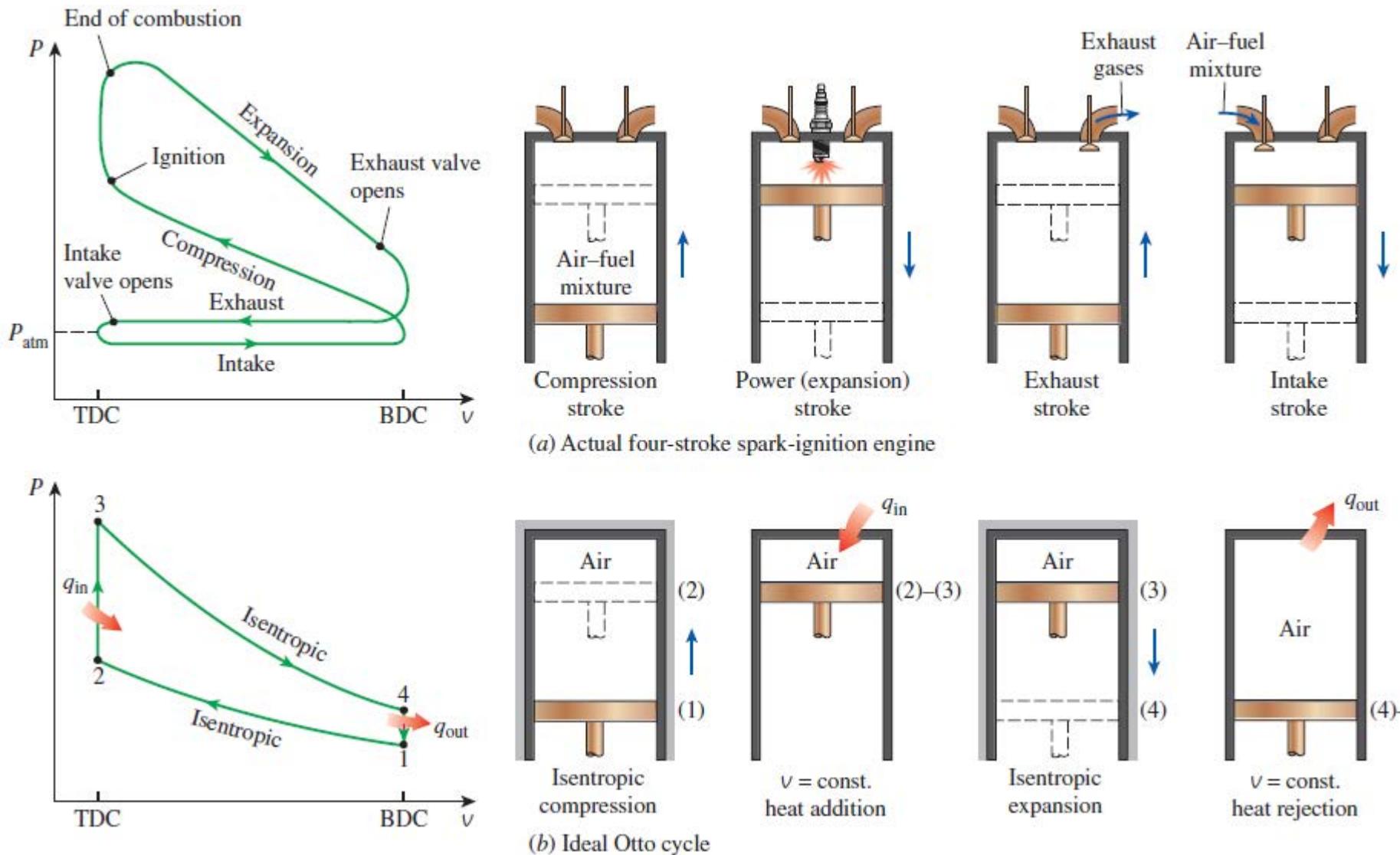
Principle of the Otto Cycle

- **Stroke 1, intake**
 - $0 \rightarrow 1$ inlet fresh air
- **Stroke 2, compression**
 - $1 \rightarrow 2$ isentropic compression (w_{in})
 - $2 \rightarrow 3$ isochoric heat addition (q_{in})
- **Stroke 3, combustion**
 - $3 \rightarrow 4$ isentropic expansion (w_{out})
 - $4 \rightarrow 1$ isochoric heat rejection (q_{out})
- **Stroke 4, exhaust**
 - $1 \rightarrow 0$ outlet air-fuel mixture



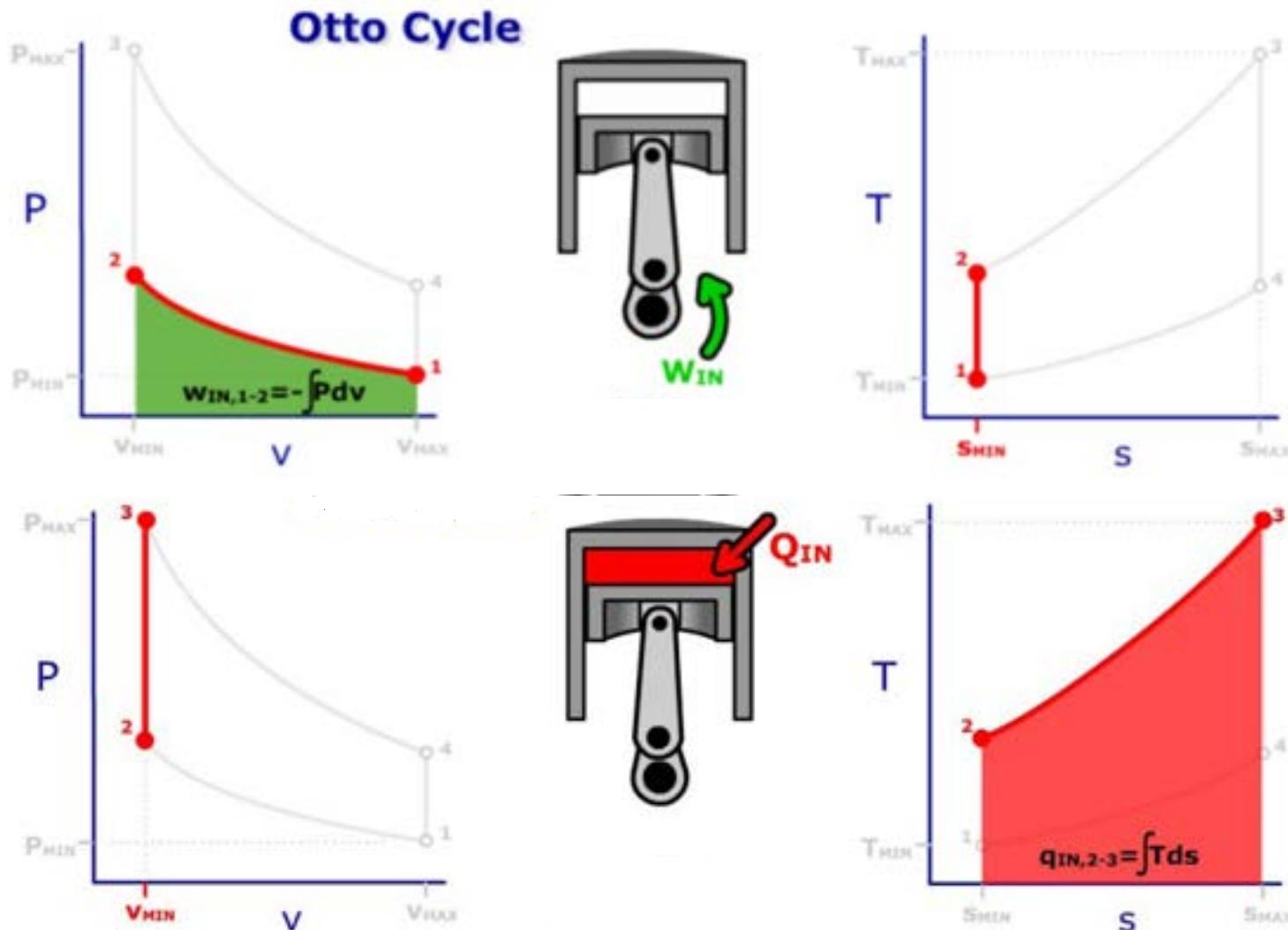
- **Stroke 1 and 4**
 - Work interactions during intake and exhaust cancel each other, and thus inclusion of the intake and exhaust processes has no effect on the net work output from the cycle
 - In modeling they are ignored, however, when calculating the power output from the cycle during, we must consider the fact that the ideal cycle has four strokes just like the actual four-stroke engine

The Actual and Ideal Otto Cycle



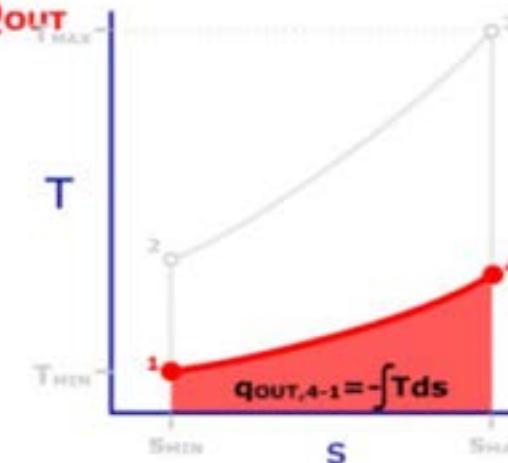
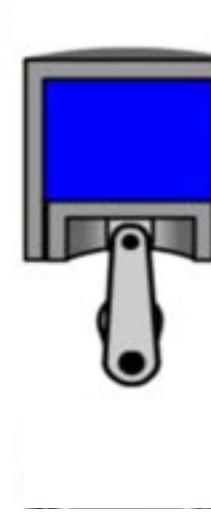
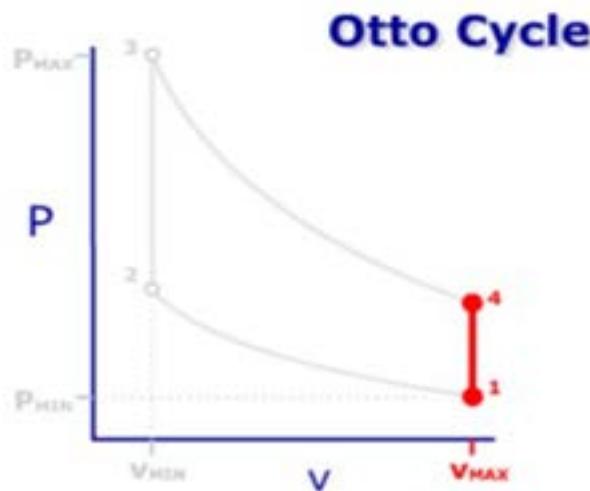
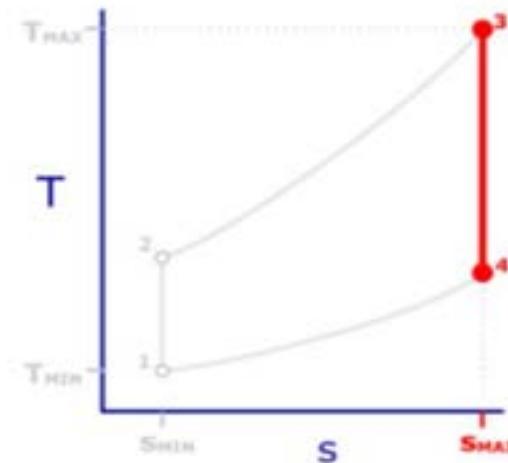
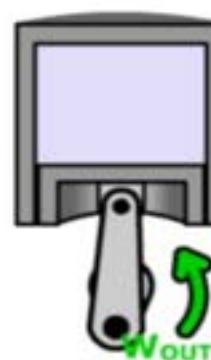
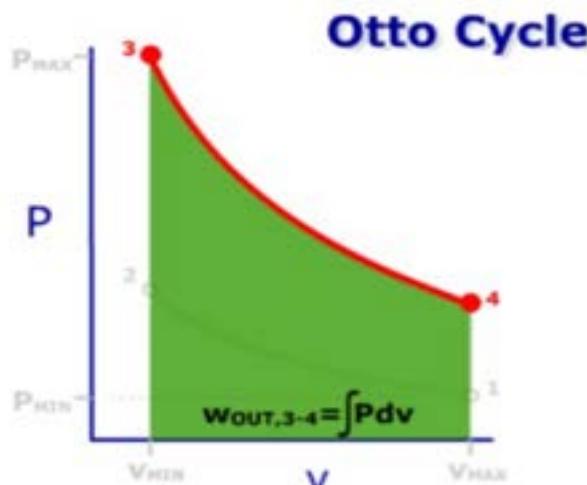
In the analysis the intake and exhaust stroke are neglected

The Otto Cycle



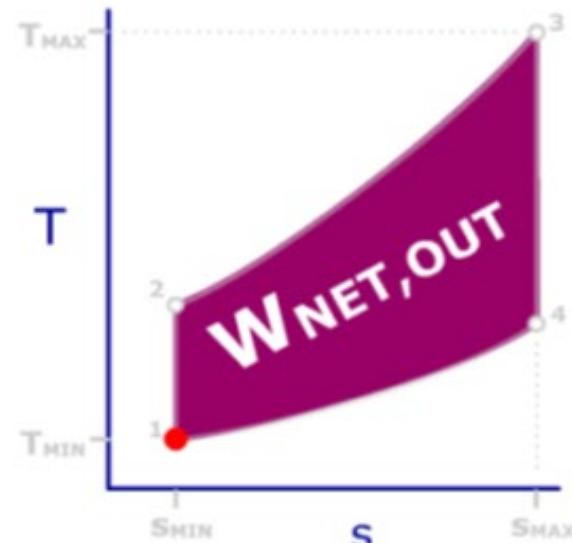
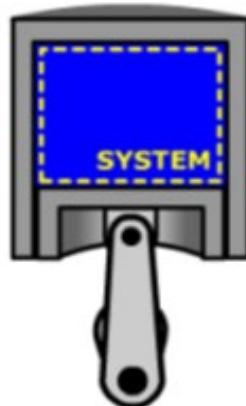
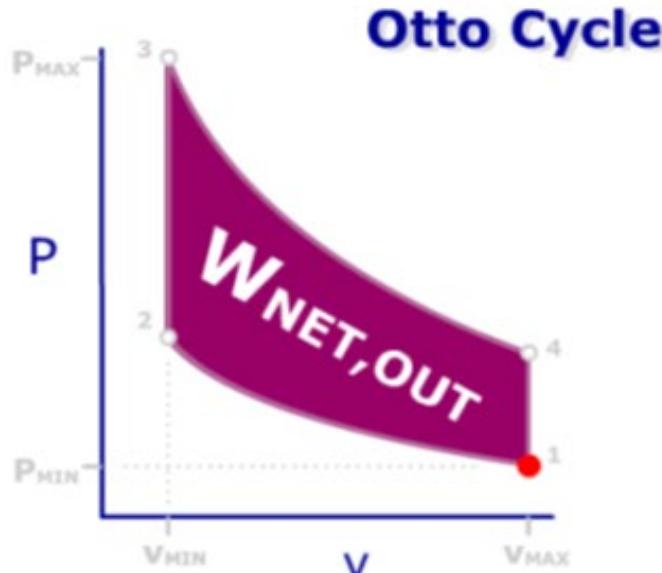
The area below the Pv diagram indicates the work input during compression and the area below the Ts diagram indicates the heat input

The Otto Cycle



The area below the Pv diagram indicates the work output during expansion and the area below the Ts diagram indicates the heat output

The Otto Cycle



Process	Q	W	Type
$1 \rightarrow 2$	0	W_{IN}	Isentropic
$2 \rightarrow 3$	Q_{IN}	0	Isometric
$3 \rightarrow 4$	0	W_{OUT}	Isentropic
$4 \rightarrow 1$	Q_{OUT}	0	Isometric

State	T	P	v	s
1	T_{MIN}	P_{MIN}		
2				$s_2 = s_1$
3	T_{MAX}	P_{MAX}	$v_3 = v_2$	
4			$v_4 = v_1$	$s_4 = s_3$

The area enclosed in the the Pv diagram indicates the net work output and the area enclosed in the Ts diagram indicates the net heat input of the cycle
 For a cycle these are the same: $w_{net} = q_{net}$

Otto Cycle Analysis

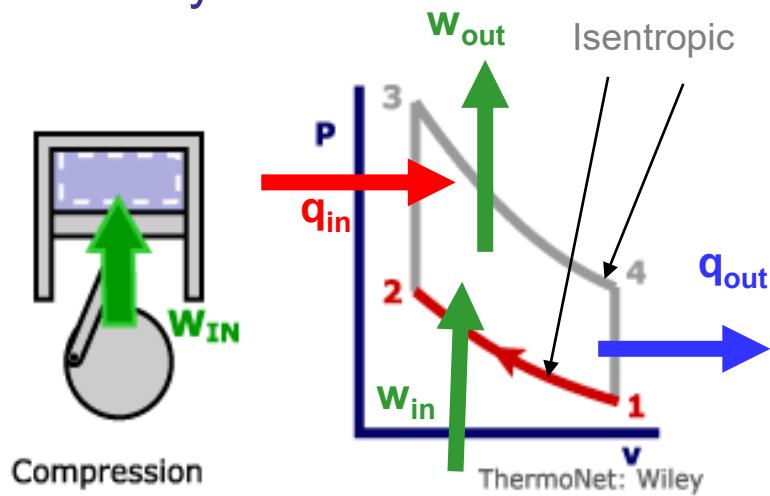
- Otto cycle modeled as a closed ideal air standard cycle
- **Important formulas (our tools)**

- Ideal gas: $Pv = RT$ (for all processes)
 - For example: $P_3T_2 = P_2 T_3$

- Isentropic processes (1 - 2 and 3 - 4):
 - $Pv^k = \text{constant}$ ($k=c_p/c_v$)
 - For example: $P_1v_1^k = P_2v_2^k$
 - $Tv^{(k-1)} = \text{constant}$
 - $TP^{(1-k)/k} = \text{constant}$

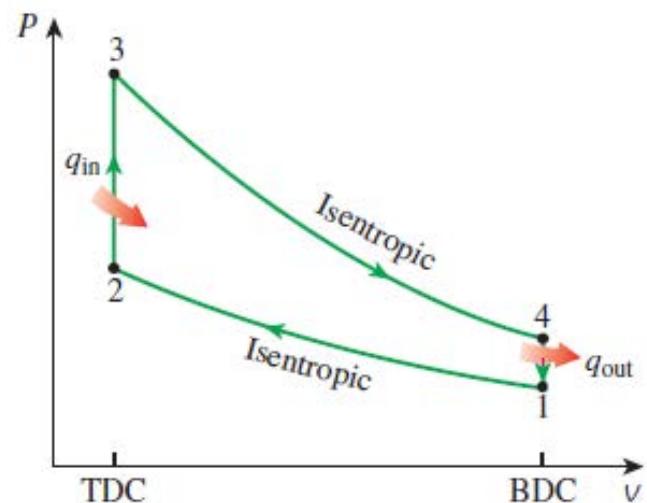
Isentropic relations:
See Class 9, and Çengel 7.9

- First law closed system: $\Delta u = (q_{in} - q_{out}) + (w_{out} - w_{in})$
- $\Delta u = c_v \Delta T$
 - For example: $w_{in} = w_{(1-2)} = \Delta u_{(1-2)} - q_{(1-2)} = u_2 - u_1 = c_v(T_2 - T_1)$
- Compression ratio: $r_v = v_{max}/v_{min} = v_1/v_2 = v_4/v_3$
- $P_{max} = P_3$, $P_{min} = P_1$ and $T_{max} = T_3$, $T_{min} = T_1$



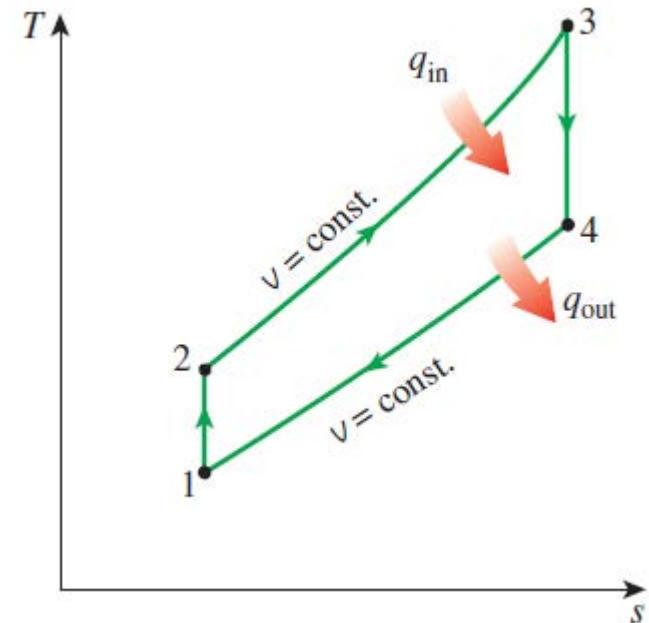
Work and Heat Otto Cycle

- Work in- and output Otto cycle: Ideal air standard analysis
- The **work input** is between point 1 and 2
- $w_{in} = w_{1-2}$, for this process the heat is zero: $q_{1-2} = 0$
- The first law states: $\Delta u_{a-b} = q_{a-b} + w_{a-b}$
- Therefore: $w_{in} = w_{1-2} = u_2 - u_1 = c_v(T_2 - T_1)$
- The **work output** is between point 3 and 4
- $w_{out} = w_{3-4}$ the heat is also zero: $q_{3-4} = 0$
- Similar, the work output is:
$$w_{out} = w_{3-4} = u_3 - u_4 = c_v(T_3 - T_4)$$
- The **net work output** is: $w_{net} = w_{3-4} - w_{1-2}$
$$w_{net} = c_v(T_3 - T_4) - c_v(T_2 - T_1)$$



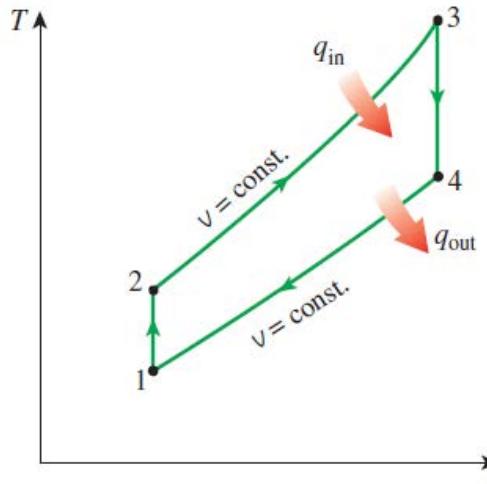
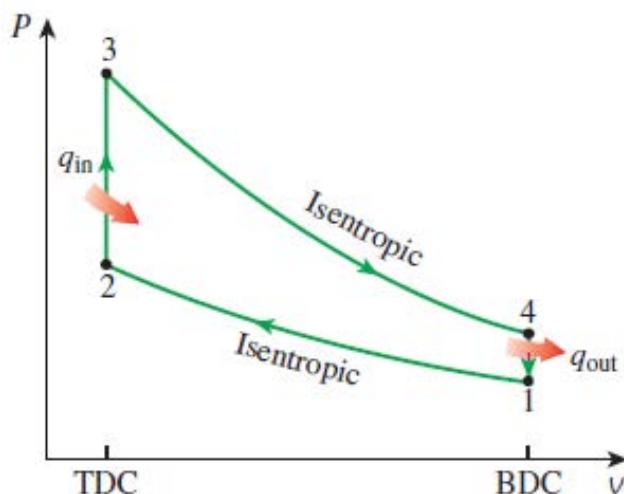
Heat in- and output Otto Cycle

- Heat in- and output Otto cycle: Ideal air standard analysis
- The **heat input** is between point 2 and 3
- $q_{in} = q_{2-3}$, for this process the work is zero as $v = \text{constant}$, $w_{2-3} = 0$
- The first law states: $\Delta u_{a-b} = q_{a-b} + w_{a-b}$
- Therefore: $q_{in} = q_{2-3} = u_3 - u_2 = c_v(T_3 - T_2)$
- The **heat output** is between point 4 and 1
- $q_{out} = q_{4-1}$ the work is also zero: $w_{4-1} = 0$
- Similar, the heat output is:
$$q_{out} = q_{4-1} = u_4 - u_1 = c_v(T_4 - T_1)$$
- The **net heat input** is $q_{net} = q_{2-3} - q_{4-1}$
$$q_{net} = c_v(T_3 - T_2) - c_v(T_4 - T_1)$$
- This is equal to the net work output



Net Work Output and Heat Input Otto Cycle

- **Net work output Otto cycle:** Ideal air standard analysis
 - $w_{net} = c_v(T_3 - T_4) - c_v(T_2 - T_1)$ [kJ/kg]
- **Heat input Otto cycle:** Ideal air standard analysis
 - $q_{in} = q_{2-3} = u_3 - u_2 = c_v(T_3 - T_2)$ [kJ/kg]
- These expressions give specific energies for one stroke only



Power Output Otto Cycle

- What is the power output of an Otto engine?
- A 4-stroke engine has 4 strokes and two turnings of the crank
- Only in one stroke and one turning power is delivered
- An Otto engine has many revolutions per minute (RPM)
- Therefore, the specific power is: $\dot{w}_{net} = w_{net} \frac{1}{2} \frac{RPM}{60}$ [kJ/kg = kW/kg]
- Otto engines mostly have more than 1 cylinder, the total mass of the gas in all cylinders should be considered to calculate the power

$$\dot{W}_{net} = m\dot{w}_{net} = mw_{net} \frac{1}{2} \frac{RPM}{60} \quad [\text{kJ/s} = \text{kW}]$$

Otto Cycle Efficiency

- The efficiency of the Otto cycle (Ideal air standard):

$$\eta_{\text{Otto, ias}} = \frac{\text{Wanted}}{\text{Payed for}} = \frac{w_{\text{net}}}{q_{\text{in}}} = \frac{w_{\text{out}} - w_{\text{in}}}{q_{\text{in}}} =$$
$$\frac{(u_3 - u_4) - (u_2 - u_1)}{(u_3 - u_2)} = \frac{c_v(T_3 - T_4) - c_v(T_2 - T_1)}{c_v(T_3 - T_2)}$$

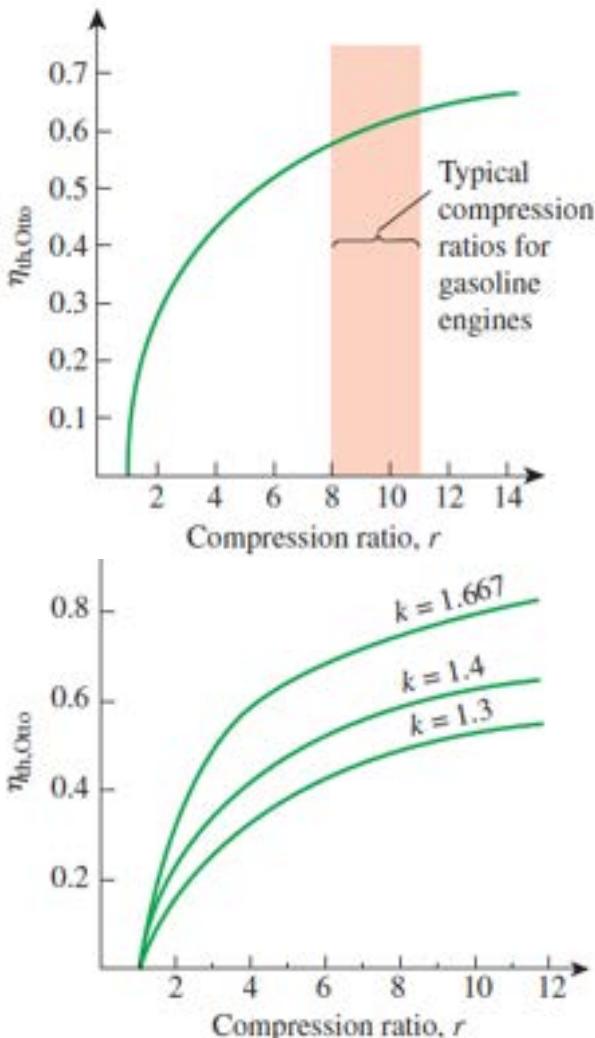
- Which can be written as:

$$\eta_{\text{Otto, ias}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_4}{T_3} = 1 - \left(\frac{v_3}{v_4}\right)^{k-1} = 1 - \frac{1}{r_v^{k-1}}$$

- The efficiency of an ideal air-standard cycle depends only on the compression ratio
- Compare with the Carnot efficiency: $\eta_{\text{CARNOT}} = 1 - \frac{T_{\text{COLD}}}{T_{\text{HOT}}} = 1 - \frac{T_1}{T_3}$
- The Otto cycle efficiency is lower because heat addition and rejection are not reversible and isothermal

Efficiency of an Ideal Otto Cycle

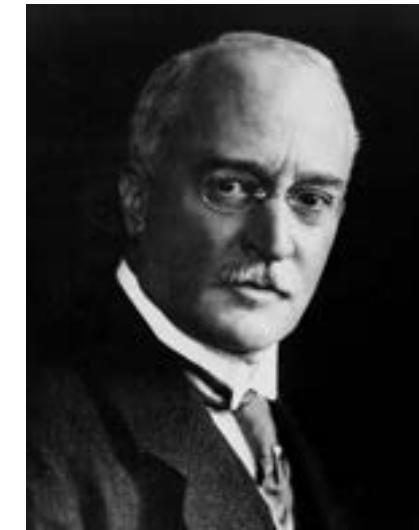
- Efficiency of the ideal Otto cycle as a function of the compression ratio (top) and as a function of the specific heat ratio k of the working fluid (bottom)



$$\eta_{\text{Otto, ias}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{1}{r_v^{k-1}}$$

- Here:
 - $r_v = \frac{v_{\max}}{v_{\min}} = \frac{v_1}{v_2}$ (Compression ratio)
 - $k = \frac{c_p}{c_v}$
- The top figure shows that the efficiency of a gasoline engine, undergoing the Otto cycle, increases with a higher compression ratio
- The bottom figure shows that the efficiency increases with a higher specific heat ratio k , so with a larger difference in c_p and c_v

Diesel Cycle



Rudolph Diesel and
the first Diesel engine



Wärtsilä-Sulzer RTA96-C

- We have seen the analysis of
 - the Stirling cycle, an external combustion reciprocating cycle
 - the Otto cycle, an internal combustion reciprocating cycle used in gasoline (petrol) engines
- Before we continue to the Diesel cycle an example to show how large they can be
- The Wärtsilä-Sulzer RTA96-C designed for large container ships that run on heavy fuel oil is the largest reciprocating engine in the world



Wärtsilä-Sulzer RTA96-C (right) used to power container ship Emma Maersk (above)



Wärtsilä-Sulzer RTA96-C

The engine has 14 massive cylinders and a huge camshaft. Its specs are given in the table

Technical data (as of 2008)



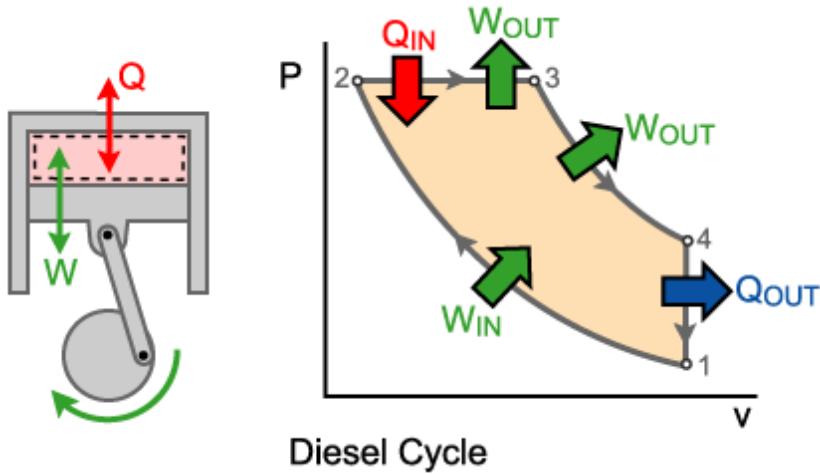
Configuration	Turbocharged two-stroke diesel straight engine, 6 to 14 cylinders
Bore	960 mm (38 in)
Stroke	2,500 mm (8.2 ft)
Displacement	1810 litres (110450 CI) per cylinder
Engine speed	22–120 RPM
Mean effective pressure	1.96 MPa @ full load, 1.37 MPa @ maximum efficiency (85% load)
Mean piston speed	8.5 meters per second
Best specific fuel consumption	160 g/(kW·h) ^{[3][a]}
Power	Up to 5,720 kW per cylinder, 34,320–80,080 kW (46,020–107,390 bhp) total
Torque	Up to 7,603,850 N·m (5,608,310 lbf·ft) @ 102 rpm
Power density	29.6–34.8 kW (39.7–46.7 bhp) per tonne, 2300 tonnes for the 14-cylinder version
Mass of fuel injected per cylinder per cycle	~160 g (5.6 oz) @ full load (Whole engine uses up to 250 tons of fuel per day.)
Crankshaft weight	300 t (660,000 lb) ^[1]
Piston weight	5.5 t (12,000 lb)
Piston height	6 m (20 ft)

https://en.wikipedia.org/wiki/W%C3%A4rtsil%C3%A4-Sulzer_RTA96-C

The Diesel Cycle

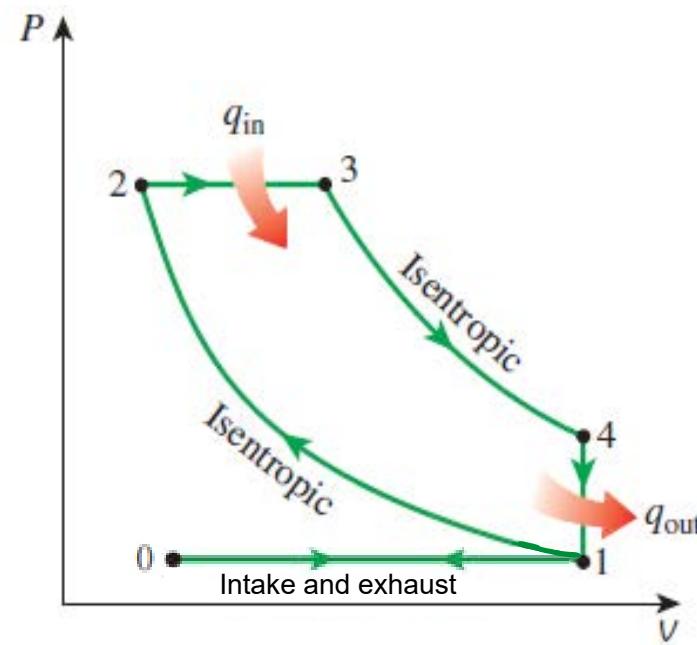
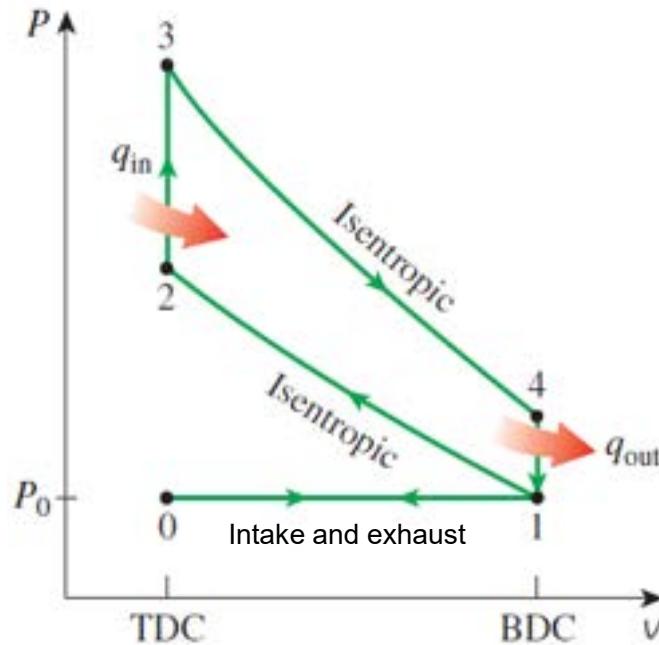
- **The Diesel cycle**

- It is an idealization of the internal combustion Diesel engine cycle developed by Rudolph Diesel (1893)
- It is executed in a reciprocating piston-cylinder device
- It is an open cycle oil-fueled internal combustion engine, however it is modeled as a closed cycle
- It consists of 2 constant entropy processes, 1 constant pressure and 1 constant volume process
- Auto-ignition occurs due to high P & T



Principle of the Diesel Cycle

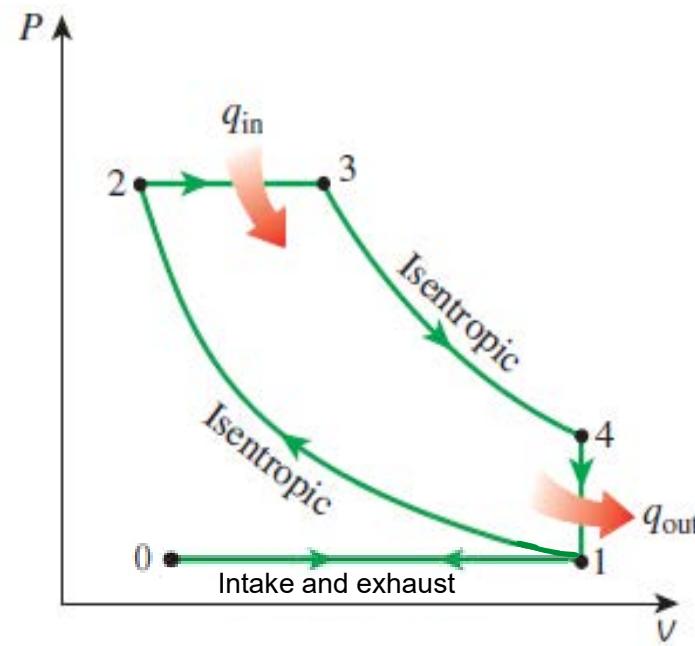
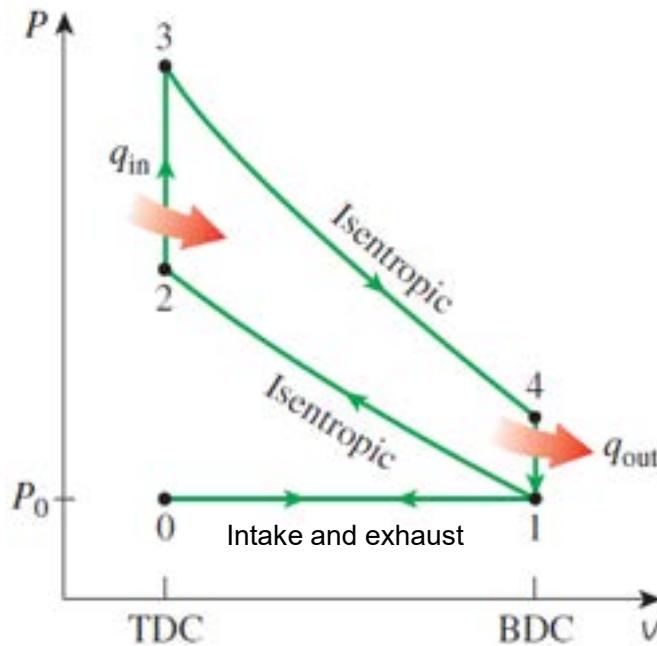
- The Diesel cycle was developed in an attempt to approach the Carnot efficiency more closely, its principle is very much alike the Otto Cycle
- The main difference with the Otto cycle is the process between 2 and 3
 - In a Diesel engine auto-ignition occurs when fuel is injected at high pressure and temperature **at constant pressure**
 - In the Otto engine the gas is **ignited by a spark at constant volume**



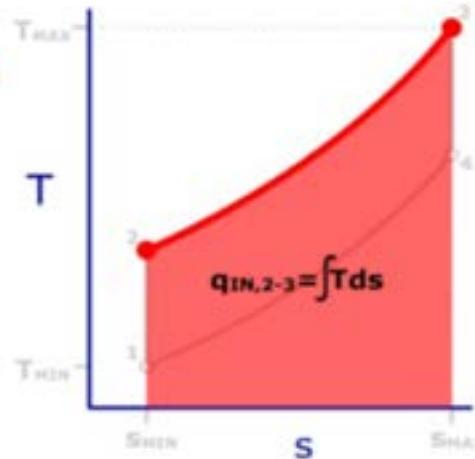
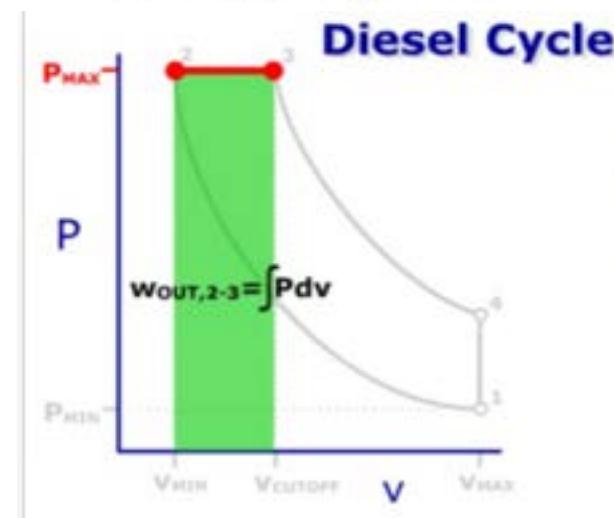
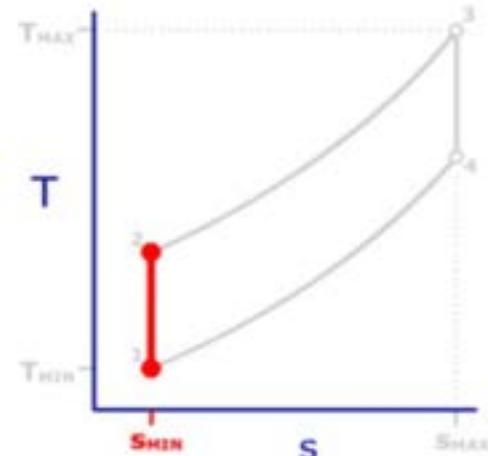
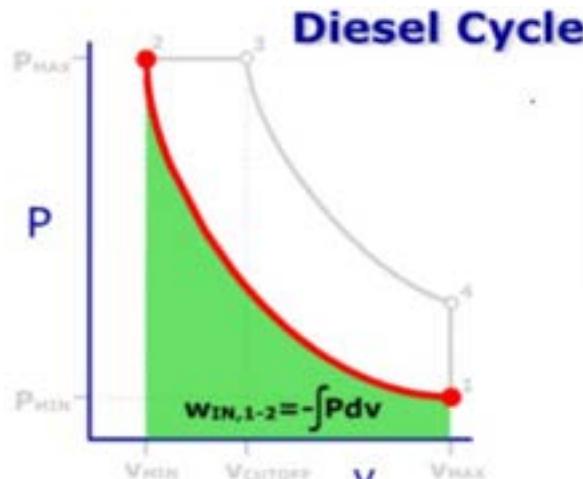
Principle of the Diesel Cycle

- The Diesel cycle was developed in an attempt to approach the Carnot efficiency more closely, its principle is very much alike the Otto Cycle

Cycle	Compression	Ignition	Combustion
Otto	Air + Fuel	Spark	Isochoric
Diesel	Air	Compression	Isobaric

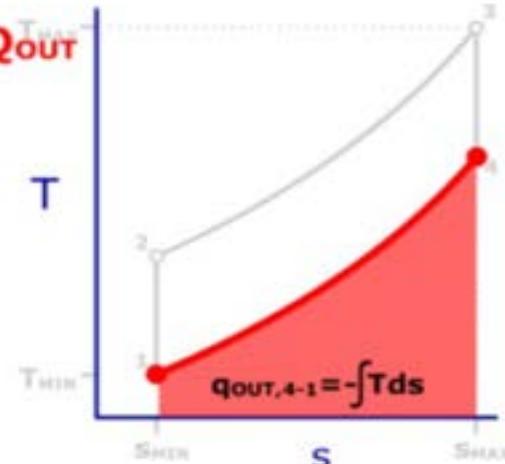
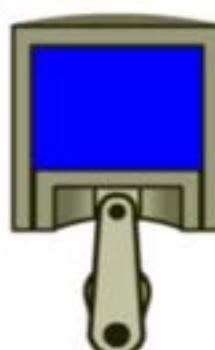
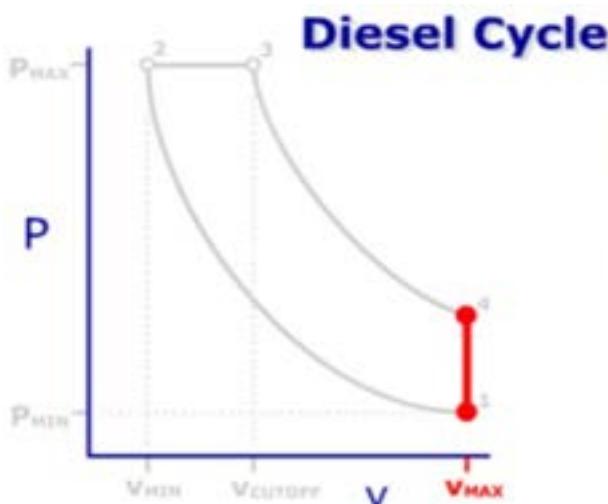
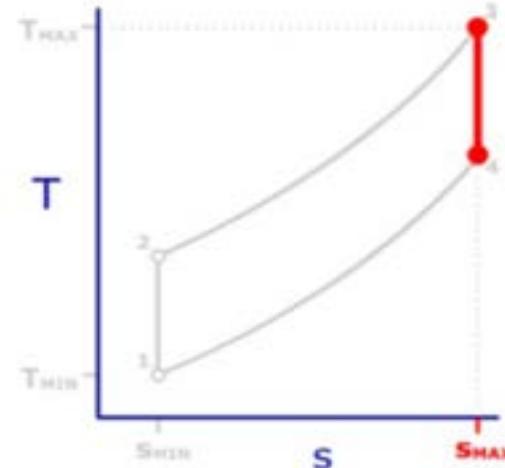
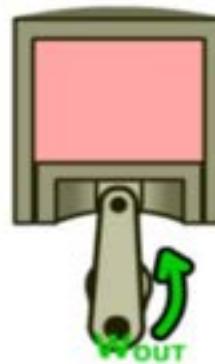
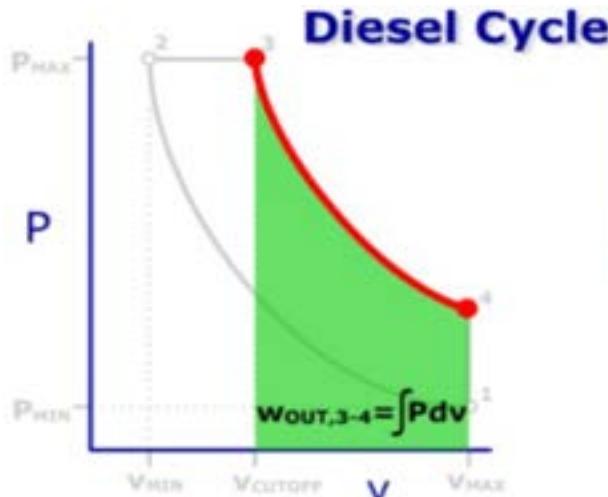


The Diesel Cycle



The area below the upper Pv diagram indicates the work input during compression. The lower Pv diagrams shows the work output during combustion. The area below the Ts diagram indicates the heat input. A

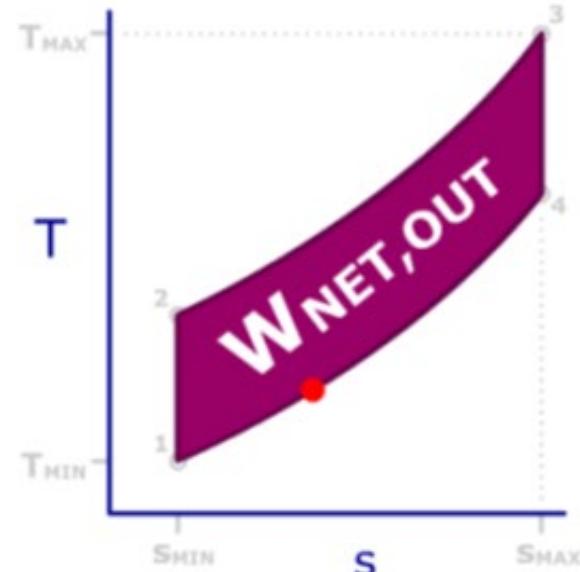
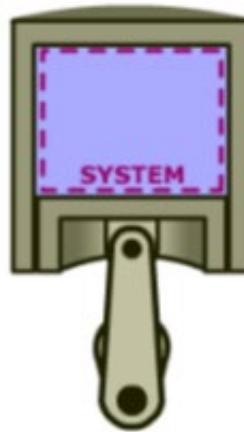
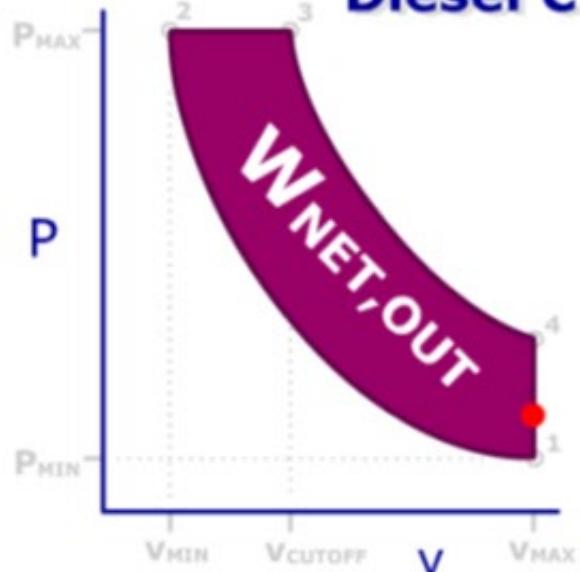
The Diesel Cycle



The area below the Pv diagram indicates the work output during expansion and the area below the Ts diagram indicates the heat output

The Diesel Cycle

Diesel Cycle



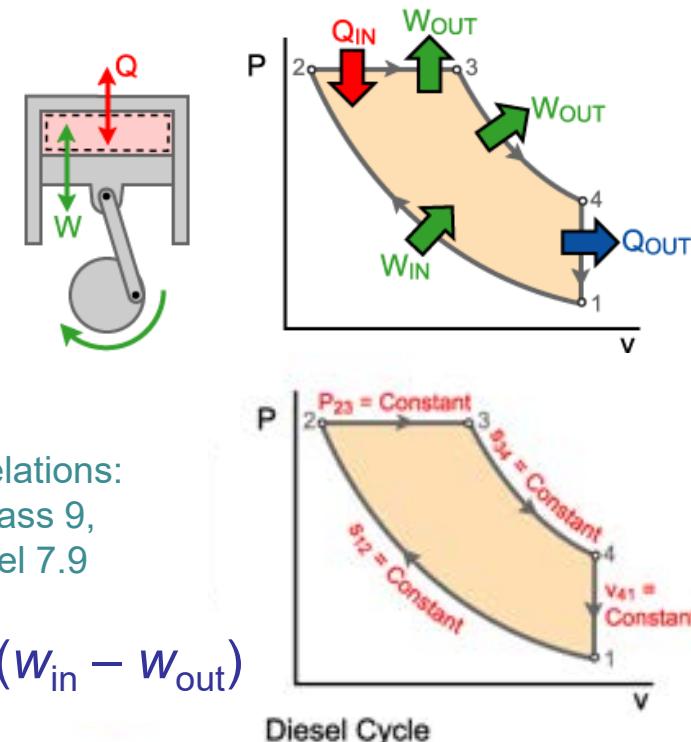
Process	Q	W	Type
$1 \rightarrow 2$	0	W_{IN}	Isentropic
$2 \rightarrow 3$	Q_{IN}	W_{OUT}	Isobaric
$3 \rightarrow 4$	0	W_{OUT}	Isentropic
$4 \rightarrow 1$	Q_{OUT}	0	Isometric

State	T	P	v	s
1	T_{MIN}	P_{MIN}		
2		P_{MAX}		$s_2 = s_1$
3	T_{MAX}	$P_3 = P_2$		
4			$v_4 = v_1$	$s_4 = s_3$

The area enclosed in the the Pv diagram indicates the net work output and the area enclosed in the Ts diagram indicates the net heat input of the cycle
 For a cycle these are the same: $w_{net} = q_{net}$

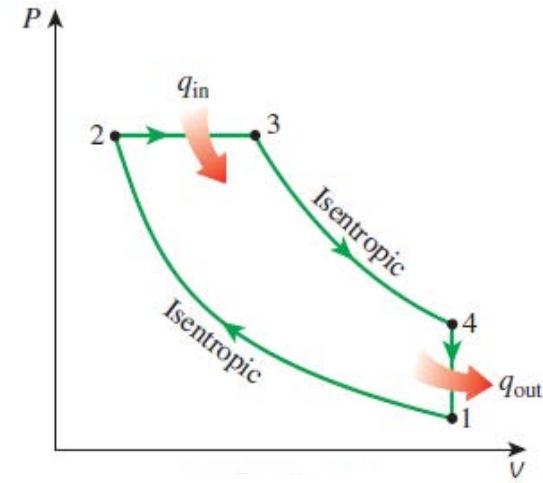
Diesel Cycle Analysis

- Diesel cycle modeled as a closed ideal air standard cycle
- Important formulas**
 - Ideal gas: $Pv = RT$
 - For example: $v_3 T_2 = v_2 T_3$
 - Isentropic processes (1-2 and 3-4):
 - $Pv^k = \text{constant}$ ($k = c_p/c_v$)
 - For example: $P_1 v_1^k = P_2 v_2^k$
 - $Tv^{(k-1)} = \text{constant}$
 - $TP^{(1-k)/k} = \text{constant}$
 - First law closed system: $\Delta u = (q_{\text{in}} - q_{\text{out}}) + (w_{\text{in}} - w_{\text{out}})$
 - $\Delta u = c_v \Delta T$ and $\Delta h = c_p \Delta T$, for example:
 - $q_{\text{in}} = q_{(2-3)} = \Delta u_{(2-3)} + w_{(2-3)} = u_3 - u_2 + (P_3 v_3 - P_2 v_2) = h_3 - h_2 = c_p(T_3 - T_2)$
 - Compression ratio: $r_v = v_{\max}/v_{\min} = v_1/v_2 = v_4/v_2$
 - Cut-off ratio: $r_{\text{cut-off}} = v_3/v_2$ (plays no role in Otto Cycle)
 - $P_{\max} = P_2 = P_3$, $P_{\min} = P_1$ and $T_{\max} = T_3$, $T_{\min} = T_1$



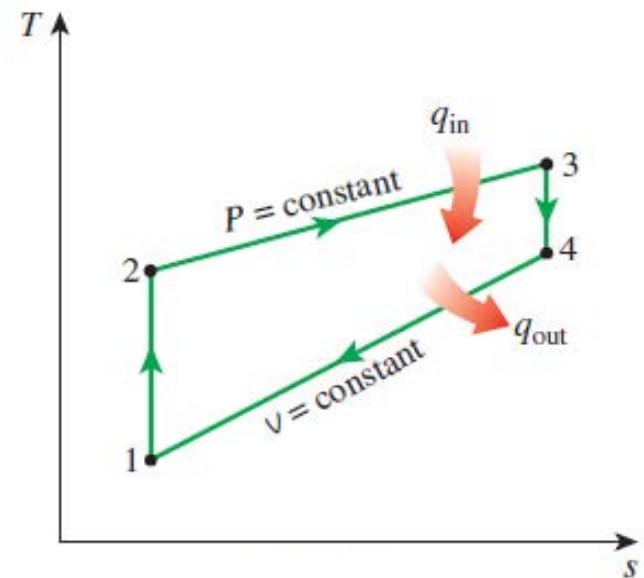
Work and Heat Diesel Cycle

- Work in- and output Diesel cycle: Ideal air standard analysis
- The **work input** is between point 1 & 2 (like the Otto cycle)
- $w_{in} = w_{1-2}$, for this process the heat is zero: $q_{1-2} = 0$
- The first law states: $\Delta u_{a-b} = q_{a-b} + w_{a-b}$ and therefore: $w_{in} = w_{1-2} = u_2 - u_1$
- The **work output** is between point 3 & 4 and **point 2 & 3**: $w_{out} = w_{3-4} + w_{2-3}$
- With $q_{3-4} = 0$ follows from the first law: $w_{3-4} = u_3 - u_4$
- From $\delta w = Pdv$ with $P_2 = P_3 = \text{constant}$ follows: $w_{2-3} = P_3v_3 - P_2v_2$
- Therefore: $w_{out} = w_{3-4} + w_{2-3} = u_3 - u_4 + P_3v_3 - P_2v_2$
- The **net work output** is:
$$\begin{aligned}w_{net} &= w_{out} - w_{in} = w_{3-4} + w_{2-3} - w_{1-2} \\&= u_3 - u_4 + P_3v_3 - P_2v_2 - (u_2 - u_1) \\&= u_3 + P_3v_3 - u_2 - P_2v_2 - u_4 + u_1 \\&= h_3 - h_2 + u_1 - u_4 = c_p(T_3 - T_2) - c_v(T_4 - T_1)\end{aligned}$$
- Note: this is different from the Otto cycle net work



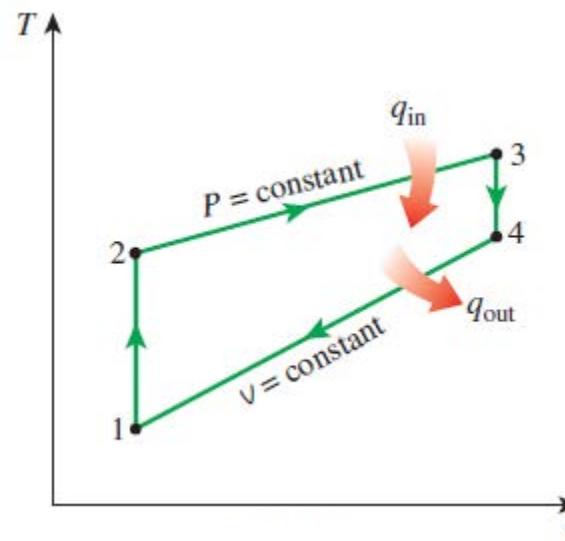
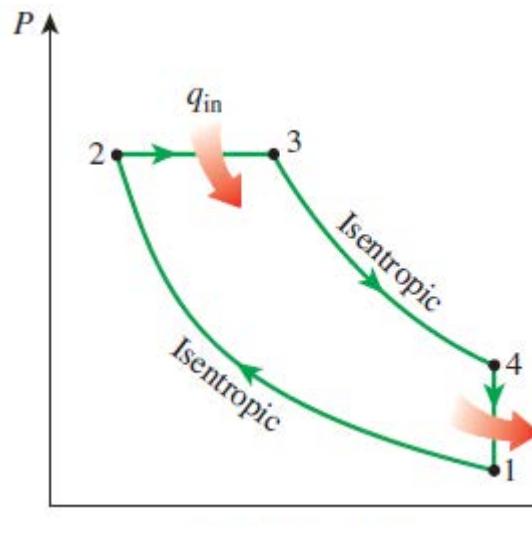
Work and Heat Diesel Cycle

- Heat in- and output Diesel cycle: Ideal air standard analysis
- The **heat input** is between point 2 and 3
- $q_{in} = q_{2-3}$, for this process the work is: $w_{2-3} = P_3v_3 - P_2v_2$
- The first law states: $\Delta U_{a-b} = q_{a-b} + w_{a-b}$
- Therefore: $q_{in} = q_{2-3} = u_3 - u_2 + P_3v_3 - P_2v_2$
 $= u_3 + P_3v_3 - u_2 - P_2v_2$
 $= h_3 - h_2 = c_p(T_3 - T_2)$
- The **heat output** is between point 4 and 1
- $q_{out} = q_{4-1}$ the work is also zero: $w_{4-1} = 0$
- From the first law follows:
$$q_{out} = q_{4-1} = u_4 - u_1 = c_v(T_4 - T_1)$$
- The **net heat input** is $q_{net} = q_{2-3} - q_{4-1}$
$$q_{net} = c_p(T_3 - T_2) - c_v(T_4 - T_1)$$
, this is equal to the net work output



Net Work Output and Heat Input Diesel Cycle

- **Net work output Diesel cycle:** Ideal air standard analysis
 - $w_{net} = c_p(T_3 - T_2) - c_v(T_4 - T_1)$ [kJ/kg]
- **Heat input Diesel cycle:** Ideal air standard analysis
 - $q_{in} = q_{2-3} = u_3 - u_2 = c_p(T_3 - T_2)$ [kJ/kg]
- These expressions give specific energies for one stroke only



Power Output Diesel Cycle

- What is the power of a Diesel engine?
- A 4-stroke engine has 4 strokes and two turnings of the crank
- Only in one stroke and one turning power is delivered
- A Diesel engine has many revolutions per minute (RPM)
- Therefore, the specific power is: $\dot{w}_{net} = w_{net} \frac{1}{2} \frac{RPM}{60}$ [kJ/kg=kW/kg]
- Diesel engines have more than 1 cylinder, the total mass of the gas in all cylinders should be considered to calculate the power

$$\dot{W}_{net} = m\dot{w}_{net} = mw_{net} \frac{1}{2} \frac{RPM}{60} \text{ [kJ/s=kW]}$$

Diesel Cycle Efficiency

- The Diesel cycle is a bit more complicated than the Otto cycle, because of **cut off ratio** that plays a role in the Diesel cycle, and not in the Otto
- The cut off ratio is the ratio between the volume before and after the heat addition: $r_{Cutoff} = \frac{v_3}{v_2} = \frac{T_3}{T_2}$ and $\frac{T_4}{T_1} = \frac{P_4}{P_1} = (r_{Cutoff}^k)_{IAS}$
- The efficiency of the Diesel cycle (Ideal air standard):

$$\eta_{Diesel,ias} = \frac{\text{Wanted}}{\text{Payed for}} = \frac{w_{netto}}{q_{in}} = \frac{w_{out} - w_{in}}{q_{in}} = \frac{w_{23} + w_{34} - w_{12}}{q_{in}} =$$
$$\frac{(P_3 V_3 - P_2 V_2) + (u_3 - u_4) - (u_2 - u_1)}{(u_3 - u_2) + (P_3 V_3 - P_2 V_2)} = \frac{(h_3 - h_2) - (u_4 - u_1)}{(h_3 - h_2)} = \frac{c_p(T_3 - T_2) - c_v(T_4 - T_1)}{c_p(T_3 - T_2)}$$

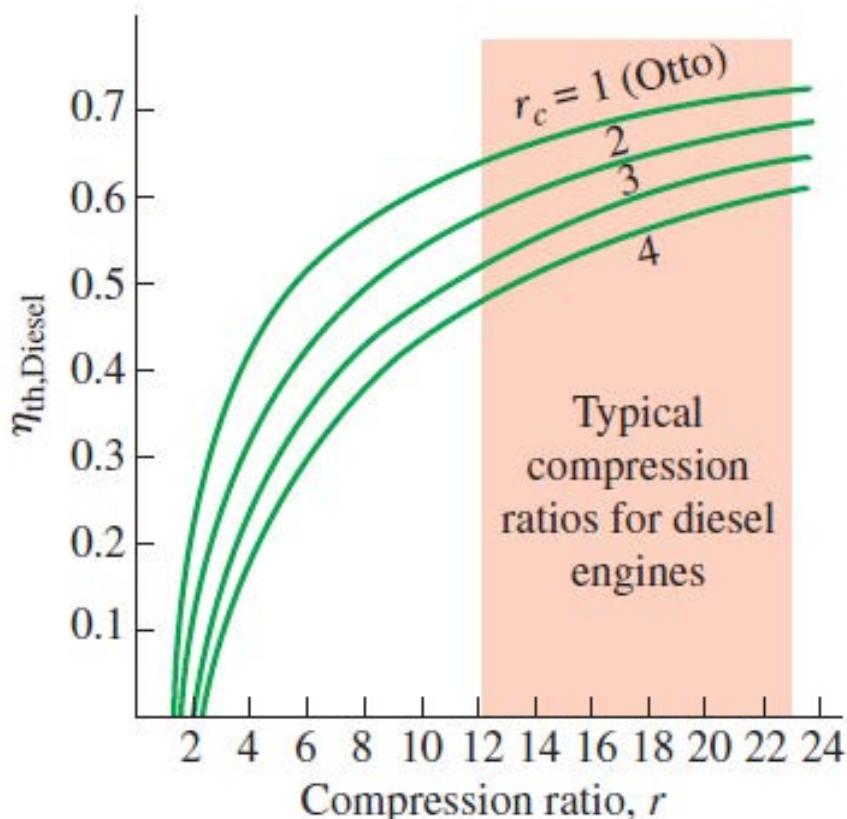
- Which can be rewritten as:

$$\eta_{Diesel,ias} = 1 - \frac{c_v(T_4 - T_1)}{c_p(T_3 - T_2)} = 1 - \frac{T_1(T_4/T_1 - 1)}{kT_2(T_3/T_2 - 1)} = 1 - \frac{1}{k} \left(\frac{1}{r_v} \right)^{k-1} \frac{(r_{cutoff}^k - 1)}{(r_{cutoff} - 1)}$$

Efficiency of the Ideal Diesel Cycle

- Efficiency of the ideal Diesel cycle as a function of the compression ratio

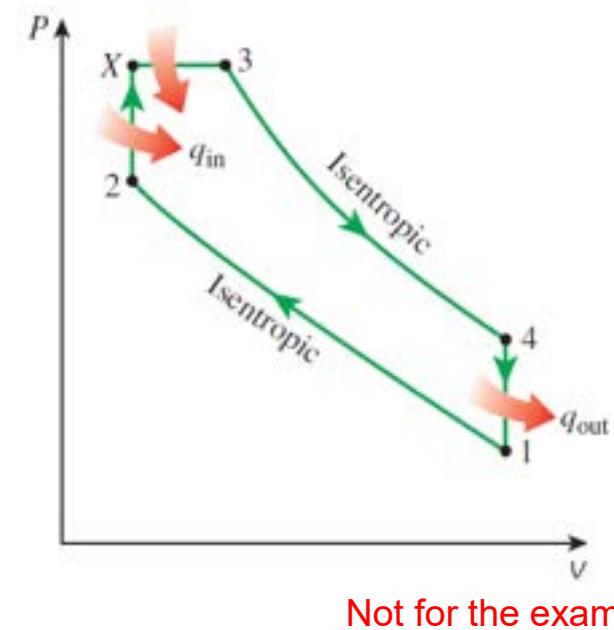
$$\eta_{\text{Diesel, ias}} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{1}{k} \left(\frac{1}{r_v} \right)^{k-1} \frac{(r_{cutoff}^k - 1)}{(r_{cutoff} - 1)}$$



- Note: in a Diesel cycle the cut off ratio, $r_c = \frac{v_3}{v_2}$ plays a role
- If $r_c = 1$ the Diesel cycle approaches the Otto cycle
- $r_v = \frac{v_1}{v_2}$ compression ratio
- The figure shows that the efficiency of a Diesel engine increases with a higher compression ratio and a lower cut off ratio

Other Piston Engine Cycles: Dual Cycle

- In modern high-speed compression ignition engines, fuel is injected into the combustion chamber much sooner compared to the early diesel engines
- Fuel starts to ignite late in the compression stroke, and consequently part of the combustion occurs almost at constant volume
- Fuel injection continues until the piston reaches the top dead centre, and combustion of the fuel keeps the pressure high well into the expansion stroke
- Thus, the entire combustion process can better be modelled as the combination of constant-volume and constant-pressure processes, the dual cycle
- The **dual cycle** is a hybrid between an Otto and a Diesel cycle and comes closer to a real cycle
 - If $v_3 = v_x \rightarrow$ Otto Cycle
 - If $P_x = P_2 \rightarrow$ Diesel Cycle
- Volume compression ratio: $r_1 = \frac{v_1}{v_2}$
- Volume expansion ratio: $r_2 = \frac{v_4}{v_3}$
- Efficiency dual cycle: $\eta_{DUAL,IAS} = 1 - \frac{\left(\frac{1}{r_1^{k-1}}\right)\left[\left(\frac{P_x}{P_2}\right)\left(\frac{r_1}{r_2}\right)^k - 1\right]}{\left(\frac{P_x}{P_2}\right) - 1 + k\left[\left(\frac{r_1}{r_2}\right) - 1\right]}$



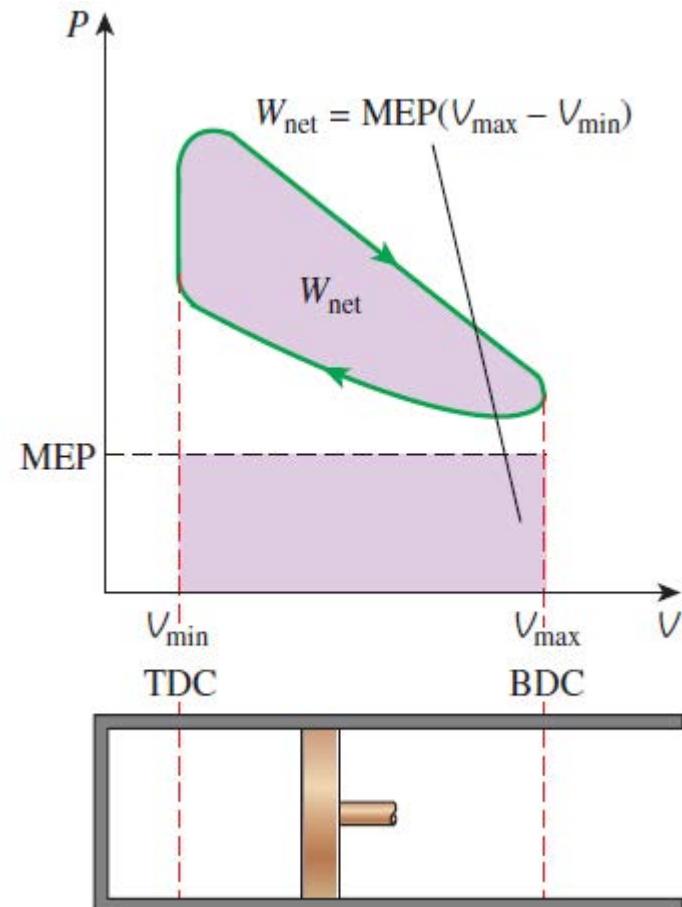
Not for the exam

Mean Effective Pressure

- The mean effective pressure (P_{ME}) is a convenient measure of the practicality of an Otto or Diesel cycle
- This is a mean pressure which multiplied by the maximum volume change gives the net cycle work output
- Definition (P_{ME})

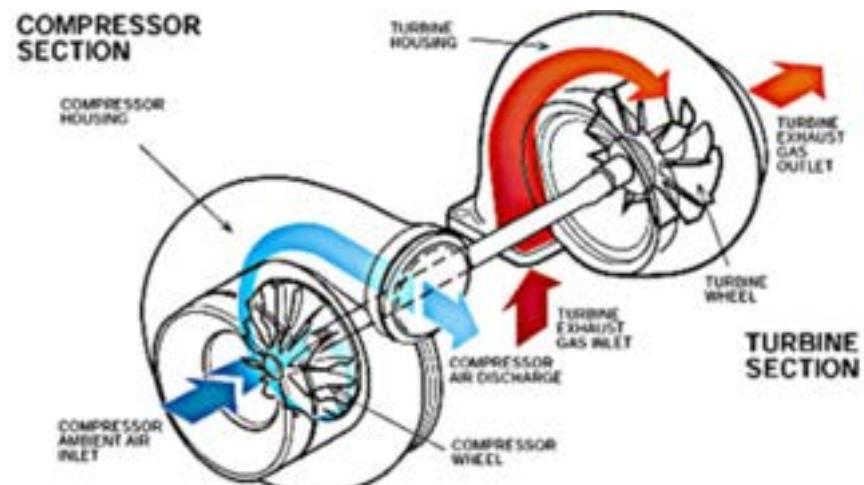
$$w_{out} - w_{in} = \oint Pdv$$
$$= P_{ME}(v_{max} - v_{min})$$

- $(v_{max} - v_{min})$ is proportional to size of engine
- Engines with larger P_{ME} produce more work per unit volume
- Engines with larger P_{ME} tend to be more practical



Turbo Charging

- Turbo charging is used to enhance the output power of the Diesel engine
- A turbo charger consists of a compressor connected to a turbine to drive the compressor
- The compressor is placed before the cylinder inlet and compresses the inlet air before it enters the cylinder
- This results in a higher density of the air in the cylinder and therefore the mass of air and oxygen is higher
- At a constant air/fuel ratio more fuel can be injected to the cylinder resulting in a higher power output
- The turbine of the turbo charger is placed after the cylinder outlet and powered by the combustion gases leaving the cylinder at high pressure



Not for the exam

Example Otto Cycle

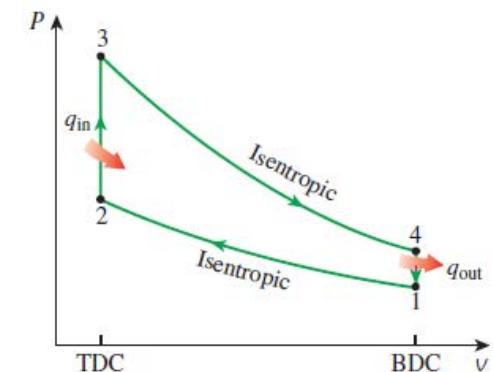
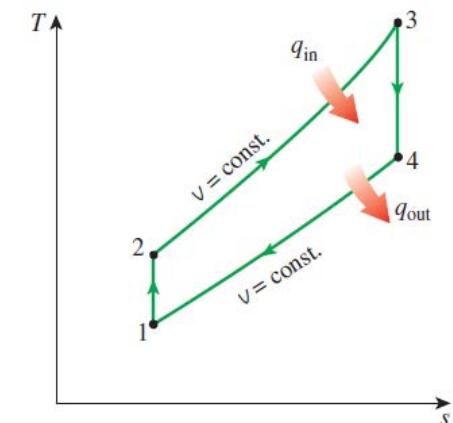
- Given is an ideal standard air Otto cycle with compression ratio 8
 - Inlet conditions $T_1 = 300 \text{ K}$, $P_1 = 100 \text{ kPa}$
 - Maximum pressure is 3.0 MPa
- Determine the net power output and the heat transferred to the engine per kg air and the thermal efficiency ($k = 1.4$, c_v at 300K)

Solution:

- P_3 is the maximum pressure = 3.0 MPa
- Compression ratio of 8 means $r_v = v_1 / v_2 = 8 = v_4 / v_3$
- Heat transferred to the engine is: $q_{in} = c_v(T_3 - T_2)$
- Net power output is: $w_{net} = c_v(T_3 - T_4) - c_v(T_2 - T_1)$
- The thermal efficiency is:

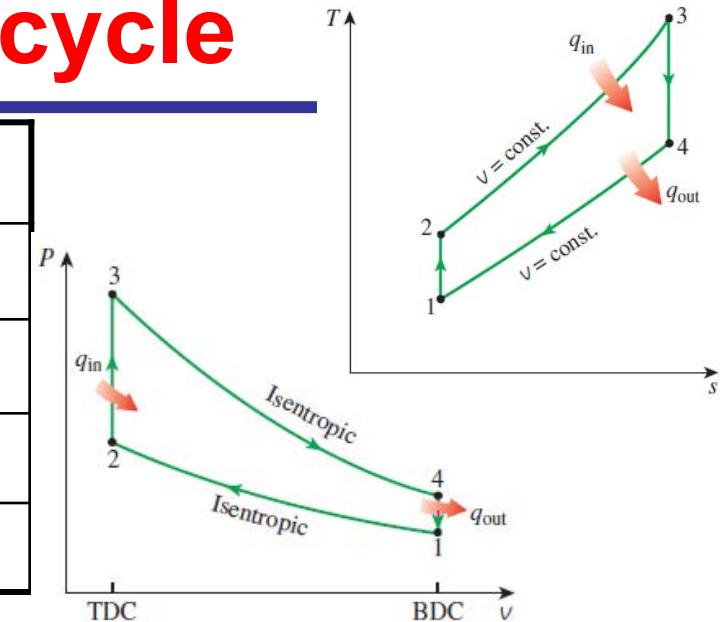
$$\eta_{Otto,ias} = \frac{c_v(T_3 - T_4) - c_v(T_2 - T_1)}{c_v(T_3 - T_2)}$$

- For this we need the temperatures on the points 1 to 4
- Therefore, we must find all the temperatures



Example Otto cycle

	$T(K)$	$P(MPa)$	Volume	Entropy
1	300	0.1	v_1	
2	689	1.84	$v_2 = v_1 / 8$	$s_2 = s_1$
3	1123	3.0	$v_3 = v_2$	
4	489	0.16	$v_4 = 8v_3 = v_1$	$s_4 = s_3$



- $1 \rightarrow 2$ isentropic: $P_2 = P_1 (v_1/v_2)^k \rightarrow P_2 = 1.84 \text{ MPa}$
- $T_2 = P_2 v_2 / R = (P_2 T_1) / (8P_1) = 689 \text{ K} \quad (v_2 = v_1 / 8 = RT_1 / 8P_1)$
- $T_3 = ((v_3 P_3) / (v_2 P_2)) T_2 = 1123 \text{ K} \quad (v_2 = v_3)$
- $3 \rightarrow 4$ isentropic: $P_4 = P_3 (v_3/v_4)^k \rightarrow P_4 = 0.16 \text{ MPa}$
- $T_4 = P_4 v_4 / R = (8P_4 T_3) / P_3 = 489 \text{ K} \quad (v_4 = 8v_3 = 8RT_3 / P_3)$

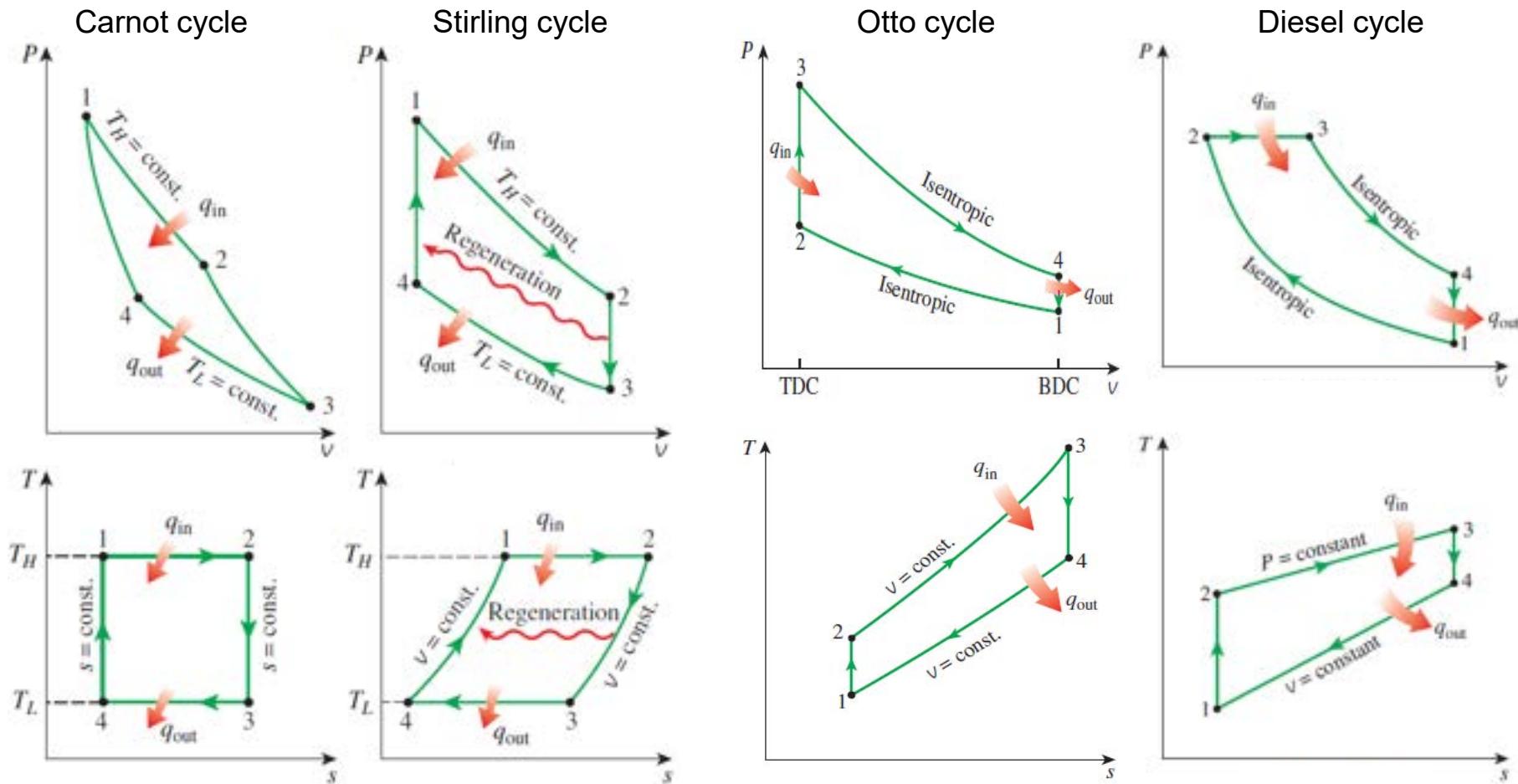
All temperatures lead to:

- $q_{\text{in}} = c_v(T_3 - T_2) = 312 \text{ kJ/kg}$
- $w_{\text{net}} = c_v(T_3 - T_4) - c_v(T_2 - T_1) = 176 \text{ kJ/kg}$

$$\eta_{\text{Otto},ias} = \frac{(T_3 - T_4) - (T_2 - T_1)}{(T_3 - T_2)} = 0.56$$

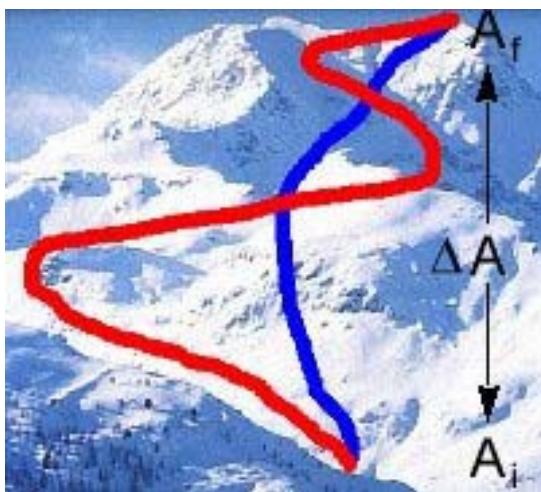
Recapitulate Class 14

- Reciprocating engine cycles, **gas power cycles**, executed in a piston cylinder device undergoing an air standard cycle are analyzed
- Stirling cycle, Otto cycle, Diesel cycle

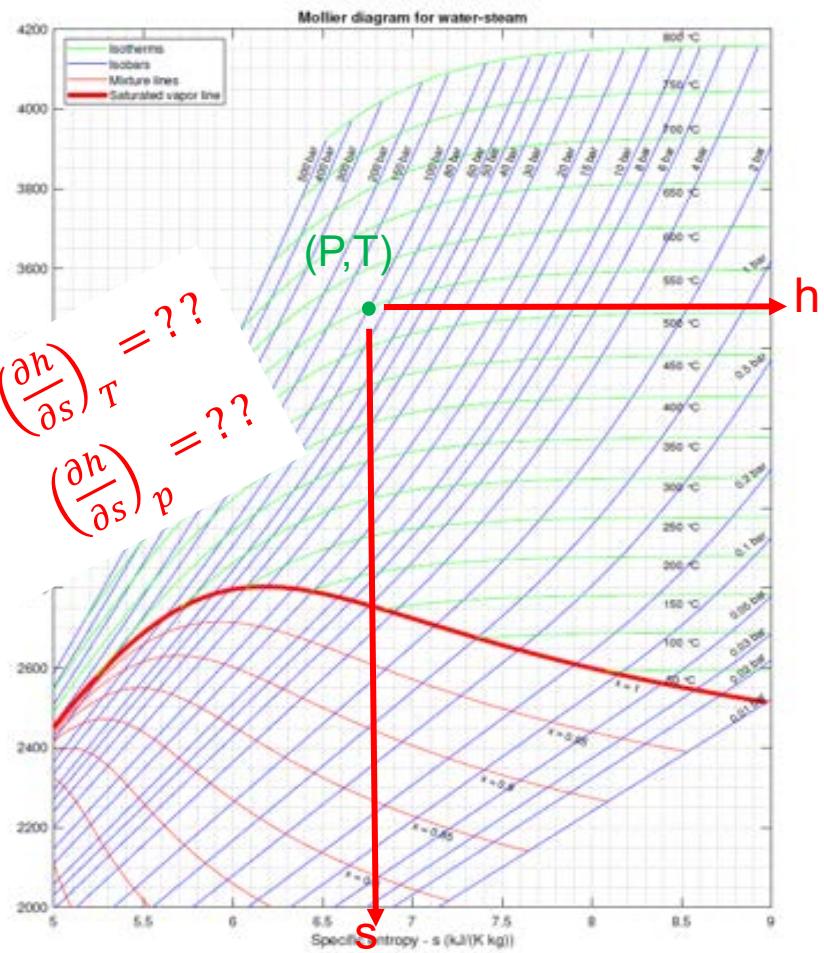


Next Classes 15, 16 & 17: Math Background

- How are tables and diagrams composed?
- How can unknown properties that can not be measured be determined from a set of limited available data?
- **Class 15** → State postulate, thermodynamics and partial derivatives, state and path functions



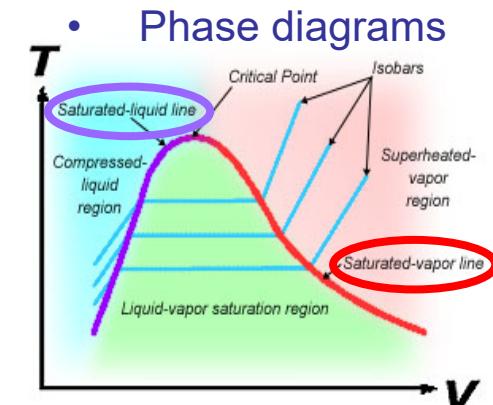
- Isotherms:
- Isobars:



$$dv(P, T) = \left(\frac{\partial v}{\partial T} \right)_p dT + \left(\frac{\partial v}{\partial P} \right)_T dP$$

Keep in mind: Important Formulas

- Specific volume $v = V/m$ [m³/kg] and density $\rho = 1/v = m/V$ [kg/m³]
- Volume work $\delta w = Pdv$
- Enthalpy $h = u + Pv$, (u internal energy, P pressure, v volume)
- Thermal efficiency $\eta_{thermal} = \frac{\text{Net electrical power output}}{\text{Rate of fuel energy input}} = \frac{\dot{W}_{net}}{\dot{Q}_{in}}$
- Mixture fraction $x = \frac{v - v_l}{v_v - v_l} \rightarrow v = v_l + x(v_v - v_l)$
- Ideal gas law $Pv = RT$, $c_p - c_v = R$
- For an ideal gas $du = c_v dT$ and $dh = c_p dT$
- Conservation of mass $m_{in} = m_{out}$, mass flow rate $\dot{m} = \rho v A$
- Conservation of energy, first law of thermodynamics
 - Closed system $du = \delta w - \delta q \rightarrow \Delta u = w - q$
 - 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 $ds \geq \frac{\delta q_{net}}{T_{res}}$ (= for reversible process)
- Reversible heat transfer $\delta q_{net,rev} = Tds$, irreversible $\delta q_{net,irrev} < Tds$
- Gibbs equations $Tds = du + Pdv$ and $Tds = dh - vdP$
- Isentropic efficiencies $\eta_{INPUT,S} = \frac{w_{IN,S}}{w_{IN,A}}$, $\eta_{OUTPUT,S} = \frac{w_{OUT,A}}{w_{OUT,S}}$
- Isentropic processes ideal gas $Pv^k = \text{constant}$, $Tv^{k-1} = \text{constant}$, $P^{(k-1)/k}/T = \text{constant}$
- Thermal efficiency power cycles $\eta_{he} = \frac{w_{out} - w_{in}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$ Carnot efficiency $\eta_{carnot} = 1 - \frac{T_{cold}}{T_{hot}}$



Class 15: Mathematics in Thermodynamics

The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top.

In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are not state functions, but path functions.



General Chemistry: Principles, Patterns, and Applications,
by Bruce Averill and Patricia Eldredge

Thermodynamics so far

- **Class 1 – 5, 9** → Concepts, definitions, energies, properties of air and water, 1 and 2 law, all tools to make and analyze thermodynamic processes en cycles
- **Class 6** → Thermodynamic cycle: a series of processes which return to the initial state
 - **Heat power cycles** produce power from heat
 - **Refrigeration / heat pump cycles** transport heat using power
- **Class 7, 8** → Vapor cycles, cycles using a working medium that undergoes a phase change during the cycle to produce power
 - Steam engine, Rankine cycle (steam turbine cycle), Combined heat and power cycle (co-generation)
- **Class 10, 11, 14** → Properties of gas, gas cycles, cycles using gas as working medium to produce power
 - Brayton cycle (gas turbine cycle, jet engine), combined cycles, Stirling, Otto and Diesel cycle
- **Class 13** → Refrigeration and heat pumps cycles

So far, we learned to use a lot of thermodynamic tools to design and analyze thermodynamic systems

Thermodynamics continued.....

- We used thermodynamic tables and diagrams in the analysis, however we tend to take the tables and diagrams for granted
- We did not ask ourselves how tables and diagrams were prepared and how some unknown properties that can not be measured can be determined from a set of limited available data
- In the **next three classes** we will focus more in depth on
 - Develop fundamental relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties
 - The background of tables and diagrams
 - Develop the Maxwell relations, which form the basis for many thermodynamic relations
 - Develop the Clapeyron equation and determine the enthalpy of vaporization from P, v, and T measurements alone
 - Develop general relations for du, dh, and ds that relate change in u, h and s to changes in P, T and v
 - Discuss the Joule-Thomson coefficient
- **Class 15** → State postulate, thermodynamics and partial derivatives, state and path functions
- **Class 16** → Fundamental relations between thermodynamic properties, Maxwell relations, Clapeyron equation
- **Class 17** → Joule-Thomson coefficient, defined partial derivatives, reduction and evaluation of partial derivatives, find relations for du and dh

Content Class 15

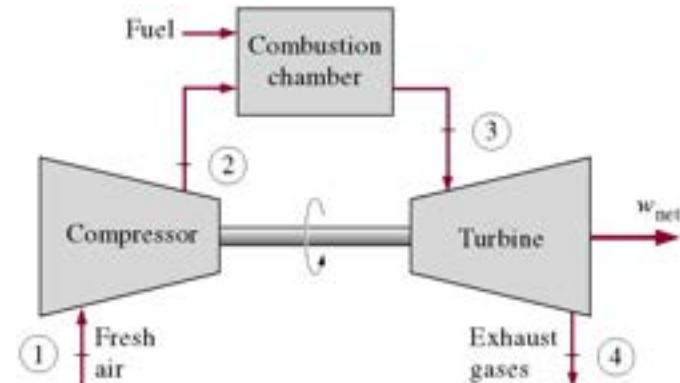
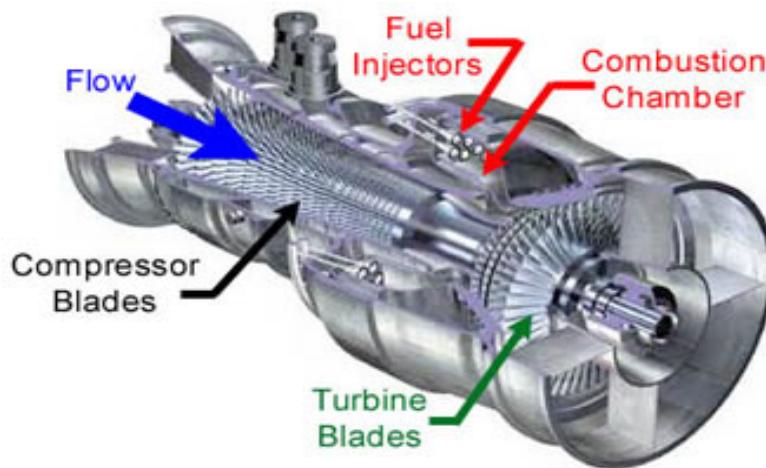
- State postulate, tables and diagrams
- Thermodynamics and partial derivatives
 - A little math: partial derivatives
 - Total differential
 - Relations between partial derivatives
 - Application to ideal gas
 - Geometric representation of partial derivatives
 - Gibbs relations
- Path and state functions
 - Different integration paths & cyclic integral
- Learning goals: Explain the importance of partial derivatives for thermodynamics and apply them to thermodynamic properties & Explain the difference between path- and state functions, determine in which category an energy or quantity fits and explain the consequences of this for the quantity.



Fokke & Sukke:
From 0 to 100
km/h in 3 sec.
Especially if you
crash into a ravine
with your bike.

Work depends on the path taken,
elevation or potential energy
depends only on the state

Example: analysis of a thermodynamic cycle



What do we want to know?

Efficiency, power in- and output,

How do we achieve that?

For this we need data for h , s ,

- Property data from Mollier diagram
- Property data from tables
- Relations e.g., essential for programming / optimization

State Postulate, Tables and Diagrams

- State Postulate:** The state of a simple, compressible substance is completely specified by any two independent, intensive properties. All other properties at that state can be expressed in terms of those two properties

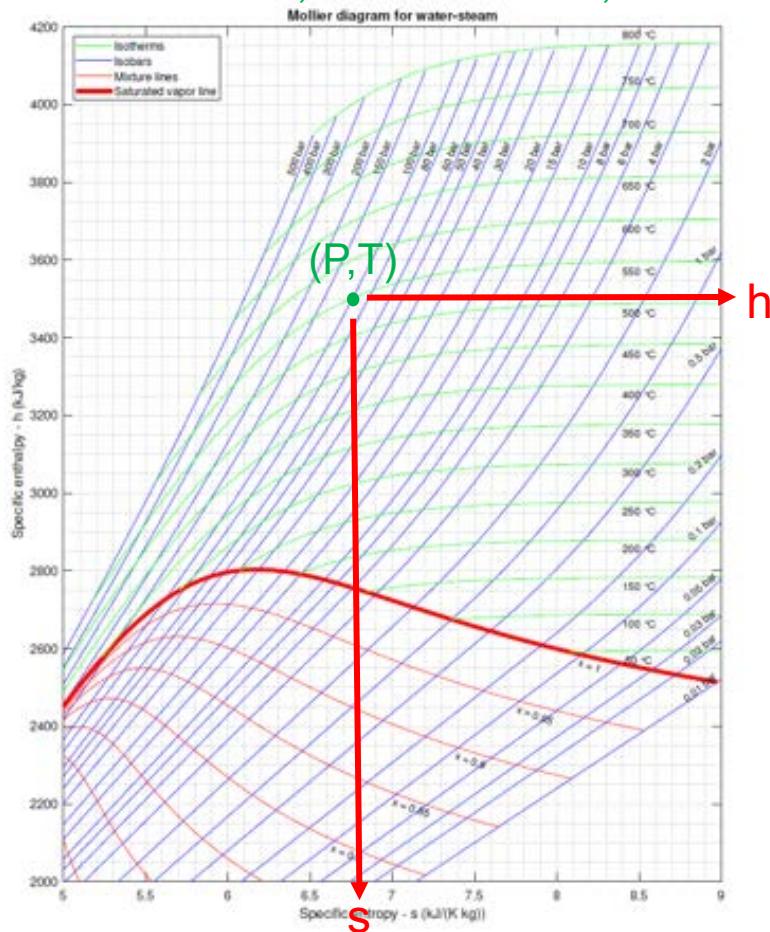
$T = 150^\circ\text{C}$, $x = 0 \rightarrow h, s ?$

Temp (°C)	Pres (Bar)	Specific volume (m³/kg)		Internal Energy (kJ/kg)		Enthalpy (kJ/kg)			Entropy (kJ/kgK)	
T	P	$v_L \times 10^3$	v_v	u_L	u_v	h_L	h_v	h_f	s_L	s_v
120	1.985	1.0603	0.8919	503.50	2529.3	503.71	2202.6	2706.3	1.5276	7.1296
130	2.701	1.0697	0.6685	546.02	2539.9	546.31	2174.2	2720.5	1.6344	7.0289
140	3.613	1.0797	0.5089	588.74	2550.0	589.13	2144.7	2733.9	1.7391	6.9299
150	4.758	1.0905	0.3928	631.68	2559.5	632.20	2114.3	2746.5	1.8418	6.8379
160	6.178	1.1020	0.3071	674.86	2568.4	675.55	2062.6	2758.1	1.9427	6.7502
170	7.917	1.1143	0.2428	718.33	2576.5	719.21	2049.5	2768.7	2.0419	6.6663
180	10.02	1.1274	0.1941	762.09	2583.7	763.22	2015.0	2778.2	2.1396	6.5857

$x = 0$

- Tables and diagrams are used extensively to find values for properties based on two known properties
- How are they build and what are the fundamental relations between the properties ?

$P = 100 \text{ bar}$, $T = 550^\circ\text{C} \rightarrow h, s ?$



Measurable and Non-Measurable Properties

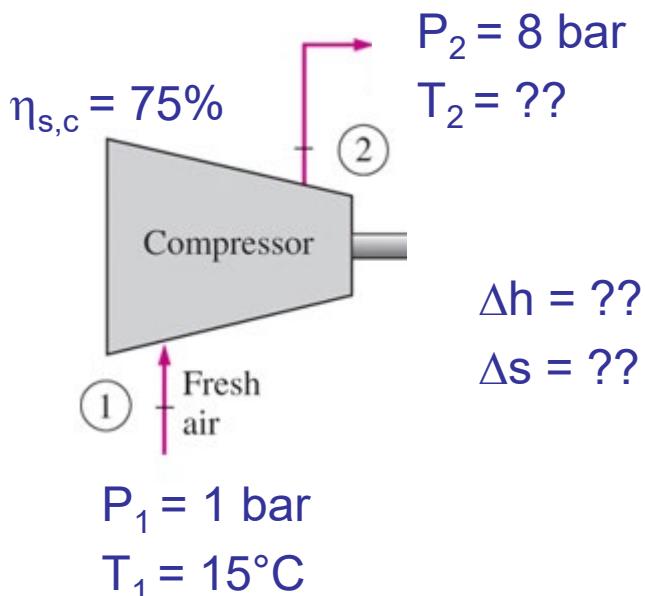
- A lot of properties can be easily measured directly:
 - Temperature
 - Pressure
 - Length (volume)
 - Mass
- Some properties can be determined from them using simple relations:
 - Density
 - Specific volume
- However, a lot of properties are not so easy to determine because they can not be measured or related to easily measurable properties through simple relations:
 - Internal energy
 - Enthalpy
 - Entropy
- Therefore, it is essential to develop relations between commonly encountered properties and express the properties that can not be measured to the ones that easily can be measured



Thermodynamics and Partial Derivatives

- Thermodynamics deals with **changes in properties**
- For calculations **quasi-equilibrium** is assumed and systems are to be expected in equilibrium at all stage of the process
- To calculate changes the total process is divided in infinitesimal small changes and evaluated using **differential mathematics**, therefore most basic thermodynamic relations involve **differentials**
(e.g. $\delta w = Pdv$, or $Tds = du + Pdv$ and $Tds = dh - vdp$ and $ds = \left(\frac{\delta q}{T}\right)_{int,rev}$)
- The state postulate states that **two independent properties** are needed to find all others, mathematically speaking: $f=f(x,y)$ or $v=v(P,T)$
- Realizing that **differentials** are involved in a lot of relations and that **two independent variables** are needed it may be evident that **partial derivatives** play an important role in the derivation of the relations to relate the properties that cannot be measured directly to the ones that easily can be measured

Thermodynamics and Partial Derivatives



- $P, T, v, m \rightarrow$ can be measured
- Sometimes equations of state $\rightarrow P = f(T, v)$ e.g., $P = RT/v$
- Density / specific volume \rightarrow simple relations
- What about: $h, u, s ???$

- **Partial derivatives:** $dh(P, T) = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial P}\right)_T dP \rightarrow \int_1^2 dh(P, T) = \Delta h$
 $\left(\frac{\partial h}{\partial T}\right)_p = ??$ and $\left(\frac{\partial h}{\partial P}\right)_T = ??$
- Using partial derivatives, we can write h as a function of T and P and when we find an expression for $\left(\frac{\partial h}{\partial T}\right)_p$ and $\left(\frac{\partial h}{\partial P}\right)_T$ we can calculate the change in h knowing the change in P and T

Thermodynamics and Partial Derivatives

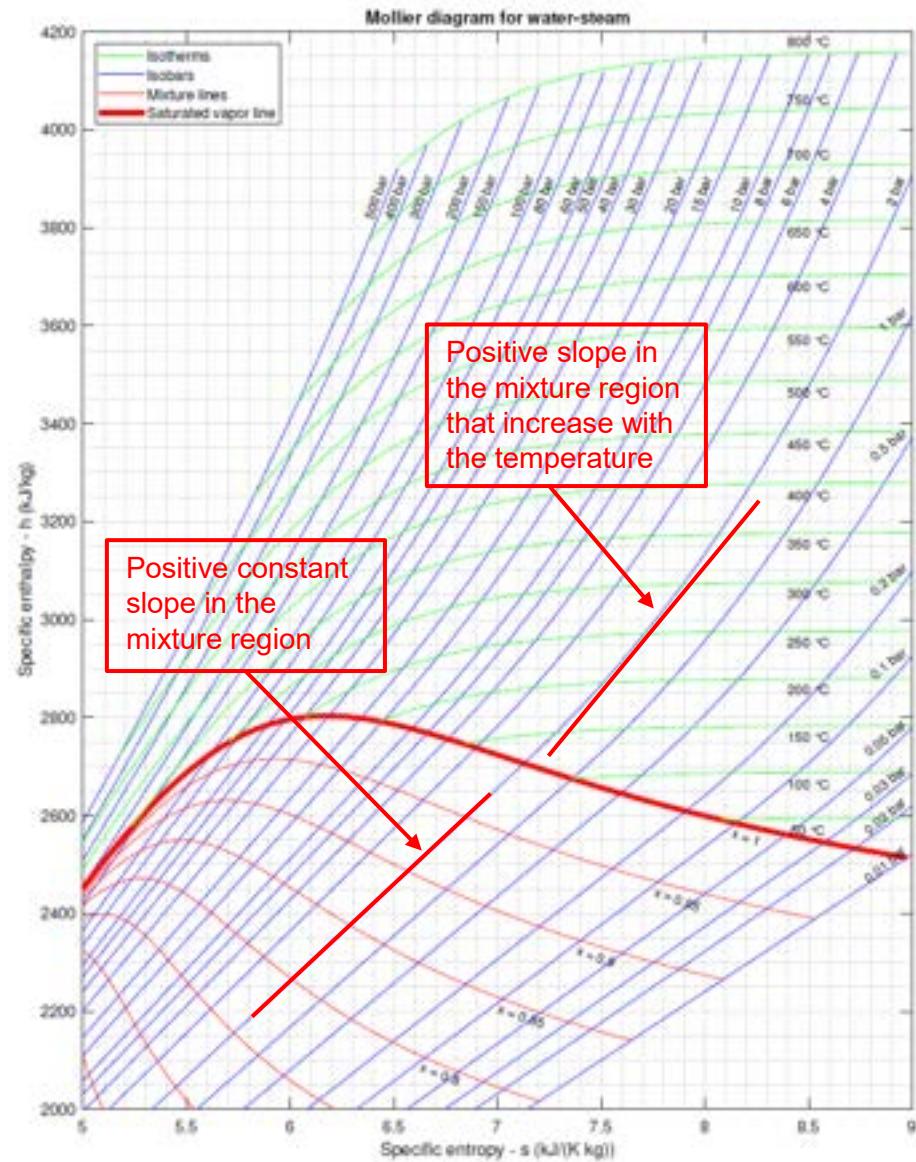
- **Mollier diagram**

- Isotherms: $\left(\frac{\partial h}{\partial s}\right)_T = ??$

- Isobars: $\left(\frac{\partial h}{\partial s}\right)_p = ??$

- Partial derivatives determine the lines in the diagrams and give insight in the behavior of fluids under different circumstances

- Note the difference of the slopes of the tangent line in the mixture and the superheated region



Review Theory of Partial Derivatives

- If you don't know it anymore, review the basic theory of partial derivatives, there are different ways to do this:

1: Refresh the theory about partial derivatives as taught in Calculus 2

2: Document *Math Background for Thermodynamics*, a small summary with an explanation about partial derivatives in the context of Thermodynamics with some small exercises:

<http://mutuslab.cs.uwindsor.ca/schurko/introphyschem/handouts/mathsh.pdf>

3: A video with a general explanation about partial derivatives (author Dale J. Brugh). First, second, and mixed partial derivatives of multi-variable functions are introduced, and geometric and physical interpretations are provided. <https://www.youtube.com/watch?v=1QuN2miiE34>

4: A video of Greg Birkett, from The university of Queensland with an explanation of partial derivatives related to thermodynamics. Why we need property relations and how partial derivatives can help. It explains the use of partial derivatives in Thermodynamics. <https://www.youtube.com/watch?v=RtnCqiskcCk&t=93s>

Thermodynamic relations and partial derivatives: better together

At the end of this video, you will be able to:

- Explain why we are interested in partial derivatives in thermodynamics
- Use partial derivatives to calculate a change in a variable

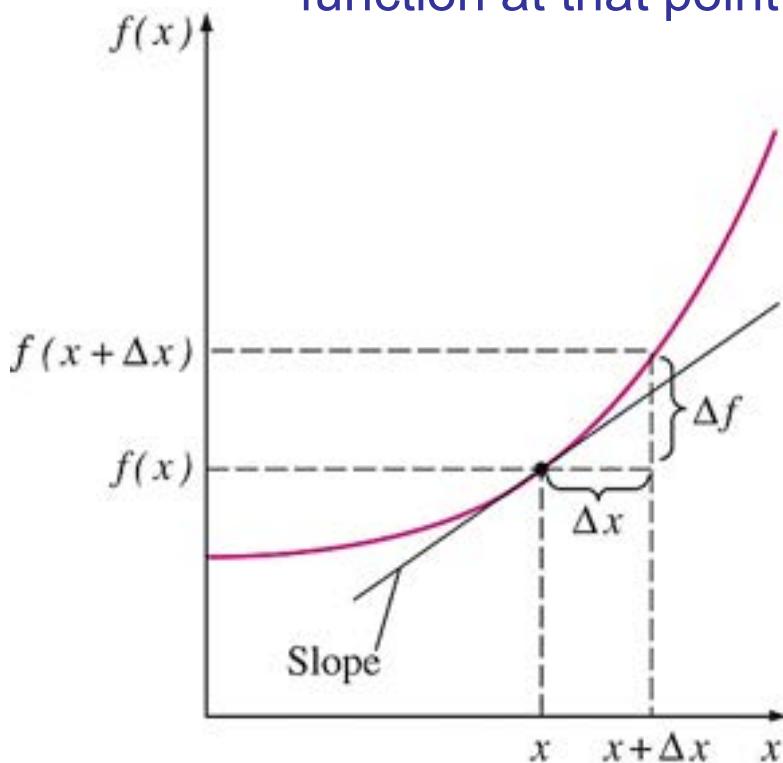
Recap

Even though we do have equations of state to relate P, T and V, we do not have equations for u, h and s. The total differential is comprised of partial differentials with respect to each other.

We are already familiar with the partial differentials of c_v and c_p .

A little Math: Derivative of a Function

- For a function $f(x)$, that depends on one variable, x , yields:
 - The steepness of the curve is a measure of the dependence of f on x
 - The steepness is measured by the slope of a line tangent to the curve at that point and equal to the derivative of the function at that point



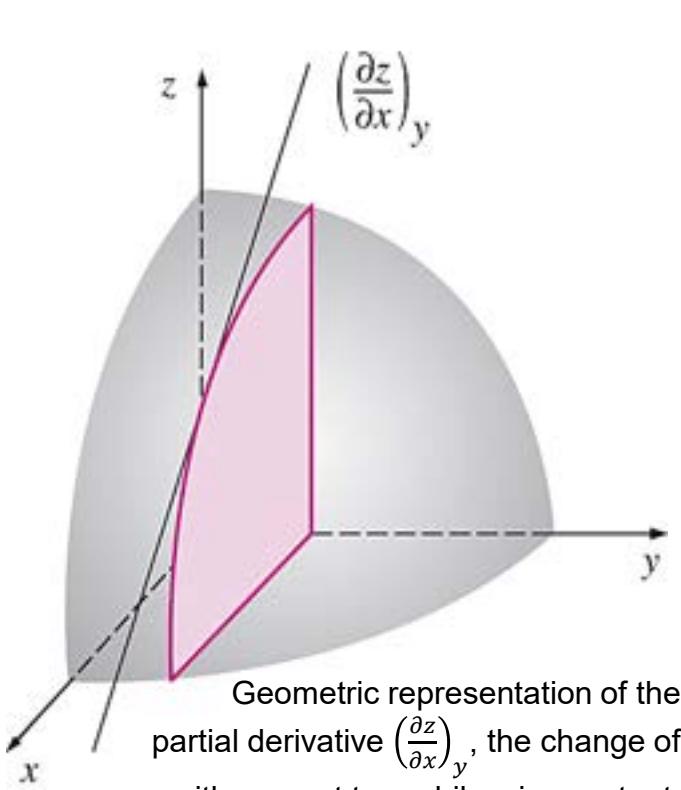
$$\frac{df}{dx} = \lim_{\Delta x \rightarrow 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

- Therefore, the derivative of a function $f(x)$ with respect to x represents the rate of change of f with x

The derivative of a function $f(x)$, that depends on only one variable, x , at a specified point represents the slope of the function

A little Math: Partial Derivatives

- However, in thermodynamics one variable is not enough so consider a function $z(x,y)$ of two variables, (x,y) :
- The variation of $z(x,y)$ with x when y is held constant is called the **partial derivative** of z with respect to x , and it is expressed as



$$\left(\frac{\partial z}{\partial x}\right)_y = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta z}{\Delta x}\right)_y = \lim_{\Delta x \rightarrow 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x}$$

- Note that the value of the partial derivative, $\left(\frac{\partial z}{\partial x}\right)_y$, in general, is different at different values of y .

The symbol ∂ represents differential changes, just like the symbol d . They differ in that the symbol d represents the *total* differential change of a function and reflects the influence of all variables, whereas ∂ represents the *partial* differential change due to the variation of a single variable.

Tower of Babel: Confusion of Tongues

- In our non-ideal world live mathematician, chemists, physicist, engineers....
- Everyone speaks his own language and uses his own notations
- Chemists like mols, engineers prefer to use (kilo) grams
- Mathematicians often use different notations than engineers
- For partial derivatives, many notations are used,
as also indicated in Calculus books:

Example:
Ideal gas law
 $Pv = RT$ or
 $PV = nR_u T$

There are many alternative notations for partial derivatives. For instance, instead of f_x we can write f_1 or $D_1 f$ (to indicate differentiation with respect to the *first* variable) or $\partial f / \partial x$. But here $\partial f / \partial x$ can't be interpreted as a ratio of differentials.

NOTATIONS FOR PARTIAL DERIVATIVES If $z = f(x, y)$, we write

Calculus: Early
Transcendentals
blz. 880

$$f_x(x, y) = f_x = \frac{\partial f}{\partial x} = \frac{\partial}{\partial x} f(x, y) = \frac{\partial z}{\partial x} = f_1 = D_1 f = D_x f$$

$$f_y(x, y) = f_y = \frac{\partial f}{\partial y} = \frac{\partial}{\partial y} f(x, y) = \frac{\partial z}{\partial y} = f_2 = D_2 f = D_y f$$



The Great Tower of Babel (Pieter Breughel the Elder, 1563, to be seen in the Museum of Art History in Vienna). The Tower of Babel is a mythical building that has never been completed because people did not understand each other as they spoke a different language.

Tower of Babel: Confusion of Tongues

- Mathematicians often use different notations than engineers and for partial derivatives many notations are used
- In mathematics you use the notation: f_x or f_y to indicate a (partial) derivative or f_{xx} and f_{yy} to indicate a double derivative
- In most disciplines in mechanical engineering (e.g., thermodynamics and fluid mechanics) preference is given to a different notation
- For derivatives $\rightarrow f_x = \left(\frac{\partial f}{\partial x}\right)_y$ and $f_y = \left(\frac{\partial f}{\partial y}\right)_x$
- For double derivatives $\rightarrow f_{xx} = \left(\frac{\partial^2 f}{\partial x^2}\right)_y$ and $f_{yy} = \left(\frac{\partial^2 f}{\partial y^2}\right)_x$
- Note that in the notation that is used in mechanical engineering is also indicated which variable is kept constant, this is especially important if more than two variables play a role, compare the specific heat at constant pressure and at constant volume: $c_p = T \left(\frac{\partial s}{\partial T}\right)_p$ and $c_v = T \left(\frac{\partial s}{\partial T}\right)_v$
- Another constant can represent another variable or have another meaning

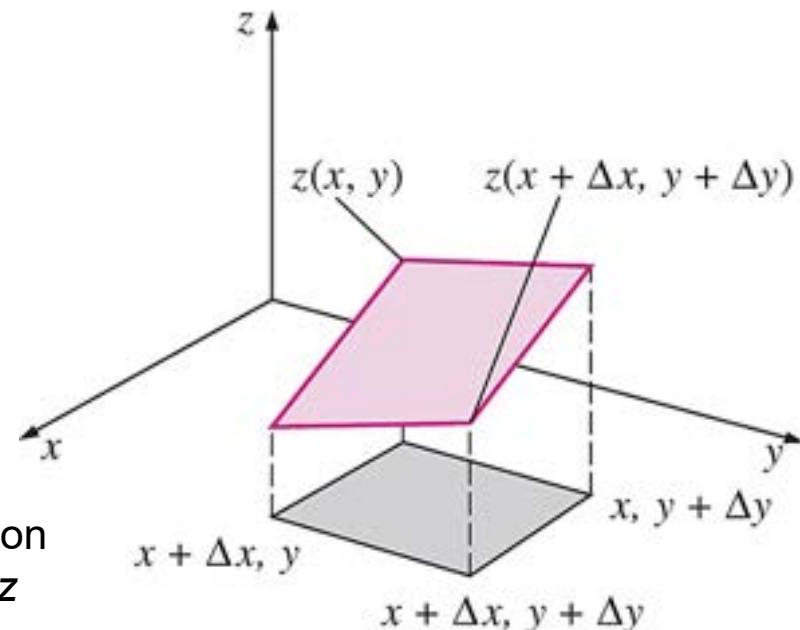
A little Math: Total Differential

- The total differential change of a variable z that depends on x and y , $z(x,y)$ for changes in both x and y , is expressed as:

$$dz(x,y) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

- Note: x, y independent variables, z dependent of x and y
- This is the **fundamental relation** for the **total differential** of a dependent variable in terms of its partial derivatives with respect to the independent variables
- It describes the change in z , with respect to changes in x and y

Geometric representation of the total derivative dz for a function $z(x, y)$.



Relations between Partial Derivatives

- Reciprocity relation:

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

- Cyclic relation (or minus one (-1) rule or triple product rule):

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

- Chain rule:

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y = \frac{\left(\frac{\partial x}{\partial w}\right)_y}{\left(\frac{\partial z}{\partial w}\right)_y}$$

A new variable is introduced

Demonstration of
the reciprocity relation for
the function $z + 2xy - 3y^2z$

Function: $z + 2xy - 3y^2z = 0$

$$1) z = \frac{2xy}{3y^2 - 1} \rightarrow \left(\frac{\partial z}{\partial x}\right)_y = \frac{2y}{3y^2 - 1}$$

$$2) x = \frac{3y^2z - z}{2y} \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{3y^2 - 1}{2y}$$

$$\text{Thus, } \left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y}$$

Relations between Partial Derivatives

- The total differential: $dz(x, y) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Mdx + Ndy$

with $M = \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$

- Differentiation of M to x and N to y results in mixed differentials:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x}\right)_y\right)_x = \frac{\partial^2 z}{\partial y \partial x}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y}\right)_x\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

- For properties the order of differentiation is immaterial since they are continuous point functions and have exact differentials:

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} \text{ and therefore } \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

- Note this relation is only valid for total or exact differentials (state functions) and NOT for non-total or non-exact differentials (path functions)

Translation to Thermodynamics

- Consider an ideal gas and analyze how the volume changes with respect to the temperature, T and the pressure, P
- Realize that this is mathematically equal to the analysis of a function for the volume v that depends on P and T , $v(P, T)$
- The **total differential** of v as function of P and T is expressed as:

$$dv(P, T) = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial P}\right)_T dP$$

Note: P, T , independent variables, v dependent of P and T



- $dv(P, T)$ describes the change of the volume
- dT and dP are the changes in pressure and temperature
- $\left(\frac{\partial v}{\partial T}\right)_p$ describes how the volume changes with respect to T if P is constant
- $\left(\frac{\partial v}{\partial P}\right)_T$ describes how the volume changes with respect to P if T is constant
- Next step is to evaluate the partial differentials

Partial Derivatives for ideal gas

- The total differential of the v as function of P and T is expressed as:

$$dv(P, T) = \left(\frac{\partial v}{\partial T} \right)_P dT + \left(\frac{\partial v}{\partial P} \right)_T dP$$

We are lucky, as for an ideal gas we know the equation of state that relates the variables: $v, P, T \rightarrow Pv = RT \rightarrow v = \frac{RT}{P}$

- This gives : $\left(\frac{\partial v}{\partial T} \right)_P = \frac{R}{P} = \frac{v}{T}$ and $\left(\frac{\partial v}{\partial P} \right)_T = -\frac{RT}{P^2} = -\frac{v}{P}$
- And the total differential can be written as

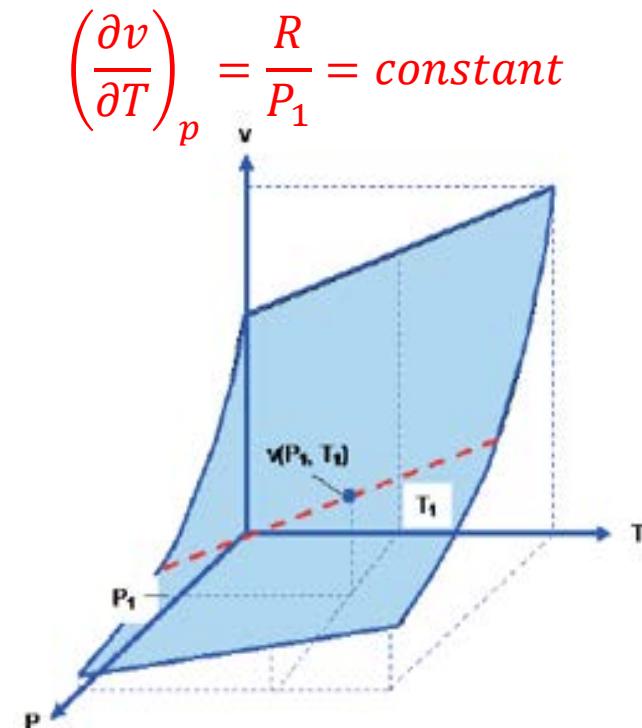
$$dv(P, T) = \frac{R}{P} dT - \frac{RT}{P^2} dP = \frac{v}{T} dT - \frac{v}{P} dP$$

- This way the volume change as a result of differential changes in temperature and pressure can be determined, approximating $dT \cong \Delta T$ and $dp \cong \Delta P$ and using average values for P and T gives:

$$\Delta v(P, T) = \frac{R}{P} \Delta T - \frac{RT}{P^2} \Delta P$$

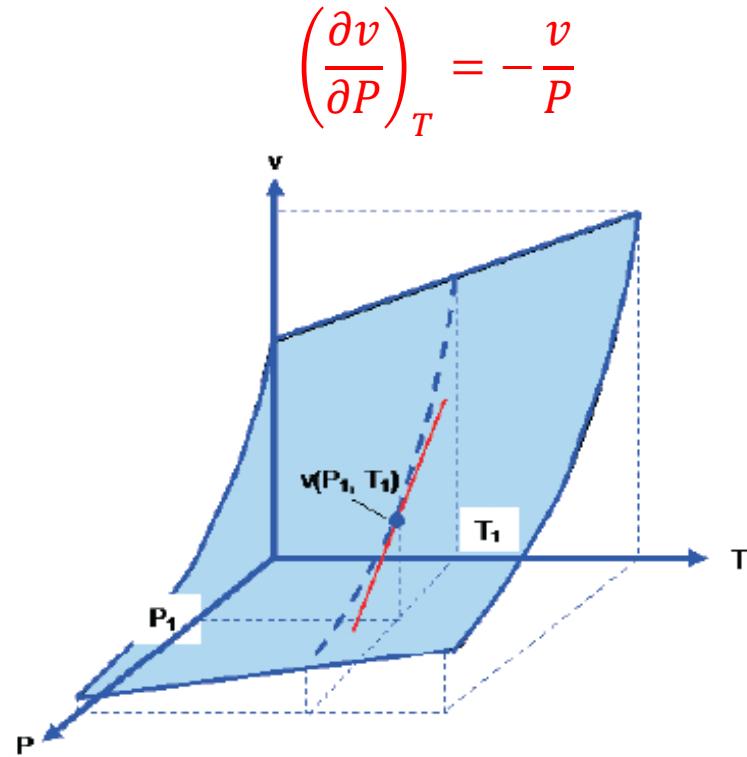
Geometric Representation

- For an ideal gas: $dv(P, T) = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial P}\right)_T dP = \frac{R}{P} dT - \frac{v}{P} dP$
- The partial derivatives can be represented in the PTv – diagram that gives the $v(P, T)$ as function of P and T
- Consider a constant arbitrary value of P (e.g. P_1) while T varies
- The slope of the line is given by the partial derivative: $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P_1}$
- In this case the slope is constant (R and P_1 are constant) and therefore the volume increases linear with T : $\Delta v(T) = \frac{R}{P_1} \Delta T$
- For an other value of P the slope is different and the relation between v and T is different
- The smaller P the steeper the slope and the larger the change in volume



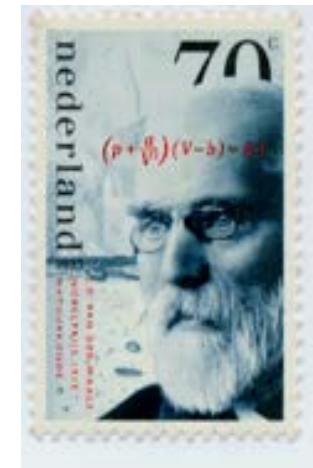
Geometric Representation

- For an ideal gas: $dv(P, T) = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial P}\right)_T dP = \frac{R}{P} dT - \frac{v}{P} dP$
- The partial derivatives can be represented in the PTv – diagram that gives the $v(P, T)$ as function of P and T
- Consider a constant arbitrary value of T (e.g. T_1) while P varies
- The slope of the line is given by the partial derivative: $\left(\frac{\partial v}{\partial P}\right)_T = -\frac{v}{P}$
- In this case the slope is not constant
- The slope depends on P and the volume decreases (- sign) with $1/P$ for an arbitrary value of T
- If P gets smaller the slope gets steeper



Partial Derivatives for Ideal Gas

- For an ideal gas: $dv(P, T) = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial P}\right)_T dP = \frac{R}{P} dT - \frac{v}{P} dP$
- In this case **we are lucky!**
- The ideal gas is very special because we know exactly how it behaves and we have a (very) simple equation of state $Pv = RT$ to describe it and therefore we can easily evaluate the partial derivative
- It already gets more complicated as we use a different (more accurate) equation of state to describe the ideal gas
- **Van der Waals equation of state:** $\left(P + \frac{a}{v^2}\right)(v - b) = RT$
- Includes two effects not considered in the ideal gas model
 1. Factor a: the intermolecular attraction forces
 2. Factor b: Volume occupied by molecules themselves
- Evaluation of the partial derivatives will result in different expressions, see assignment → 3.6



Partial Derivatives for Ideal Gas

- But still we are lucky!
- Even with a more complicated equation of state like the Van der Waals equation we are able to evaluate the partial derivatives
- For a lot of other cases we do not have (simple) equations that relate the variables, e.g. for water / steam or for variables like energies and entropy
- What if we want to relate changes in entropy, s to changes in pressure, P and temperature, T
- Total differential: $ds(P, T) = \left(\frac{\partial s}{\partial P}\right)_T dP + \left(\frac{\partial s}{\partial T}\right)_P dT$
- What is the expression for $\left(\frac{\partial s}{\partial P}\right)_T$ or $\left(\frac{\partial s}{\partial T}\right)_P$?
- Or the change of the enthalpy with changes of entropy and temperature ?
- Total differential: $dh(T, s) = \left(\frac{\partial h}{\partial s}\right)_T ds + \left(\frac{\partial h}{\partial T}\right)_s dT$

Recall The Gibbs Relations

- The Gibbs equations were used before
- They are derived from simple basic thermodynamic relations

- First law: $du = \delta q - \delta w$
- Volume work: $\delta w = Pdv$
- Clausius inequality: $ds = \left(\frac{\delta q}{T}\right)_{int,rev}$

Internal energy → $u(s,v)$
 $du = Tds - Pdv$

- **Enthalpy** → $h(s,P)$
 $h = u + Pv \rightarrow dh = du + d(Pv) = Tds - Pdv + Pdv + vdP = Tds + vdP$
- **Gibbs relations**
 - $Tds = du + Pdv \rightarrow du = Tds - Pdv$
 - $Tds = dh - vdP \rightarrow dh = Tds + vdP$
- They can be used to determine some important partial derivatives

The Gibbs Relations

- Compare Gibbs equations with total derivatives of $u(s,v)$ & $h(s,P)$
- Int. energy $\rightarrow u(s,v) \rightarrow du(s,v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv = Tds - Pdv$
- Enthalpy $\rightarrow h(s,P) \rightarrow dh(s,P) = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP = Tds + vdp$

→ This gives for the partial derivatives:

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_s = -P$$

$$\left(\frac{\partial h}{\partial s}\right)_P = T \quad \text{and} \quad \left(\frac{\partial h}{\partial P}\right)_s = v$$

Definition of temperature

$$\left(\frac{\partial u}{\partial s}\right)_v \equiv T$$

So, we already have an expression for 4 different partial derivatives

Note that $\left(\frac{\partial h}{\partial s}\right)_P = T$ is the expression for the isobar in the Mollier diagram

The Gibbs Relations

- Instead of $u(s, v)$ we can look at $s(u, v)$:
- Entropy as a function of internal energy and volume, $s(u, v)$
 - Total differential: $ds(u, v) = \left(\frac{\partial s}{\partial u}\right)_v du + \left(\frac{\partial s}{\partial v}\right)_u dv$
- From the Gibbs equations: $du = Tds - Pdv \rightarrow ds = \frac{1}{T}du + \frac{P}{T}dv$
- Comparing both equations gives for the partial derivatives:
$$\left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_u = \frac{P}{T}$$
- Note: $\left(\frac{\partial s}{\partial u}\right)_v = \left(\frac{\partial u}{\partial s}\right)^{-1}_v = T^{-1} = \frac{1}{T}$ Here you see that this part. derv. also, could have been found from the one on the previous page and the reciprocity relation
- Note: these partial derivatives meet observations / expectations for entropy
 - Increasing internal energy \rightarrow increasing entropy
 - Increasing volume \rightarrow increasing entropy

In Conclusion

1. **State postulate:** we need two independent properties to describe a simple system
2. The change of a third property can be determined using the total differential of the property as a function of the known properties, e.g. for the internal energy as a function of entropy and volume, $u(s,v)$:

$$du(s,v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv = Tds - Pdv$$

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_s = -P$$

3. Knowing $u(s,v)$ we can find T and P but also $h (= u+Pv)$ and v and s
- A function like $u(s,v)$ or $h(s,P)$ that contains all thermodynamic data for properties is called a **fundamental thermodynamic equation**
 - $u(s,v)$ is a fundamental equation in the energy representation
 - $s(u,v)$ is a fundamental equation in the entropy representation
 - In class 16 we will meet two more fundamental equations
 - Helmholtz energy, $a(T,v)$ and Gibbs energy, $g(T,P)$

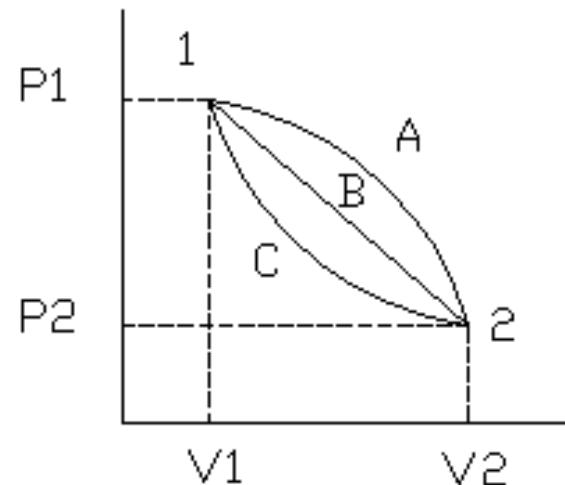
Path and State Functions

- Travel from The Netherlands to Monaco
- Different methods of transportation
- Different variables are involved:
 - Travel time
 - Used fuel
 - Distance NL – Monaco
 - Costs
 - Travel distance
 - Height difference NL – Monaco
 - Difference in temperature / pressure
 - Irritation
- Some are the same for all ways to travel others are different for every transportation



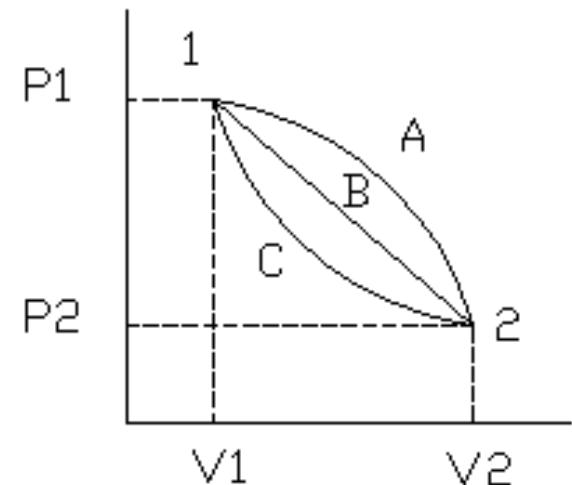
State Function

- In thermodynamics, a **state function, point function, state/point quantity or state/point variable** is a property of a system that depends only on the current state of the system and not on the way in which the system acquired that state (independent of path)
- A state function describes the equilibrium state of a system
- Examples of state quantities are temperature, pressure, internal energy, enthalpy and entropy because they describe an equilibrium state of a thermodynamic system, independently of how the system arrived at that state
- There are two states (P_1, V_1) and (P_2, V_2)
- Pressure and volume are state functions
- These are definite values for a given state
- The change in these properties is independent of the path followed and depends only on the initial and final state of the process



Path Function

- In thermodynamics, a **path function, process function, path/process quantity or path/process variable** is a quantity whose value depends on the path of a process through the equilibrium state space of a thermodynamic system
- Path functions depend on the path or process a system undergoes to reach one state from another, they describe the transition between equilibrium states of a thermodynamic system and different routes (processes or paths) give different value for the quantities
- Examples of path functions include work, heat transfer and entropy generation
- There are three paths A, B, and C
- The area below the curve gives the amount of work involved in each process / path
- Thus, the value of work depends upon the path and not on the end state of the process
- Hence work (but also heat) is a path function



Mathematics of Path and State Functions

- Work and heat are process or path functions because their values depend on the specific process or path between two equilibrium states
- In contrast to path functions, state functions or point functions are independent of the path taken and depend only on the state properties
- The path between two states plays a key role to mathematically determine between path and state functions, let us have a look at infinitesimal changes of the variables
- Infinitesimal changes in a process function may be integrated, but the integral between two states depends on the particular path taken between the two states, whereas the integral of a state function is simply the difference of the state function at the two points, independent of the path taken
- Infinitesimal changes in a process function x are often indicated by δx to distinguish them from infinitesimal changes in a state function y which is written dy
- The quantity dy is an exact differential, while δx is not an exact differential

Mathematics of Path and State Functions

- How to distinguish between path and state functions mathematically?
- State functions have exact or total differentials → dx
- Path functions non-exact or non-total differentials → δx
- What are the properties of exact or total differentials?
 - Only one solution, which is independent of the integration path
 - For a closed path (returning to the initial value) the integral is zero
- What are the properties of non-exact or non-total differentials?
 - The solution depends on the integration path
 - For a closed path the integral returns a value which is not zero
- Let us have a look at two differential functions:
$$\delta z(x, y) = xydx + (x^2 + 2y)dy$$
$$dz(x, y) = \textcircled{2}xydx + (x^2 + 2y)dy$$
- But first: Take notation of all the different symbols: d, δ , ∂ , Δ

All different Symbols: d , δ , ∂ , Δ

- x is a path function and y is a state function
- δ differential change of path function $\rightarrow \delta x$ (non exact differential)
- d total differential change of a state function that takes into account the variation of all variables $\rightarrow dy$ (exact or total differential)
- ∂ partial differential change of a function due to the variation of a single variable $\rightarrow \partial y$ (partial differential)
- Δ indicates a difference between two states, e.g., the initial and the final state of a process $\rightarrow y_{final} - y_{initial} = \Delta y$ (difference)
- Integration between two states 1 and 2
- Path function: $\int_1^2 \delta x = x$ (note: **not** Δx , there is no difference but only one value for the integration path, therefore $\int_1^2 \delta q = q$ or $\int_1^2 \delta w = w$)
- State function: $\int_1^2 dy = y_2 - y_1 = \Delta y$
- $dy, \partial y, \delta y$ are infinitesimal small changes that must be integrated
- Δy is a finite change after integration

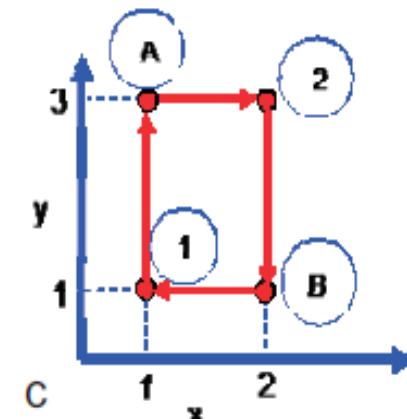
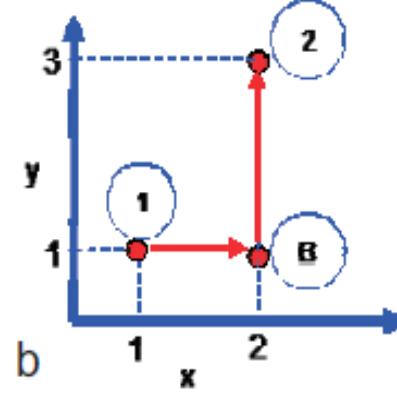
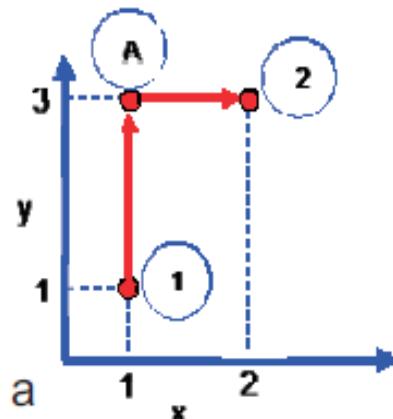
Mathematics of Path and State Functions

- Let us have a look at two differential functions:

First one: $\delta z(x, y) = xydx + (x^2 + 2y)dy$

Second one: $dz(x, y) = \cancel{2}xydx + (x^2 + 2y)dy$

- Consider the change from state 1 to state 2 via two different paths, A and B, i.e., perform the integration $1 \rightarrow A \rightarrow 2$ & $1 \rightarrow B \rightarrow 2$ for both functions
- Consider a closed cycle and perform the cyclic integral (denoted by $\oint dx$) over the closed path, i.e., perform the integration $1 \rightarrow A \rightarrow 2 \rightarrow B \rightarrow 1$

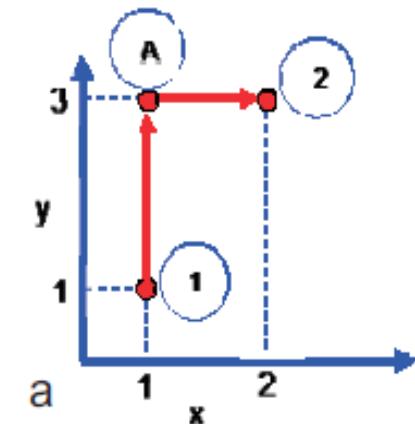


Two different paths to go from state 1 to state 2

A closed path, cyclic integral

Mathematics of Path and State Functions

- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- First path: $1 \rightarrow A \rightarrow 2$ is $(1,1) \rightarrow (1,3) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow A$ and $A \rightarrow 2$ which are evaluated and added



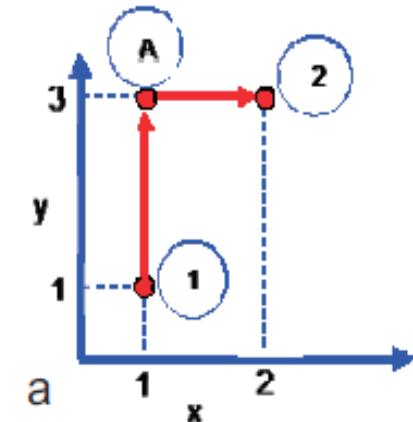
$$\int_1^A \delta z = \left[\int_{x=1}^{x=1} xydx \right] + \left[\int_{y=1}^{y=3} (x^2 + 2y)dy \right]_{x=1, dx=0} =$$

$$\int_A^2 \delta z = \left[\int_1^2 xydx \right]_{y=3, dy=0} + \left[\int_3^3 (x^2 + 2y)dy \right] =$$

- Work out the differentials

Mathematics of Path and State Functions

- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- First path: $1 \rightarrow A \rightarrow 2$ is $(1,1) \rightarrow (1,3) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow A$ and $A \rightarrow 2$ which are evaluated and added



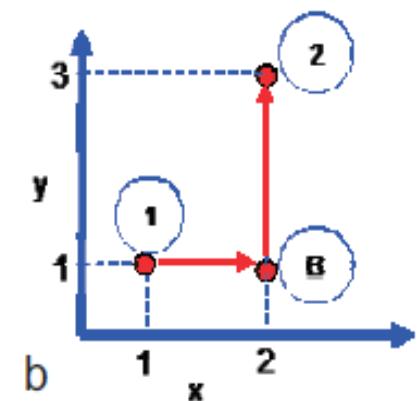
$$\int_1^A \delta z = \left[\int_{x=1}^{x=1} xydx \right] + \left[\int_{y=1}^{y=3} (x^2 + 2y)dy \right]_{x=1, dx=0} = \frac{1}{2}x^2y \Big|_1^1 + x^2y \Big|_1^3 + y^2 \Big|_1^3 = 0 + (3 - 1) + (3^2 - 1^2) = 10$$

$$\int_A^2 \delta z = \left[\int_1^2 xydx \right]_{y=3, dy=0} + \left[\int_3^2 (x^2 + 2y)dy \right] = \frac{1}{2}x^2y \Big|_1^2 + x^2y \Big|_3^2 + y^2 \Big|_3^2 = (6 - \frac{3}{2}) + 0 + 0 = 4.5$$

- Addition results in a value of 14.5 for the total path: $\int_{1-A-2} \delta z = 10 + 4.5 = 14.5$

Mathematics of Path and State Functions

- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- Second path: 1 → B → 2 is $(1,1) \rightarrow (2,1) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow B$ and $B \rightarrow 2$ which are evaluated and added



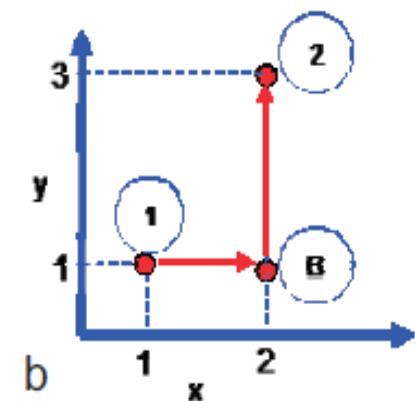
$$\int_{1-B} \delta z = \left[\int_1^2 xy dx \right]_{y=1, dy=0} + \left[\int_1^1 (x^2 + 2y) dy \right] =$$

$$\int_{B-2} \delta z = \left[\int_2^2 xy dx \right] + \left[\int_1^3 (x^2 + 2y) dy \right]_{x=2, dx=0} =$$

- Work out the differentials

Mathematics of Path and State Functions

- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- Second path: 1 → B → 2 is $(1,1) \rightarrow (2,1) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow B$ and $B \rightarrow 2$ which are evaluated and added



$$\int_{1-B} \delta z = \left[\int_1^2 xy dx \right]_{y=1, dy=0} + \left[\int_1^1 (x^2 + 2y) dy \right] = \frac{1}{2} x^2 y \Big|_1^2 + (x^2 y + y^2) \Big|_1^1 = (\frac{1}{2} 2^2 - \frac{1}{2}) + 0 = 1.5$$

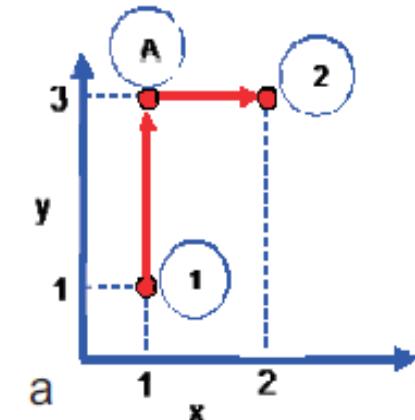
$$\int_{B-2} \delta z = \left[\int_2^2 xy dx \right] + \left[\int_1^3 (x^2 + 2y) dy \right]_{x=2, dx=0} = \frac{1}{2} x^2 y \Big|_2^2 + (x^2 y + y^2) \Big|_1^3 = 0 + (2^2 \cdot 3 + 3^2) - (2^2 \cdot 1 + 1^2) = 21 - 5 = 16$$

- Addition results in a value of 17.5 for the total path:

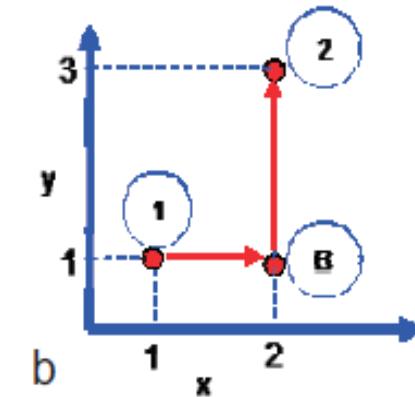
$$\int_{1-B-2} \delta z = 16 + 1.5 = 17.5$$

Mathematics of Path and State Functions

- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- State $1 \rightarrow 2$ is $(1,1) \rightarrow (2,3)$
- First path: $1 \rightarrow A \rightarrow 2$ is $(1,1) \rightarrow (1,3) \rightarrow (2,3)$
- The result is: 14.5 for the total path

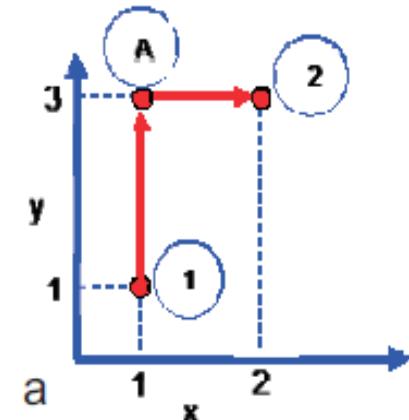


- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- State $1 \rightarrow 2$ is $(1,1) \rightarrow (2,3)$
- Second path: $1 \rightarrow B \rightarrow 2$ is $(1,1) \rightarrow (2,1) \rightarrow (2,3)$
- The result is: 17.5 for the total path
- If we compare the results of both paths we see that their value is **different** and thus we can conclude that the result depends on the path of integration and therefore the differential is not-exact and the function is a path function



Mathematics of Path and State Functions

- Second function: $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- First path: $1 \rightarrow A \rightarrow 2$ is $(1,1) \rightarrow (1,3) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow A$ and $A \rightarrow 2$ which are evaluated and added



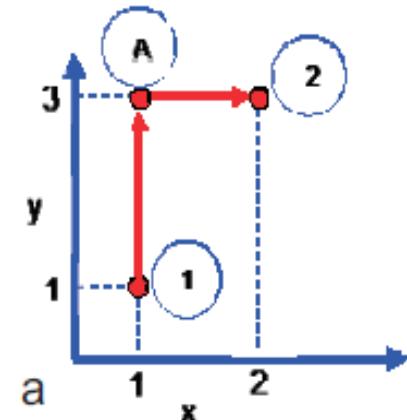
$$\int_{1-A} dz = \left[\int_1^1 2xy dx \right] + \left[\int_1^3 (x^2 + 2y) dy \right]_{x=1, dx=0} =$$

$$\int_{A-2} dz = \left[\int_1^2 2xy dx \right]_{y=3, dy=0} + \left[\int_3^3 (x^2 + 2y) dy \right] =$$

- Work out the partial differentials

Mathematics of Path and State Functions

- Second function: $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- First path: $1 \rightarrow A \rightarrow 2$ is $(1,1) \rightarrow (1,3) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow A$ and $A \rightarrow 2$ which are evaluated and added



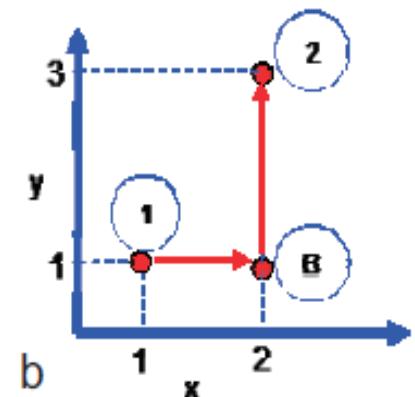
$$\int_{1-A} dz = \left[\int_1^1 2xy dx \right] + \left[\int_1^3 (x^2 + 2y) dy \right]_{x=1, dx=0} = x^2 y \Big|_1^1 + (x^2 y + y^2) \Big|_1^3 = 0 + (3 + 3^2) - (1 + 1^2) = 10$$

$$\int_{A-2} dz = \left[\int_1^2 2xy dx \right]_{y=3, dy=0} + \left[\int_3^3 (x^2 + 2y) dy \right] = x^2 y \Big|_1^2 + (x^2 y + y^2) \Big|_3^3 = (12 - 3) + 0 = 9$$

- Addition results in a value of 19 for the total path: $\int_{1-A-2} dz = 10 + 9 = 19$

Mathematics of Path and State Functions

- Second function: $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- Second path: 1 → B → 2 is $(1,1) \rightarrow (2,1) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow B$ and $B \rightarrow 2$ which are evaluated and added



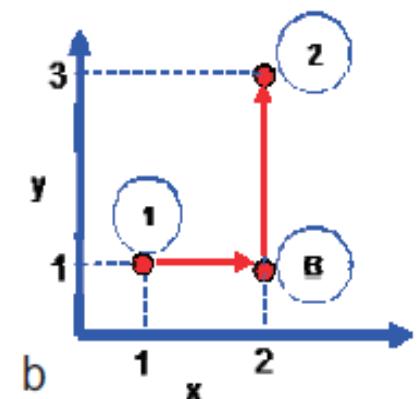
$$\int_{1-B} dz = \left[\int_1^2 2xy dx \right]_{y=1, dy=0} + \left[\int_1^1 (x^2 + 2y) dy \right] =$$

$$\int_{B-2} dz = \left[\int_2^2 2xy dx \right] + \left[\int_1^3 (x^2 + 2y) dy \right]_{x=2, dx=0} =$$

- Work out the partial differentials

Mathematics of Path and State Functions

- **Second** function: $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- State 1 → 2 is $(1,1) \rightarrow (2,3)$
- **Second** path: 1 → B → 2 is $(1,1) \rightarrow (2,1) \rightarrow (2,3)$
- This is divided in two separate integrals $1 \rightarrow B$ and $B \rightarrow 2$ which are evaluated and added



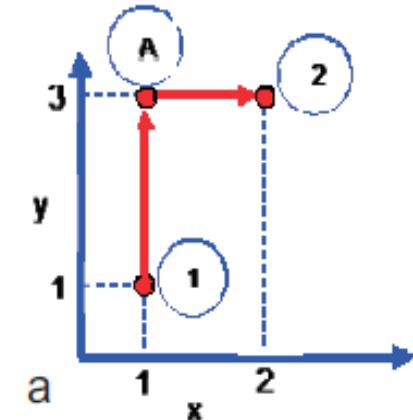
$$\int_{1-B} dz = \left[\int_1^2 2xy dx \right]_{y=1, dy=0} + \left[\int_1^1 (x^2 + 2y) dy \right] = x^2 y \Big|_1^2 + (x^2 y + y^2) \Big|_1^1 = (2^2 - 1) + 0 = 3$$

$$\int_{B-2} dz = \left[\int_2^2 2xy dx \right] + \left[\int_1^3 (x^2 + 2y) dy \right]_{x=2, dx=0} = x^2 y \Big|_2^2 + (x^2 y + y^2) \Big|_1^3 = 0 + (2^2 \cdot 3 + 3^2) - (2^2 \cdot 1 + 1^2) = 21 - 5 = 16$$

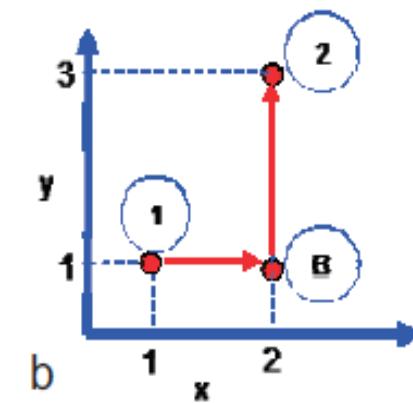
- Addition results in a value of 19 for the total path: $\int_{1-B-2} dz = 3 + 16 = 19$

Mathematics of Path and State Functions

- **Second function:** $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- State $2 \rightarrow 1$ is $(2,3) \rightarrow (1,1)$
- **First path:** $2 \rightarrow B \rightarrow 1$ is $(2,3) \rightarrow (2,1) \rightarrow (1,1)$
- The result is: 19 for the total path

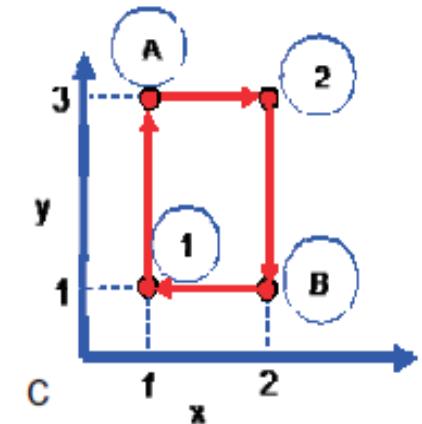


- **Second function:** $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- State $1 \rightarrow 2$ is $(1,1) \rightarrow (2,3)$
- **Second path:** $1 \rightarrow B \rightarrow 2$ is $(1,1) \rightarrow (2,1) \rightarrow (2,3)$
- The result is: 19 for the total path
- If we compare the results of both paths we see that their value is **the same** and thus we can conclude that the result not depends on the path of integration and therefore the differential is exact and the function is a state function



Mathematics of Path and State Functions

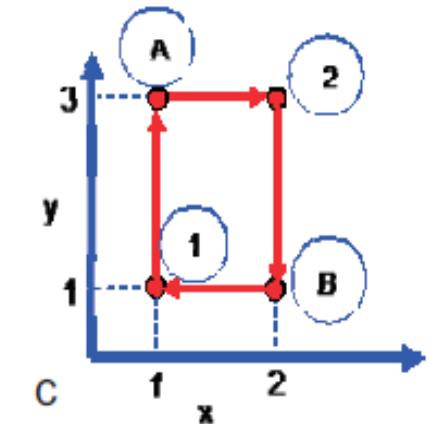
- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- Closed path
- State $1 \rightarrow 1$ is $(1,1) \rightarrow (1,1)$
- Closed path: $1 \rightarrow A \rightarrow 2 \rightarrow B \rightarrow 2$ or $(1,1) \rightarrow (1,3) \rightarrow (2,1) \rightarrow (2,3) \rightarrow (1,1)$
- This is divided in four separate integrals $1 \rightarrow A$, $A \rightarrow 2$, $2 \rightarrow B$ and $B \rightarrow 2$ which have to be evaluated and added
- These separate integrals were already evaluated in the previous slides and it results in:



Work out, what is the conclusion?

Mathematics of Path and State Functions

- First function: $\delta z(x, y) = xydx + (x^2 + 2y)dy$
- Closed path
- State $1 \rightarrow 1$ is $(1,1) \rightarrow (1,1)$
- Closed path: $1 \rightarrow A \rightarrow 2 \rightarrow B \rightarrow 2$ or $(1,1) \rightarrow (1,3) \rightarrow (2,1) \rightarrow (2,3) \rightarrow (1,1)$
- This is divided in four separate integrals $1 \rightarrow A$, $A \rightarrow 2$, $2 \rightarrow B$ and $B \rightarrow 2$ which have to be evaluated and added
- These separate integrals were already evaluated in the previous slides and it results in:

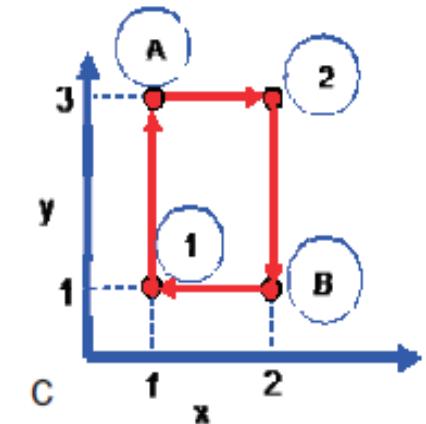


$$\oint \delta z(x, y) = \int_1^A \delta z(x, y) + \int_A^2 \delta z(x, y) + \int_2^B \delta z(x, y) + \int_B^1 \delta z(x, y)$$
$$= 10 + 4.5 - 16 - 1.5 = -3$$

- Thus: $\oint \delta z(x, y) = -3 \neq 0$
- The integral over the closed path is not zero → **path function**

Mathematics of Path and State Functions

- Second function: $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- Closed path
- State $1 \rightarrow 1$ is $(1,1) \rightarrow (1,1)$
- Closed path: $1 \rightarrow A \rightarrow 2 \rightarrow B \rightarrow 2$ or $(1,1) \rightarrow (1,3) \rightarrow (2,1) \rightarrow (2,3) \rightarrow (1,1)$
- This is divided in four separate integrals $1 \rightarrow A$, $A \rightarrow 2$, $2 \rightarrow B$ and $B \rightarrow 2$ which have to be evaluated and added
- These separate integrals were already evaluated in the previous slides and it results in:



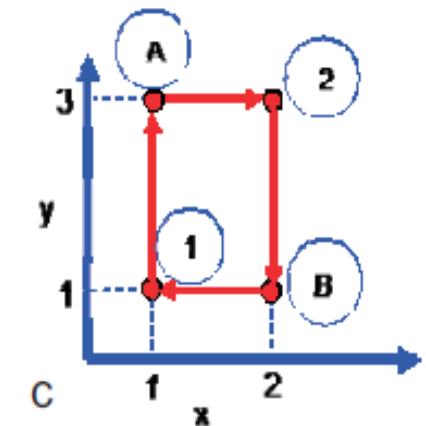
Work out, what is the conclusion?

Mathematics of Path and State Functions

- Second function: $dz(x, y) = 2xydx + (x^2 + 2y)dy$
- Closed path
- State $1 \rightarrow 1$ is $(1,1) \rightarrow (1,1)$
- Closed path: $1 \rightarrow A \rightarrow 2 \rightarrow B \rightarrow 2$ or $(1,1) \rightarrow (1,3) \rightarrow (2,1) \rightarrow (2,3) \rightarrow (1,1)$
- This is divided in four separate integrals $1 \rightarrow A$, $A \rightarrow 2$, $2 \rightarrow B$ and $B \rightarrow 2$ which have to be evaluated and added
- These separate integrals were already evaluated in the previous slides and it results in:

$$\oint dz(x, y) = \int_1^A dz(x, y) + \int_A^2 dz(x, y) + \int_2^B dz(x, y) + \int_B^1 dz(x, y)$$
$$= 10 + 9 - 3 - 16 = 0$$

- Thus: $\oint \delta z(x, y) = 0$
- The integral over the closed path is zero → **state function**



Mathematics of Path and State Functions

- Three ways to check if a differential is total or exact and the function is a state function:

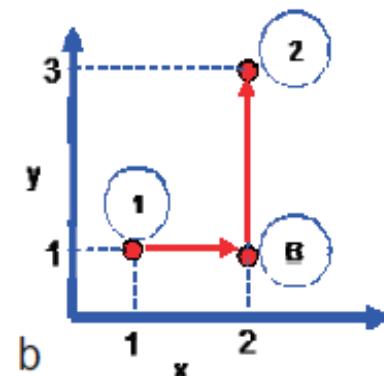
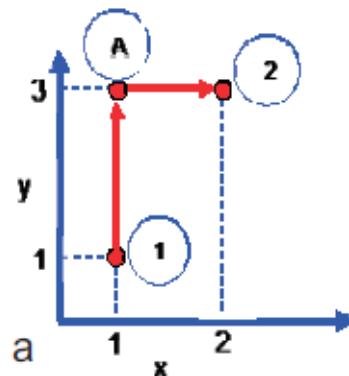
- For mixed differentials the order of differentiation is not important

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

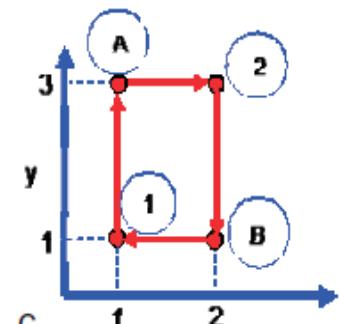
- The integral over the closed path is zero:

$$\oint dz(x, y) = 0$$

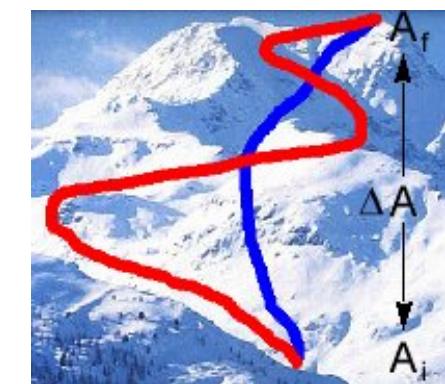
- The integration does not depend on the integration path



Two different paths to go from state 1 to state 2

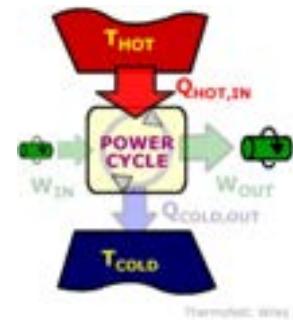


A closed path



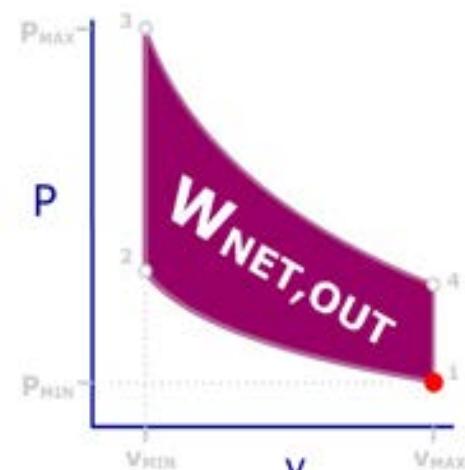
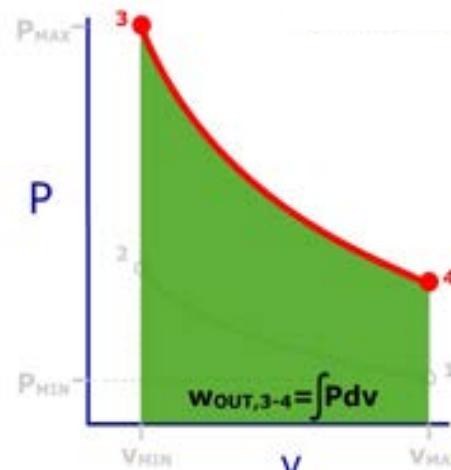
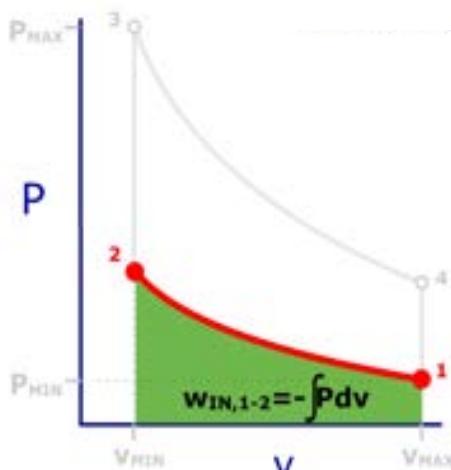
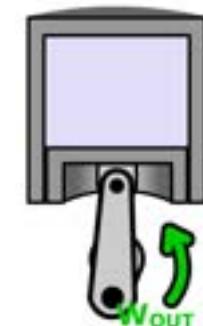
Path and State Functions in Thermodynamics

- Most thermodynamic heat and refrigeration systems to produce work and cold are closed cycles where 4 or more different states and processes can be distinguished
 - Rankine / steam turbine cycle
 - Brayton / gas turbine cycle
 - Reciprocating engines / Diesel and Otto cycle
 - Reversed Rankine / cooling cycle
- The cyclic integral over the closed path for the differential for work, δw , or heat transfer, δq , returns a value for work or heat transfer which is not zero as these are path or process functions whose differentials are not total (fortunately, otherwise it would not be possible to build a power cycle)
- The cyclic integral over the closed path for the differentials of properties like pressure, temperature, volume, entropy, internal energy and enthalpy is zero as these are state or point functions whose differentials are total or exact



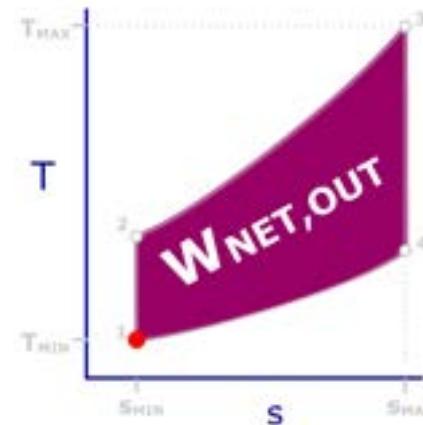
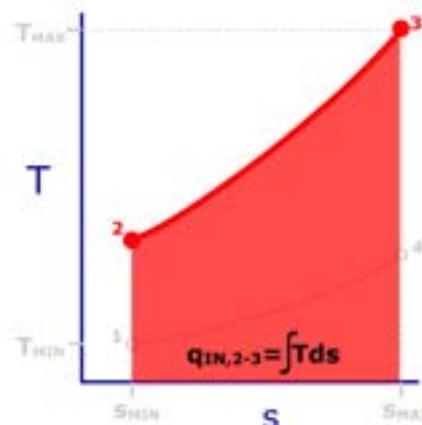
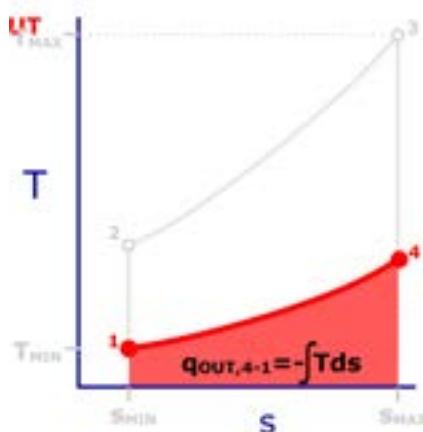
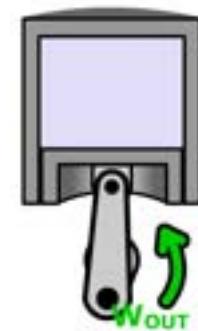
Path and State Functions in Thermodynamics

- **Otto cycle:** 4 states & 4 processes → added for a closed cycle
 - 1 → 2: - work in (volume decreases)
 - 2 → 3: no work (no volume change)
 - 3 → 4: + work out (volume increases)
 - 4 → 1: no work (no volume change)
- Total process: Net work = work out – work in
- The work can be indicated in the Pv-diagram, the net work is the area enclosed in the cycle which is not zero after a round trip while P and v return to their original value



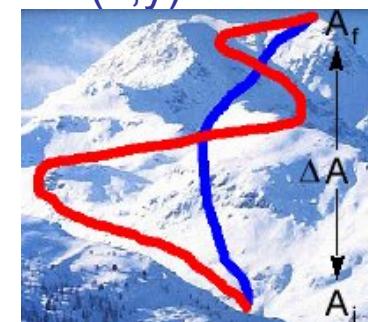
Path and State Functions in Thermodynamics

- **Otto cycle:** 4 states & 4 processes → added for a closed cycle
 - $1 \rightarrow 2$: no heat transfer
 - $2 \rightarrow 3$: + heat transfer in
 - $3 \rightarrow 4$: no heat transfer
 - $4 \rightarrow 1$: - heat transfer out
- Total process: Net heat transfer = heat in – heat out
- The heat transfer can be indicated in the Ts-diagram, the net heat transfer is equal to the net work produced and is the area enclosed in the cycle which is not zero after a round trip while T and s return to their original value



Recapitulate Class 15

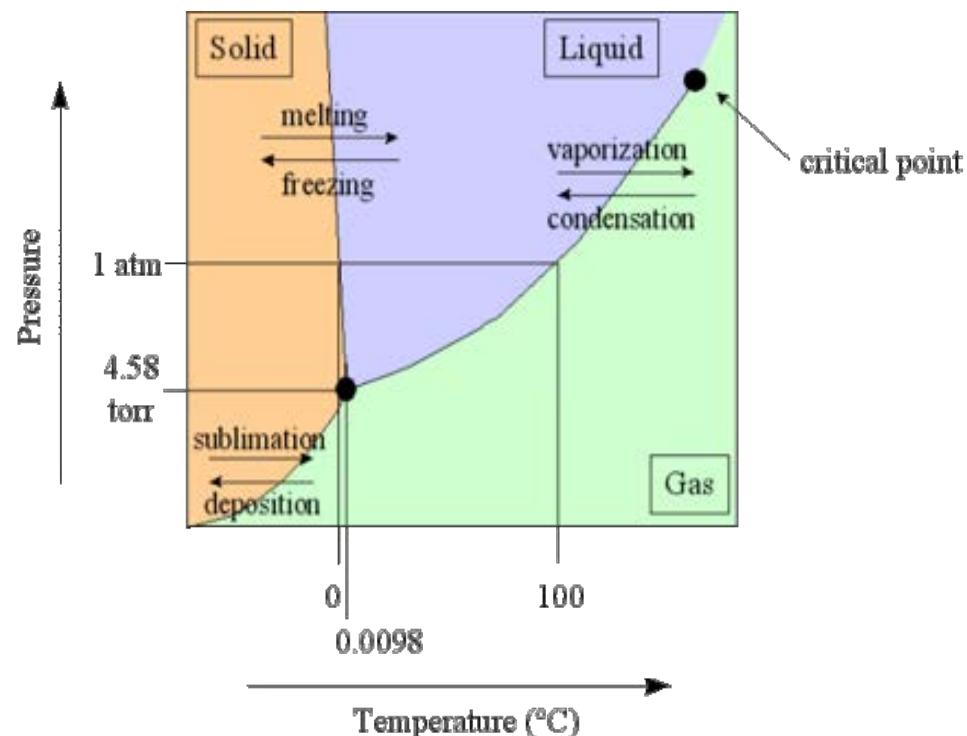
- **State Postulate:** simple system, two properties are enough to find all others
- **Total differential:** $dz(x, y) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$ describes the change of the property, x as a function of the change of both properties y and z , where the partial derivatives $\left(\frac{\partial z}{\partial x}\right)_y$ and $\left(\frac{\partial z}{\partial y}\right)_x$ denote the slope of the tangent in the point (x, y)
 - Reciprocity relation: $\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = 1 / \left(\frac{\partial z}{\partial x}\right)_y$
 - Cyclic relation (or -1 rule / minus one rule): $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$
 - Chain rule: $\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y / \left(\frac{\partial z}{\partial w}\right)_y$
- Work and heat are **process or path functions** because their values depend on the specific process or path between two equilibrium states
- In contrast to path functions, **state functions or point functions** are independent of the path taken and depend only on the state properties
- State functions have total/exact differentials, those of path functions non-total/exact
- **Total differential / state function:** Combined differentials are equal $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$, cyclic integral is zero $\oint dz(x, y) = 0$, integration is independent of the path



Different paths, different work,
same change potential energy

Next Class 16

- Develop fundamental thermodynamics relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties
- **Fundamental thermodynamic equations:** functions that contains all thermodynamic data for properties
- Thermodynamic energies
 - Internal energy: $u(s,v)$
 - Enthalpy: $h(s,P)$
 - Helmholtz energy: $a(T,v)$
 - Gibbs energy: $g(T,P)$
- Maxwell relations
- Clapeyron equation
- Clausius-Clapeyron equation



The Clapeyron equation can be used to determine enthalpy changes associated with a phase change

Class 16: Fundamental Equations & Maxwell Relations



Statue of the German physician and physicist Helmholtz in front of Humboldt University in Berlin (left).

American physicist and chemist Josiah Willard Gibbs (upper right).

The Scottish mathematical physicist James Clark Maxwell at Trinity College in Cambridge. He is holding one of his colour wheels (lower right).

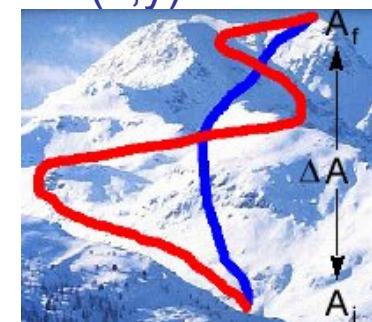


Thermodynamics continued.....

- We used thermodynamic tables and diagrams in the analysis, however we tend to take the tables and diagrams for granted
- We did not ask ourselves how tables and diagrams were prepared and how some unknown properties that can not be measured can be determined from a set of limited available data
- In the **next three classes** we will focus more in depth on
 - Develop fundamental relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties
 - The background of tables and diagrams
 - Develop the Maxwell relations, which form the basis for many thermodynamic relations
 - Develop the Clapeyron equation and determine the enthalpy of vaporization from P, v, and T measurements alone
 - Develop general relations for du, dh, and ds that relate change in u, h and s to changes in P, T and v
 - Discuss the Joule-Thomson coefficient
- **Class 15** → State postulate, thermodynamics and partial derivatives, state and path functions
- **Class 16** → Fundamental relations between thermodynamic properties, Maxwell relations, Clapeyron equation
- **Class 17** → Joule-Thomson coefficient, defined partial derivatives, reduction and evaluation of partial derivatives, find relations for du and dh

Recapitulate Class 15

- **State Postulate:** simple system, two properties are enough to find all others
- **Total differential:** $dz(x, y) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$ describes the change of the property, x as a function of the change of both properties y and z , where the partial derivatives $\left(\frac{\partial z}{\partial x}\right)_y$ and $\left(\frac{\partial z}{\partial y}\right)_x$ denote the slope of the tangent in the point (x, y)
 - Reciprocity relation: $\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = 1 / \left(\frac{\partial z}{\partial x}\right)_y$
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 - Chain rule: $\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y / \left(\frac{\partial z}{\partial w}\right)_y$
- Work and heat are **process or path functions** because their values depend on the specific process or path between two equilibrium states
- In contrast to path functions, **state functions or point functions** are independent of the path taken and depend only on the state properties
- State functions have total/exact differentials, path functions non-total/in-exact
- **Total differential / state function:** Combined differentials are equal $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$, cyclic integral is zero $\oint dz(x, y) = 0$, integration is independent of the path



Different paths, different work,
same change potential energy

Recapitulate Class 15

1. **State postulate:** we need two independent properties to describe a simple system
2. The change of a third property can be determined using the total differential of the property as a function of the known properties, e.g. for the internal energy as a function of entropy and volume, $u(s,v)$:

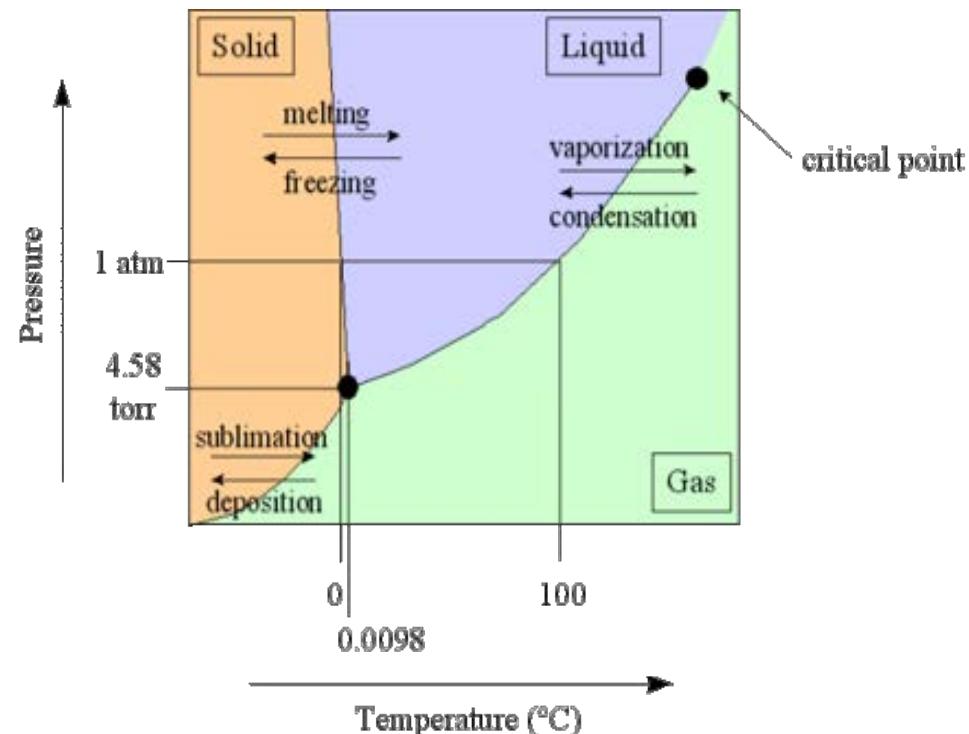
$$du(s,v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv = Tds - Pdv$$

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_s = -P$$

3. Knowing $u(s,v)$ we can find T and P but also $h (= u+Pv)$ and v and s
- A function like $u(s,v)$ or $h(s,P)$ that contains all thermodynamic data for properties is called a **fundamental thermodynamic equation**
 - $u(s,v)$ is a fundamental equation in the energy representation
 - $s(u,v)$ is a fundamental equation in the entropy representation
 - In class 16 we will meet two more fundamental equations
 - Helmholtz energy, $a(T,v)$ and Gibbs energy, $g(T,P)$

Content Class 16

- Develop fundamental thermodynamics relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties
- **Fundamental thermodynamic equations:** functions that contains all thermodynamic data for properties
- Thermodynamic energies
 - Internal energy: $u(s,v)$
 - Enthalpy: $h(s,P)$
 - Helmholtz energy: $a(T,v)$
 - Gibbs energy: $g(T,P)$
- Maxwell relations
- Clapeyron equation
- Clausius-Clapeyron equation



The Clapeyron equation can be used to determine enthalpy changes associated with a phase change

Video about part of the content of class 16

- The video <https://www.youtube.com/watch?v=ZeijeoZ1-j8> of Greg Birkett, from The university of Queensland covers a part of the theory of this class and is very instructive. All thermodynamic properties are related and this allows us to calculate things from equations of state (e.g. the ideal gas law is an equation of state).
- **Thermodynamic properties: they are related**
 - At the end of this video, you will be able to
 - Explain what fundamental property relations and Maxwell equations are
 - Substitute an equation of state into the equations for du
- **Fundamental property relations are defined coming from the combination of:**
 - First law of thermodynamics
 - Definitions of thermodynamics variables, e.g., $h = u + Pv$
 - Total derivatives of those variables.
- **Four fundamental property relations:**
 - $du = Tds - Pdv$ (follows from the first law $du = dq + dw = Tds - Pdv$)
 - $dh = Tds + vdP$ (follows from $h = u + Pv$)
 - $da = -sdT - PdV$ (follows from $a = u - Ts$)
 - $dg = -sdT + vdP$ (follows from $g = h - Ts = u + Pv - Ts$)
- **Maxwell relations:** Changes in the internal energy u can be determined, applied to the Van der Waals equation of state.
- **Recap:** All thermodynamic properties are related to each other in one way or the other.
- It is possible to derive these relationships from the first law of thermodynamics, definitions of thermodynamics variables and partial differentials.
- Using this is possible to derive an equation for du that uses c_v and an equation of state.

Internal Energy (Recap)

- **Internal energy:** the energy of a substance due to the motion and vibration of molecules in the substance
- Internal energy as a function of entropy and volume, $u(s,v)$
 - Total differential: $du(s,v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$
- Compare to the first Gibbs equation: $du = Tds - Pdv$
- This gives for the partial derivatives: $\left(\frac{\partial u}{\partial s}\right)_v = T$ and $\left(\frac{\partial u}{\partial v}\right)_s = -P$

Definition of temperature

$$\left(\frac{\partial u}{\partial s}\right)_v \equiv T$$

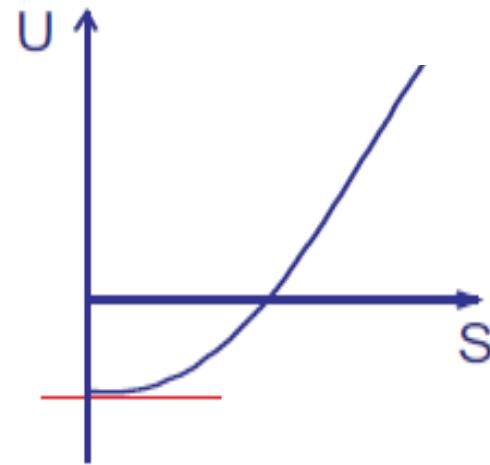
And for pressure

$$\left(\frac{\partial u}{\partial v}\right)_s \equiv -P$$

Internal Energy: Temperature

Definition of temperature

$$\left(\frac{\partial u}{\partial s}\right)_v \equiv T$$

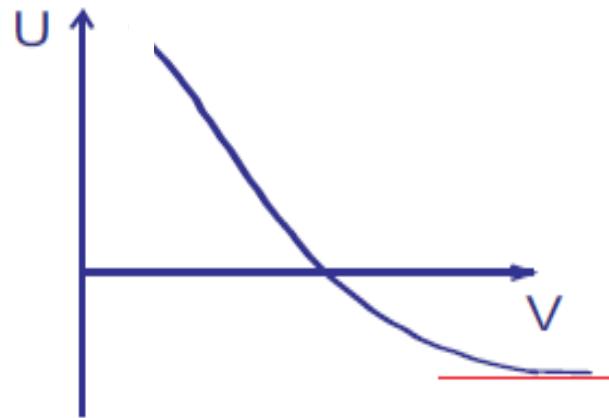


- If $s \rightarrow 0$ then also $T \rightarrow 0$ and thus $\left(\frac{\partial u}{\partial s}\right)_v = T \rightarrow 0$
- At absolute zero temperature no motion of molecules no change in internal energy
- Tangent at $s \rightarrow 0$ has slope zero
- u is a continuous increasing function of s as T is always positive
- u increases as T increases

Internal Energy: Pressure

And for pressure

$$\left(\frac{\partial u}{\partial v}\right)_s \equiv -P$$



- If $v \rightarrow \infty$ then $P \rightarrow 0$ and thus $\left(\frac{\partial u}{\partial v}\right)_s = -P \rightarrow 0$
- For an infinite large volume, the pressure goes to zero
- Tangent at $v \rightarrow \infty$ has slope zero
- u is a continuous decreasing function of the volume v as P is always positive so $-P$ is always negative
- The slope of the tangent decreases as v increases, i.e. the pressure decreases as the volume increases (as also follows from observations)

Enthalpy (Recap)

- **Enthalpy:** is a combination property of the internal energy u and the flow work $Pv \rightarrow h = u + Pv$
- Enthalpy as a function of entropy and pressure, $h(s, P)$
 - Total differential: $dh(s, P) = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP$
- Combining:
 - First Gibbs equation: $du = Tds - Pdv$
 - Definition of enthalpy: $h = u + Pv$
- Results in the second Gibbs equation:
$$dh = du + Pdv + vdP = Tds - \cancel{Pdv} + \cancel{Pdv} + vdP = Tds + vdP$$
- Comparing gives for the partial derivatives: $\left(\frac{\partial h}{\partial s}\right)_P = T$ and $\left(\frac{\partial h}{\partial P}\right)_s = v$

Free Energies

- Besides internal energy and enthalpy there are two more, important energies → Internal energy and enthalpy minus a term Ts
- These are called **free energies** and they represent the energy that can be converted to work in a physical system
 - Helmholtz free energy: $a = u - Ts$
 - Gibbs free energy: $g = h - Ts = u + Pv - Ts$
- In equilibrium free energies tend to go to a minimum value where entropy tends to go to a maximum
- **Conclusion:** a spontaneous process always results in an increase in entropy and a decrease in free energy
- Free energies are, like entropy, a measure for the direction in which a spontaneous process proceeds (used mainly in chemistry)

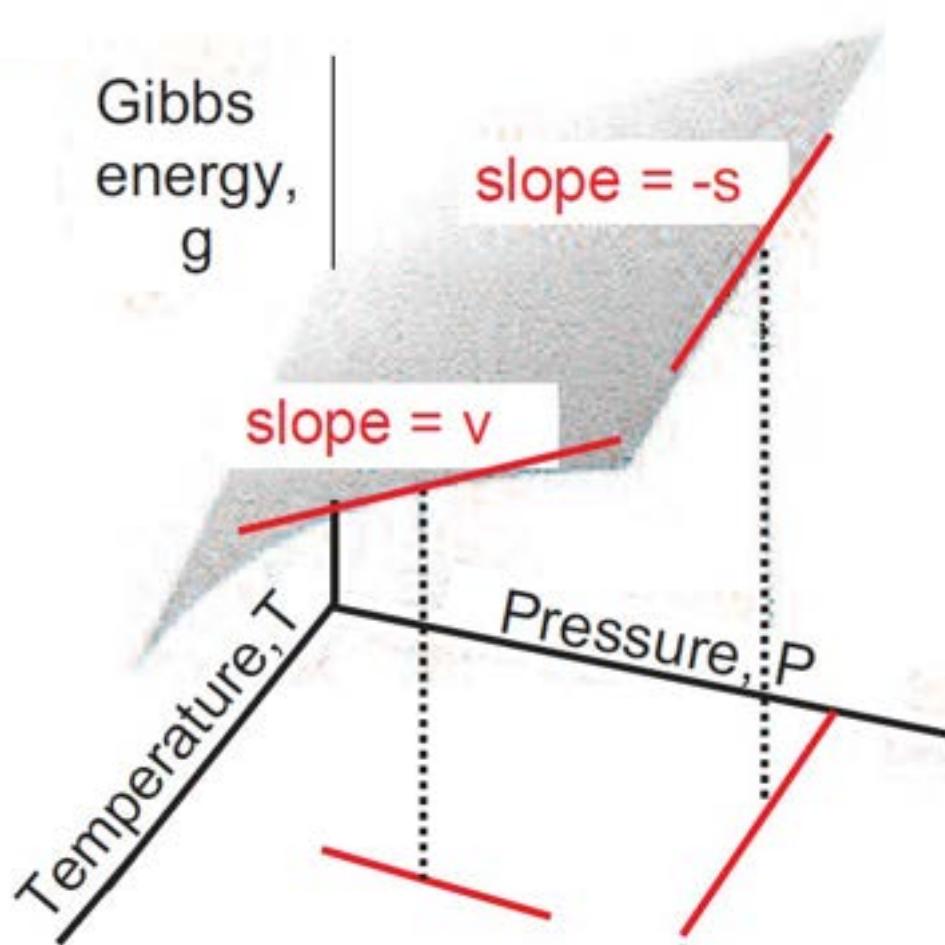
Helmholtz Energy

- **Helmholtz energy:** amount of useful work that can be subtracted from a closed thermodynamical system at constant temperature and volume (e.g., chemical energy concerned with explosions in closed volumes)
- **Helmholtz energy:** is a combination property of the internal energy u minus a term $Ts \rightarrow a = u - Ts$
- Helmholtz energy as a function of temperature and volume, $a(T,v)$
 - Total differential: $da(T,v) = \left(\frac{\partial a}{\partial T}\right)_v dT + \left(\frac{\partial a}{\partial v}\right)_T dv$
- Combining:
 - First Gibbs equation: $du = Tds - Pdv$
 - Definition of Helmholtz energy: $a = u - Ts$
- Results in a third Gibbs equation:
$$da = du - Tds - sdT = \cancel{Tds} - \cancel{Pdv} - Tds - sdT = -sdT - Pdv$$
- Comparing gives for the partial derivatives: $\left(\frac{\partial a}{\partial T}\right)_v = -s$ and $\left(\frac{\partial a}{\partial v}\right)_T = -P$

Gibbs Energy

- **Gibbs energy:** maximum amount non volume work*, that can be subtracted from a thermodynamically closed system at constant pressure and temperature (* e.g., electrical work in a electro chemical fuel cell)
- **Gibbs energy:** is a combination property of the enthalpy h minus a term $Ts \rightarrow g = u + Pv - Ts = h - Ts$
- Gibbs energy as a function of temperature and pressure, $g(T,P)$
 - Total differential: $dg(T,P) = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP$
- Combining:
 - Second Gibbs equation: $dh = Tds + vdP$
 - Definition of Gibbs energy: $g = h - Ts$
- Results in a fourth Gibbs equation:
$$dg = dh - Tds - sdT = \cancel{Tds} + vdP - \cancel{Tds} - sdT = -sdT + vdP$$
- Comparing gives for the partial derivatives: $\left(\frac{\partial g}{\partial T}\right)_P = -s$ and $\left(\frac{\partial g}{\partial P}\right)_T = v$

Gibbs Energy Geometrical Representation

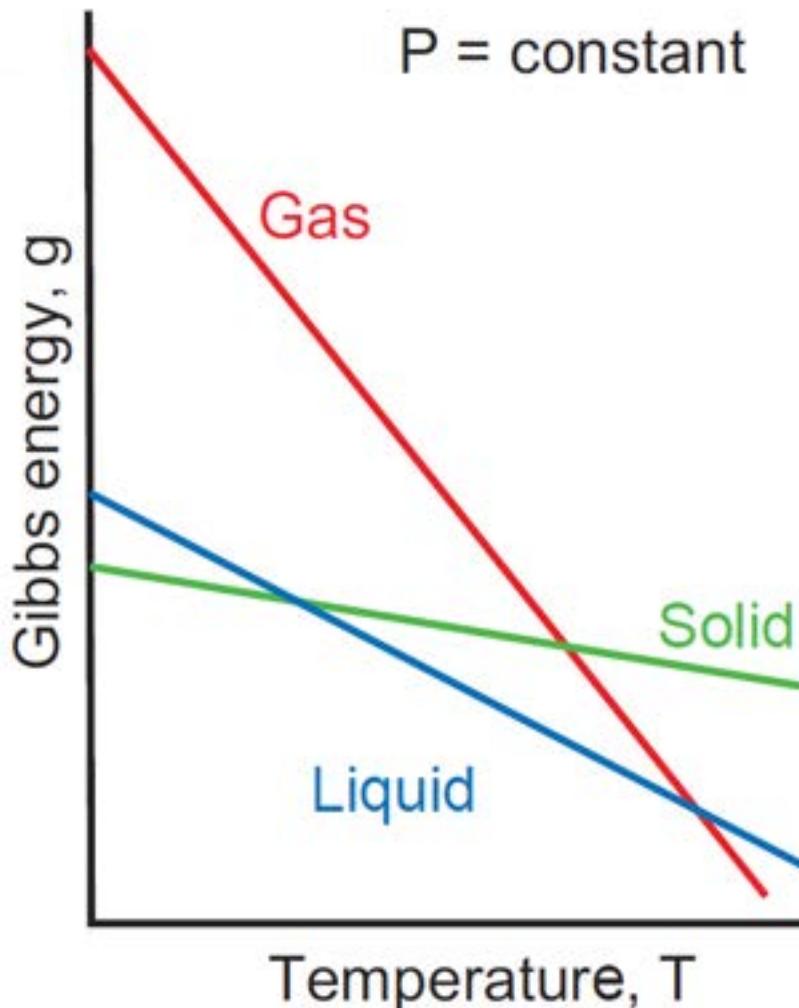


- The partial derivatives describe the slope of the tangents:

$$\left(\frac{\partial g}{\partial P} \right)_T = v$$

$$\left(\frac{\partial g}{\partial T} \right)_P = -s$$

Gibbs Energy at Constant Pressure

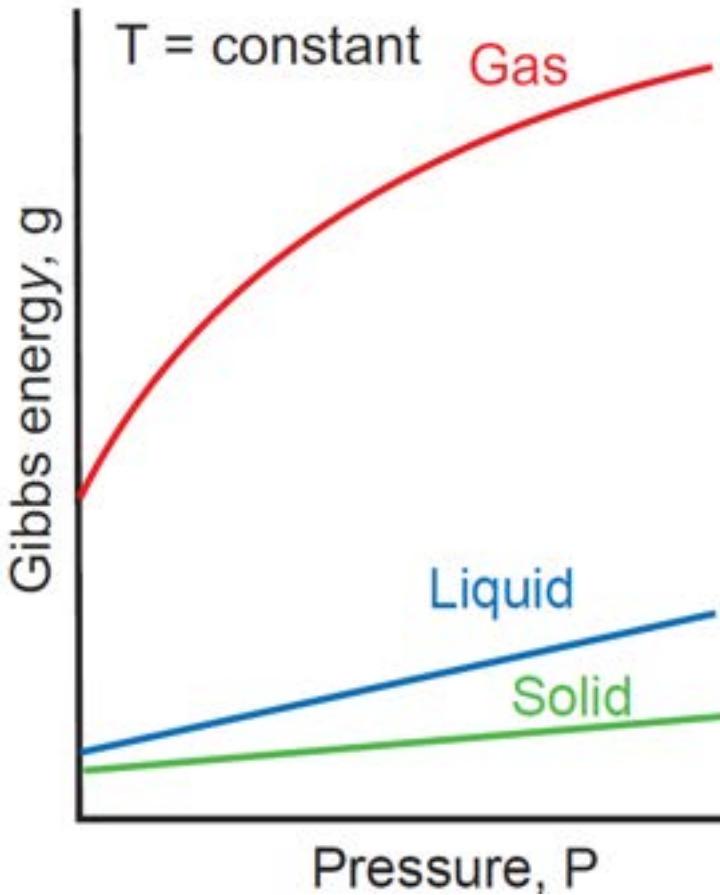


- Change of the Gibbs energy as a function of the temperature at constant pressure:

$$\left(\frac{\partial g}{\partial T} \right)_P = -s$$

- Slope is proportional to the entropy
- All lines decrease (minus sign, negative slope)
- Entropy of a gas is larger than the entropy of a solid therefore the slope of the gas line is more steep

Gibbs Energy at Constant Temperature



- Change of the Gibbs energy as a function of the pressure at constant temperature:

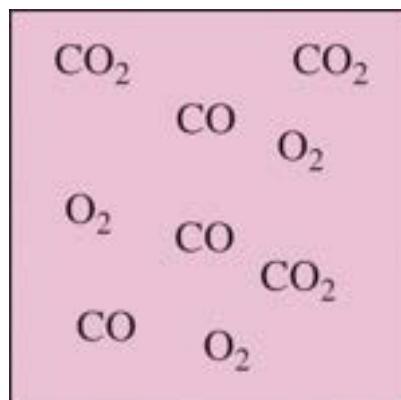
$$\left(\frac{\partial g}{\partial P} \right)_T = v$$

- Slope is proportional to the volume
- All lines increase (positive slope, as v is always positive)
- Volume of a liquid and a solid do not change with pressure → the slope of those lines is constant
- For a gas the volume changes as the pressure changes → the slope is not constant, higher pressure → smaller volume and the slope is less steep for higher pressures
- Compared to a liquid and a solid the volume of a gas is larger → the slope of the gas line is steeper

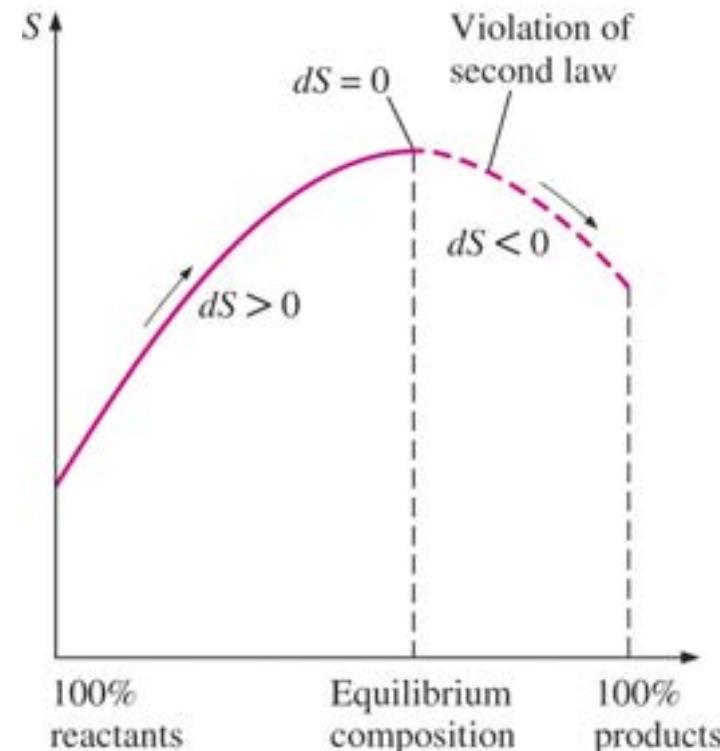
Criterion for Chemical Equilibrium

- If temperature, pressure, and composition (thus the state) of a system is known: **how can be predicted if the system is in chemical equilibrium ?**
- Take the laws of thermodynamics into account:
 - First law (energy is conserved): $du = \delta q + \delta w = \delta q - PdV$
 - Second law (increase of entropy principle): Entropy always increases in a spontaneous reaction; in equilibrium the entropy is at a maximum:

$$ds_{\text{system}} \geq \frac{\delta q}{T}$$



A chemical reaction in an adiabatic chamber proceeds in the direction of increasing entropy. When the entropy reaches a maximum, the reaction stops. Decrease of the entropy is impossible

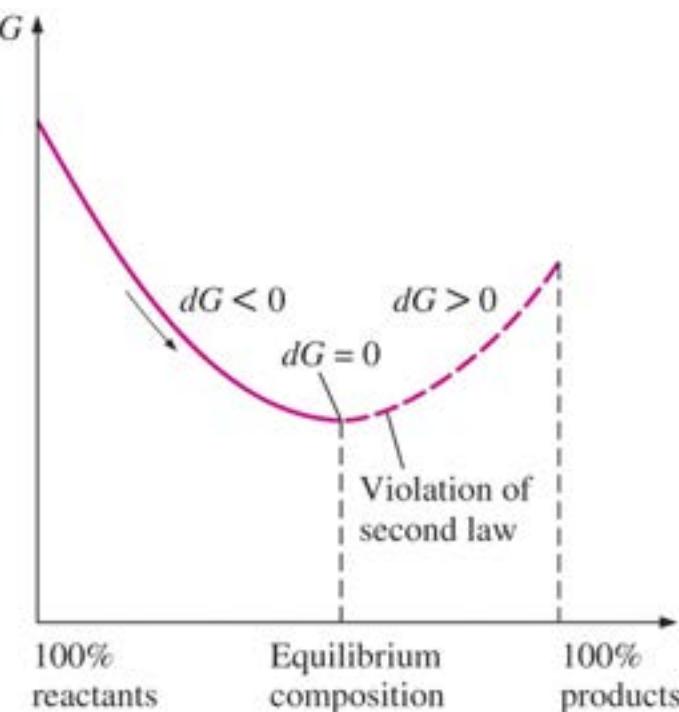


Criterion for Chemical Equilibrium

- Combining the first and second law: $du = \delta q - Pdv$ and $ds_{\text{system}} \geq \frac{\delta q}{T}$ gives $du + Pdv - Tds \leq 0$
- The differential of the Gibbs function ($g=u+Pv-Ts$) for constant temperature and pressure:

$$(dg)_{T,P} = du + Pdv + \cancel{vdP}^0 - Tds - \cancel{sdT}^0 = du + Pdv - Tds$$

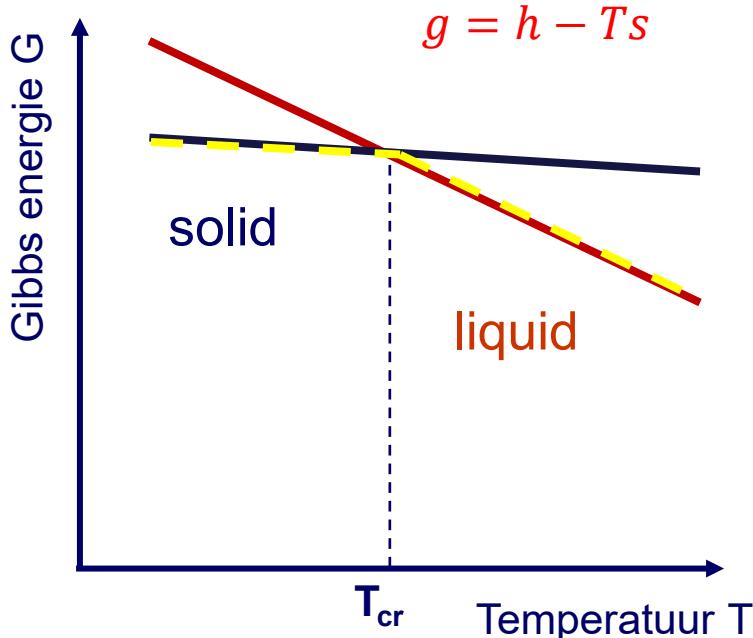
- Comparing: $(dg)_{T,P} \leq 0$
- A chemical reaction at a specified T and P proceeds in the direction of a decreasing Gibbs function, the reaction stops, and chemical equilibrium is established when the Gibbs function attains a minimum value
- Therefore, the criterion for chemical equilibrium is: $(dg)_{T,P} = 0$



Gibbs Energy during Phase Change

- The Gibbs energy decreases as the temperature increases (at higher temperatures the system is in a state of higher disorder (randomness))
- At a critical temperature where phase change takes place (e.g., the melt temperature of a solid) the Gibbs energy ($g=h-Ts$) is constant and $dg=0$:

$$dg = dh - Tds - sdT = dh - Tds = 0 \rightarrow dh = T_{cr}ds \rightarrow \Delta h = T_{cr}\Delta s$$



- **Example: Melting** → no change Gibbs energy
 - $T < T_s$: Gibbs energy of the solid lower than Gibbs energy of the liquid
 - $T > T_s$: Gibbs energy of the liquid lower than Gibbs energy of the solid

Overview Thermodynamic Energies

- **Internal energy:** the energy of a substance due to the motion and vibration of molecules in the substance
- **Enthalpy:** combination property of the internal energy u and the flow work Pv
- **Helmholtz energy:** combination property of the internal energy u and Ts
- **Gibbs energy:** combination property of the enthalpy h and Ts

Energy	Symbol, variables	Total differential	Partial Derivatives
Internal energy	$u(s, v)$	$du = Tds - Pdv$	$T = \left(\frac{\partial u}{\partial s}\right)_v$ and $-P = \left(\frac{\partial u}{\partial v}\right)_s$
Enthalpy	$h(s, P) = u + Pv$	$dh = Tds + vdP$	$T = \left(\frac{\partial h}{\partial s}\right)_P$ and $v = \left(\frac{\partial h}{\partial P}\right)_s$
Helmholtz energy	$a(T, v) = u - Ts$	$da = -sdT - Pdv$	$-s = \left(\frac{\partial a}{\partial T}\right)_v$ and $-P = \left(\frac{\partial a}{\partial v}\right)_T$
Gibbs energy	$g(T, P) = u + Pv - Ts$	$dg = -sdT + vdP$	$-s = \left(\frac{\partial g}{\partial T}\right)_P$ and $v = \left(\frac{\partial g}{\partial P}\right)_T$

- All four thermodynamic energies are:
 - State functions
 - Exact / total differentials
 - Fundamental equations of state

In Conclusion 1

- **Four thermodynamic energies (state functions / exact differentials)**
 - Internal energy: u
 - Enthalpy: h
 - Helmholtz energy: a
 - Gibbs energy: g
- **Other properties (state functions / exact differentials)**
 - Temperature: T
 - Pressure: P
 - Volume: v
 - Entropy: s
- This gives 8 important properties → $8^3 = 512$ partial derivatives !!!!
- **Besides these there are the path functions / non-exact differentials**
 - Work
 - Heat
 - Entropy generation

In Conclusion 2

- $8^3 = 512$ partial derivatives, we want to know them all
- Some of them are trivial, e.g., $\left(\frac{\partial x}{\partial x}\right)_y = 1$, $\left(\frac{\partial x}{\partial y}\right)_x = 0$
- Some of them are already evaluated, e.g., $\left(\frac{\partial u}{\partial s}\right)_v = T$ and $\left(\frac{\partial g}{\partial P}\right)_T = v$
- Some of them are easy to evaluate if the equation of state is known, e.g., for an ideal gas: $\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$
- But what about the others, e.g., $\left(\frac{\partial s}{\partial v}\right)_T$ or $\left(\frac{\partial P}{\partial s}\right)_v$??
- Specially entropy is difficult to measure
- Relate unknown partial derivatives to partial derivatives that are known or can be measured
- Maxwell relations relate s to P, v and T



Maxwell Relations

- Making use of the exactness of the differentials of thermodynamic properties, relations between the partial derivatives of the properties P, v, T, and s of a simple compressible system can be derived
- Applying the relation of the combined derivatives to the four Gibbs equations results in the so called Maxwell relations that relate P, v, T, and s



The James Clerk Maxwell Monument in Edinburgh, where he studied.

https://en.wikipedia.org/wiki/James_Clerk_Maxwell

Maxwell Relations

- Recapitulate: Mixed derivatives (Class 15)

- Exact differential: $dz(x, y) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Mdx + Ndy$
with $M = \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$
- Differentiation of M to x and N to y results in combined differentials:
$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x}\right)_y\right)_x = \frac{\partial^2 z}{\partial y \partial x} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y}\right)_x\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$
- For exact differentials (Theorem of Clairaut):
$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and therefore} \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Maxwell Relation from Internal Energy

- Internal energy $u(s, v)$, total differential: $du(s, v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$
- Compare to the first Gibbs equation: $du = Tds - Pdv$
- Partial derivatives: $\left(\frac{\partial u}{\partial s}\right)_v = T$ and $\left(\frac{\partial u}{\partial v}\right)_s = -P$

- Two variables, take the combined derivative, v and s or s and v

$$\left(\frac{\partial}{\partial v} \left(\frac{\partial u}{\partial s}\right)_v\right)_s = \left(\frac{\partial}{\partial v} T\right)_s = \left(\frac{\partial T}{\partial v}\right)_s \quad \text{and} \quad \left(\frac{\partial}{\partial s} \left(\frac{\partial u}{\partial v}\right)_s\right)_v = \left(\frac{\partial}{\partial s} (-P)\right)_v = -\left(\frac{\partial P}{\partial s}\right)_v$$

- Because the internal energy is a state function (exact differential) the order of differentiation is not important ($\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$):

$$\left(\frac{\partial}{\partial v} \left(\frac{\partial u}{\partial s}\right)_v\right)_s = \left(\frac{\partial}{\partial s} \left(\frac{\partial u}{\partial v}\right)_s\right)_v \rightarrow \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

First Maxwell equation: $\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$

Maxwell Relation from Enthalpy

- Enthalpy $h(s, P)$, total differential: $dh(s, P) = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP$
- Compare to the second Gibbs equation: $dh = Tds + vdP$
- Partial derivatives: $\left(\frac{\partial h}{\partial s}\right)_P = T$ and $\left(\frac{\partial h}{\partial P}\right)_s = v$

- Two variables, take the combined derivative, P and s or s and P

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial h}{\partial s}\right)_P\right)_s = \left(\frac{\partial}{\partial P} T\right)_s = \left(\frac{\partial T}{\partial P}\right)_s \quad \text{and} \quad \left(\frac{\partial}{\partial s} \left(\frac{\partial h}{\partial P}\right)_s\right)_P = \left(\frac{\partial}{\partial s} v\right)_P = \left(\frac{\partial v}{\partial s}\right)_P$$

- Because the internal energy is a state function (exact differential) the order of differentiations is not important ($\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$):

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial h}{\partial s}\right)_P\right)_s = \left(\frac{\partial}{\partial s} \left(\frac{\partial h}{\partial P}\right)_s\right)_P \rightarrow \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

Second Maxwell equation: $\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$

Maxwell Relations

- Similarly follow the third and fourth Maxwell relation from the Helmholtz energy, $a(T,v)$ and the Gibbs energy, $g(T,P)$

First Maxwell relation: $\left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_v$

Second Maxwell relation: $\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$

Third Maxwell relation: $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$

Fourth Maxwell relation: $\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P$

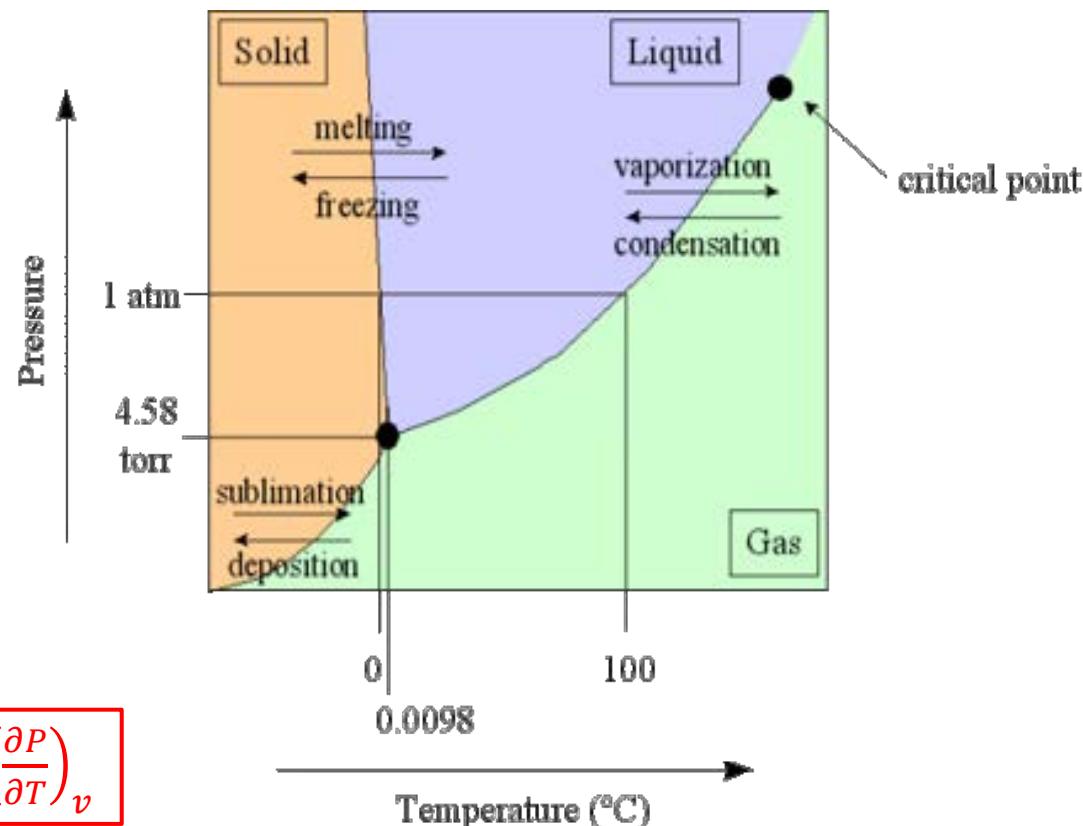


The Maxwell relations are named after the Scottish mathematical physicist James Clark Maxwell (1831 – 1879), fascinated by light and colors he also made the first color picture

- The Maxwell relations are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties P , v , and T , they are frequently used to derive useful thermodynamic relations

Application Maxwell Relations

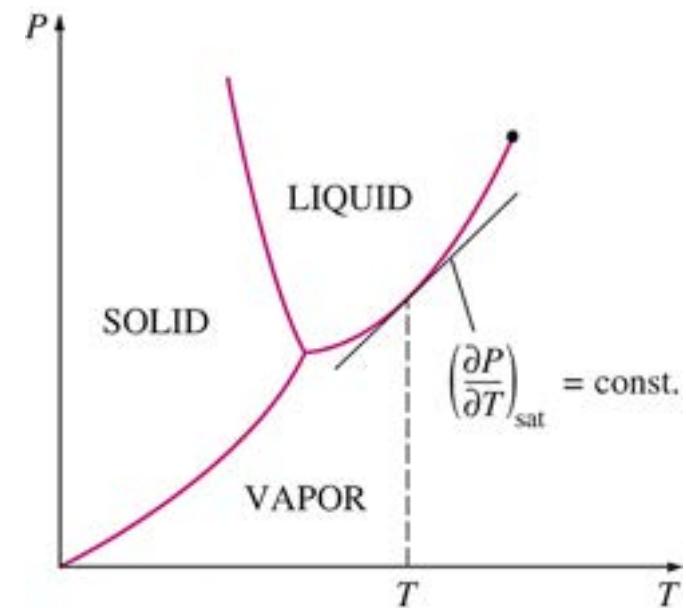
- The third Maxwell relation can be used to determine the enthalpy change associated with a phase change from P, T and v data alone, i.e., the enthalpy of vaporization h_{fg} (but also the change in enthalpy for melting or sublimation)
- This relation is called the **Clapeyron equation**
- With some approximations it can be reduced to the **Clausius Clapeyron equation**



$$\text{Third Maxwell relation: } \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

Clapeyron Equation

- Consider the third Maxwell relation: $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$
- Analyze the right-hand side: $\left(\frac{\partial P}{\partial T}\right)_v$
- During a phase change process, $P = P_{\text{sat}}$ which depends on the saturation temperature, T_{sat} only and is independent of the volume
- Both properties are related $P_{\text{sat}} = f(T_{\text{sat}})$ (line in the diagram)
- No other variables
- Therefore $\left(\frac{\partial P}{\partial T}\right)_v$ can be expressed as the total derivative $\left(\frac{dP}{dT}\right)_{\text{sat}}$
- This, constant value, is the slope of the saturation curve of the PT-diagram which is independent of the volume



The slope of the saturation curve on a P-T diagram is constant at constant T or P

Clapeyron Equation

- Consider the third Maxwell relation: $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$
- Analyze the **left-hand side**: $\left(\frac{\partial s}{\partial v}\right)_T$
- During a phase change process, $T = T_{\text{sat}}$ is constant (isothermal process)
- For a phase change at constant T : $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{s_g - s_f}{v_g - v_f}\right)_{T_{\text{sat}}} = \frac{s_{fg}}{v_{fg}}$

With: s_{fg} = the entropy change liquid – vapor, v_{fg} = the volume change liquid – vapor

- Using the second Gibbs equation an expression for s_{fg} can be found
- During a phase change also the pressure is constant, P_{sat} therefore

$$dh = Tds + vdP = Tds \rightarrow \int_f^g dh = \int_f^g Tds \rightarrow h_{fg} = T_{\text{sat}} s_{fg}$$

With: h_{fg} = the enthalpy change liquid – vapor (enthalpy of vaporization)

- Thus, the left hand side is equal to: $\left(\frac{\partial s}{\partial v}\right)_T = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{T_{\text{sat}} v_{fg}}$

Clapeyron Equation

- Consider the third Maxwell relation: $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$
- Combining the result for the left and the right hand side gives:

$$\text{Clapeyron equation: } \left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{T_{sat}v_{fg}}$$

called after the French engineer en physicist E. Clapeyron (1799-1864)

- The Clapeyron equation is an important thermodynamic relation which gives the possibility to determine the enthalpy of vaporization h_{fg} at a given temperature by simply measuring the slope of the saturation curve on a P - T diagram and the specific volume of saturated liquid and saturated vapor at the given temperature
- The Clapeyron equation is applicable to any phase-change process that occurs at constant temperature and pressure, in general form it is expressed as, with 1 and 2 the two phases

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{12}}{T_{sat}v_{12}}$$

Clausius - Clapeyron Equation

- **Clapeyron equation:** $\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{T_{sat}v_{fg}}$
- The Clapeyron equation can be simplified for liquid–vapor and solid–vapor phase changes by utilizing some approximations
 - Low pressure $v_g \gg v_l$ thus $v_g \cong v_{fg}$, vapor treated as ideal gas $v_g = RT/P$
- Substituting into the Clapeyron relations yields:

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{T_{sat}v_g} = \frac{Ph_{fg}}{R(T_{sat})^2} \quad \text{or} \quad \left(\frac{dP}{P}\right)_{sat} = \frac{h_{fg}}{R} \left(\frac{dT}{T^2}\right)_{sat}$$

- For small temperature intervals h_{fg} can be treated as constant, integrating between 2 saturations states gives the Clausius - Clapeyron equation :

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} \cong \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{sat}$$

- This equation can be used to determine the variation of saturation pressure with temperature, it can also be used in the solid–vapor region by replacing h_{fg} by h_{ig} (the enthalpy of sublimation) of the substance

Recapitulate Class 16

- Overview thermodynamic energies (state functions / exact differentials)

Energy	Symbol, variables	Total differential	Partial Derivatives
Internal energy	$u(s, v)$	$du = Tds - Pdv$	$T = \left(\frac{\partial u}{\partial s}\right)_v$ and $-P = \left(\frac{\partial u}{\partial v}\right)_s$
Enthalpy	$h(s, P) = u + Pv$	$dh = Tds + vdp$	$T = \left(\frac{\partial h}{\partial s}\right)_P$ and $v = \left(\frac{\partial h}{\partial P}\right)_s$
Helmholtz energy	$a(T, v) = u - Ts$	$da = -sdT - Pdv$	$-s = \left(\frac{\partial a}{\partial T}\right)_v$ and $-P = \left(\frac{\partial a}{\partial v}\right)_T$
Gibbs energy	$g(T, P) = u + Pv - Ts$	$dg = -sdT + vdp$	$-s = \left(\frac{\partial g}{\partial T}\right)_P$ and $v = \left(\frac{\partial g}{\partial P}\right)_T$

- Maxwell relations
- The enthalpy change associated with a phase change can be determined using:

First (u)	$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$
Second (h)	$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$
Third (a)	$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$
Fourth (g)	$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$

- Clapeyron equation: $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_{fg}}{T_{sat}v_{fg}}$
- Clausius – Clapeyron equation (less exact):

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{Ph_{fg}}{R(T_{sat})^2} \quad \text{or} \quad \left(\frac{dp}{P}\right)_{sat} = \frac{h_{fg}}{R} \left(\frac{dT}{T^2}\right)_{sat}$$

Formulas (WaTT)

- Most important relations summarized on one page
- Formula form is supplied at the exam

Differentiaal uitdrukkingen voor thermodynamische energieën

Energie	Symbool, variabelen	Differentiaal
Interne energie	$u(s, v)$	$du = Tds - Pdv$
Enthalpie	$h(s, P) = u + Pv$	$dh = Tds + vdP$
Helmholtz energie	$a(T, v) = u - Ts$	$da = -sdT - Pdv$
Gibbs energie	$g(T, P) = u - Ts + Pv$	$dg = -sdT + vdP$

Maxwell relaties

$$\left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial v}{\partial T}\right)_P = - \left(\frac{\partial s}{\partial P}\right)_T$$

Thermodynamische coëfficiënten

$$\text{Isotherme compressibiliteit coëfficiënt: } \kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T$$

$$\text{Thermische expansie coëfficiënt: } \beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$$

$$\text{Joule-Thomson coëfficiënt: } \mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$$

$$\text{Specifieke warmte voor een constant-volume proces: } c_v = \left(\frac{\partial q}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$$

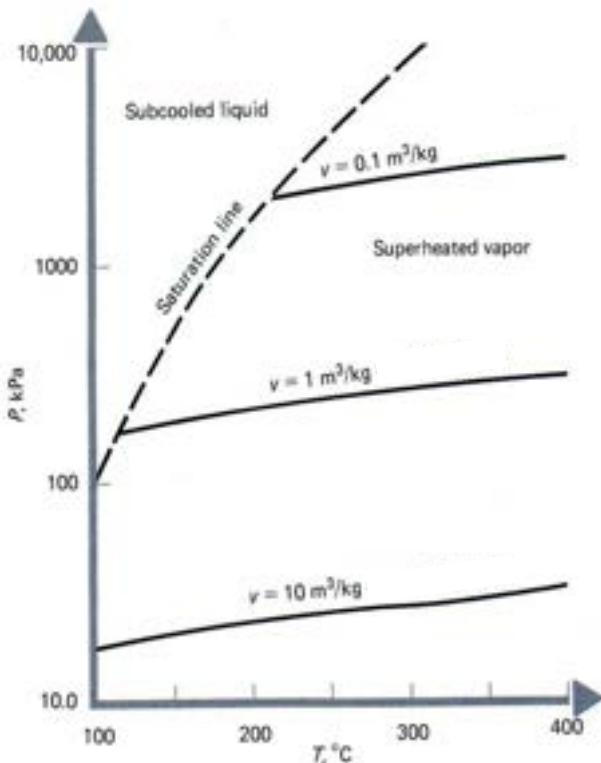
$$\text{Specifieke warmte voor een constant-druk proces: } c_p = \left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$$

$$\text{Relatie van Nernst-Lindeman: } c_v = c_P - \frac{T v \beta^2}{\kappa}$$

$$\text{Clapeyron relatie: } \left(\frac{dP}{dT}\right)_{sat} = \left(\frac{h_{12}}{T v_{12}}\right)$$

$$\text{Clausius-Clapeyron relatie: } \left(\frac{dP}{T^2}\right)_{sat} = \frac{h_{12}}{R} \left(\frac{dT}{T^2}\right)_{sat} \text{ of } \left(\frac{d(\ln P)}{dT}\right)_{sat} = \frac{h_{12}}{RT_{sat}^2}$$

Class 17: Defined Partial Derivatives & Reduction of Partial Derivatives



Joule Thomson effect in a snow cannon. Small droplets of water are mixed with compressed air. This mixture expands in a throttling valve. The gas cools down and the water droplets turn into ice

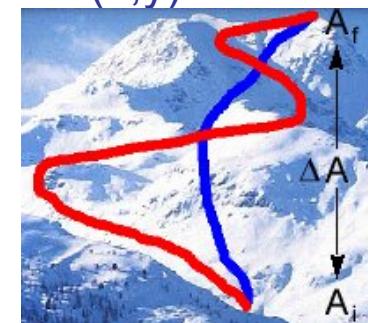
P , T and v data are relatively easy to find experimentally. The figure shows data for water over a portion of the P - T - v surface. Changes in internal energy, enthalpy and entropy can be determined from this data if relations between these properties and the P , T and v data are known.

Thermodynamics continued.....

- We used thermodynamic tables and diagrams in the analysis, however we tend to take the tables and diagrams for granted
- We did not ask ourselves how tables and diagrams were prepared and how some unknown properties that can not be measured can be determined from a set of limited available data
- In the **next three classes** we will focus more in depth on
 - Develop fundamental relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties
 - The background of tables and diagrams
 - Develop the Maxwell relations, which form the basis for many thermodynamic relations
 - Develop the Clapeyron equation and determine the enthalpy of vaporization from P, v, and T measurements alone
 - Develop general relations for du, dh, and ds that relate change in u, h and s to changes in P, T and v
 - Discuss the Joule-Thomson coefficient
- **Class 15** → State postulate, thermodynamics and partial derivatives, state and path functions
- **Class 16** → Fundamental relations between thermodynamic properties, Maxwell relations, Clapeyron equation
- **Class 17** → Joule-Thomson coefficient, defined partial derivatives, reduction and evaluation of partial derivatives, find relations for du and dh

Recapitulate Class 15

- **State Postulate:** simple system, two properties are enough to find all others
- **Total differential:** $dz(x, y) = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$ describes the change of the property, x as a function of the change of both properties y and z , where the partial derivatives $\left(\frac{\partial z}{\partial x}\right)_y$ and $\left(\frac{\partial z}{\partial y}\right)_x$ denote the slope of the tangent in the point (x, y)
 - Reciprocity relation: $\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = 1 / \left(\frac{\partial z}{\partial x}\right)_y$
 - Cyclic relation (or -1 rule / minus one rule): $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$
 - Chain rule: $\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y / \left(\frac{\partial z}{\partial w}\right)_y$
- Work and heat are **process or path functions** because their values depend on the specific process or path between two equilibrium states
- In contrast to path functions, **state functions or point functions** are independent of the path taken and depend only on the state properties
- State functions have total/exact differentials, those of path functions non-total/exact
- **Total differential / state function:** Combined differentials are equal $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$, cyclic integral is zero $\oint dz(x, y) = 0$, integration is independent of the path



Different paths, different work,
same change potential energy

Recapitulate Class 15

1. **State postulate:** we need two independent properties to describe a simple system
2. The change of a third property can be determined using the total differential of the property as a function of the known properties, e.g. for the internal energy as a function of entropy and volume, $u(s,v)$:

$$du(s,v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv = Tds - Pdv$$

$$\left(\frac{\partial u}{\partial s}\right)_v = T \quad \text{and} \quad \left(\frac{\partial u}{\partial v}\right)_s = -P$$

3. Knowing $u(s,v)$ we can find T and P but also $h (= u+Pv)$ and v and s
- A function like $u(s,v)$ or $h(s,P)$ that contains all thermodynamic data for properties is called a **fundamental thermodynamic equation**
 - $u(s,v)$ is a fundamental equation in the energy representation
 - $s(u,v)$ is a fundamental equation in the entropy representation
 - In class 16 we will meet two more fundamental equations
 - Helmholtz energy, $a(T,v)$ and Gibbs energy, $g(T,P)$

Recapitulate Class 16

- Overview thermodynamic energies (state functions / exact differentials)

Energy	Symbol, variables	Total differential	Partial Derivatives
Internal energy	$u(s, v)$	$du = Tds - Pdv$	$T = \left(\frac{\partial u}{\partial s}\right)_v$ and $-P = \left(\frac{\partial u}{\partial v}\right)_s$
Enthalpy	$h(s, P) = u + Pv$	$dh = Tds + vdp$	$T = \left(\frac{\partial h}{\partial s}\right)_P$ and $v = \left(\frac{\partial h}{\partial P}\right)_s$
Helmholtz energy	$a(T, v) = u - Ts$	$da = -sdT - Pdv$	$-s = \left(\frac{\partial a}{\partial T}\right)_v$ and $-P = \left(\frac{\partial a}{\partial v}\right)_T$
Gibbs energy	$g(T, P) = u + Pv - Ts$	$dg = -sdT + vdp$	$-s = \left(\frac{\partial g}{\partial T}\right)_P$ and $v = \left(\frac{\partial g}{\partial P}\right)_T$

- Maxwell relations

First (u)	$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$
Second (h)	$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$
Third (a)	$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$
Fourth (g)	$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$

- Application of the third Maxwell equation
The enthalpy change associated with a phase change can be determined using:

- Clapeyron equation: $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_{fg}}{T_{sat}v_{fg}}$
- Clausius – Clapeyron equation (less exact):

$$\left(\frac{dp}{dT}\right)_{sat} = -\frac{Ph_{fg}}{R(T_{sat})^2} \quad \text{or} \quad \left(\frac{dp}{P}\right)_{sat} = \frac{h_{fg}}{R} \left(\frac{dT}{T^2}\right)_{sat}$$

Content Class 17

- The **state postulate** established that the state of a simple compressible system is completely specified by two independent, intensive properties, i.e., all the properties of a system, such as internal energy, enthalpy, and entropy at any state can be determined once **two independent**, properties are available
- The calculation of these properties from **measurable ones** depends on the availability of simple and accurate relations between the two groups
- In class 17 general relations will be developed for changes in internal energy, enthalpy, and entropy in terms of pressure, specific volume, temperature, and specific heats alone, based upon the theory and using relations derived in class 15 and 16
- Partial derivatives that are easy to measure
 - Volume expansivity / thermal expansion: β (thermische expansiecoëfficiënt)
 - Isothermal compressibility: κ (isotherme compressibiliteitscoëfficiënt)
 - Isochoric pressure coefficient: α (isochoore drukcoëfficiënt)
 - Specific heat at constant pressure and volume: c_p and c_v
- Systematic evaluation of partial derivatives: partial derivatives that can not be measured have to be rewritten into expressions with P , T , v , s , κ , β , c_p
- Relations for changes in internal energy, enthalpy and entropy
- Joule-Thomson coefficient, μ_{JT}

Thermal Expansion, β

- Class 15: **total differential** of v as function of P and T is expressed as:

$$dv(P, T) = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial P}\right)_T dP$$

- Relative change, divide by the volume:

$$\frac{dv}{v} = \boxed{\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p dT + \frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T dP}$$



- Percentage change of volume at an isobaric ($dP=0$) temperature change:

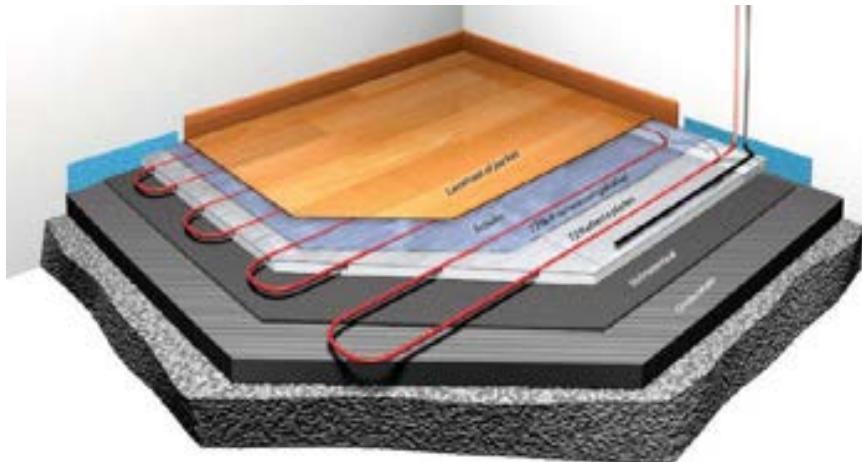
$$\frac{dv}{v} = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P dT = \beta dT$$

- **Thermal expansion:** $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$

- Volume and temperature are proportional
- The value of the partial derivative is positive, volume increases if the temperature increases
- β is a quantity that easily can be measured

Thermal Expansion, β

- Applications thermal expansion: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$



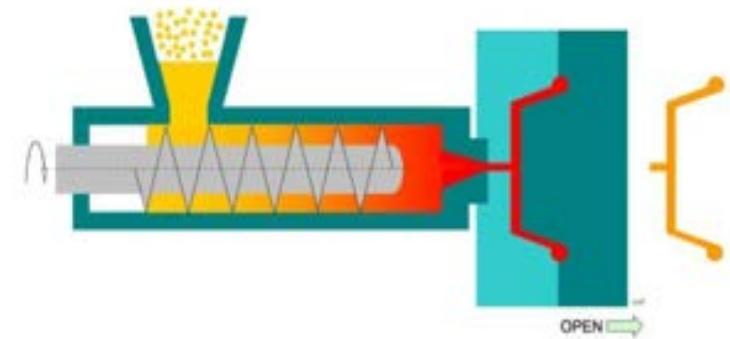
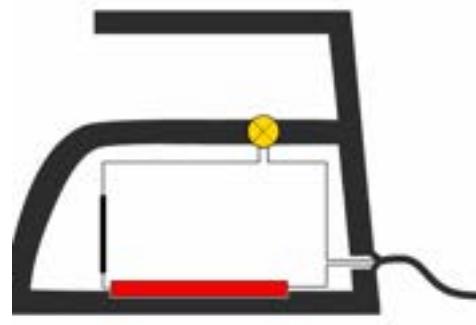
Thermal expansion in constructions



Deformation of the tracks as a result of expansion of steel
(Landgraaf, juli 2006)



Bimetallic strips



Process technology

Isothermal Compressibility, κ

- Class 15: **total differential** of v as function of P and T is expressed as:

$$dv(P, T) = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial P}\right)_T dP$$

- Relative change, divide by the volume

$$\frac{dv}{v} = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p dT + \boxed{\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T dP}$$



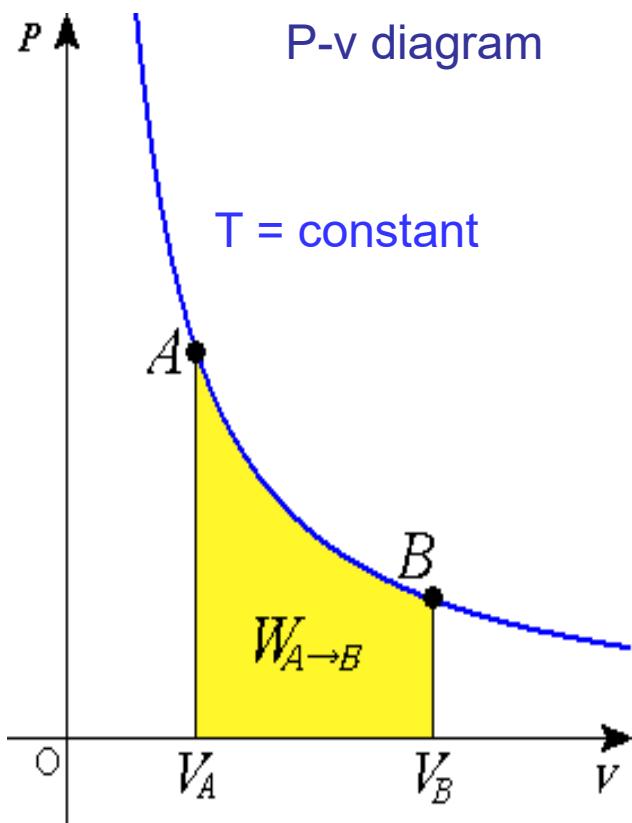
- Percentage change of volume at an isothermal ($dT=0$) pressure change:

$$\frac{dv}{v} = \frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T dP = -\kappa dP$$

- **Isothermal compressibility:** $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T$
 - Volume and pressure are inversely proportional
 - The value of the partial derivative is negative, volume decreases if the pressure increases, a minus is added to give positive κ values
- κ is a quantity that easily can be measured, like β

Isothermal Compressibility, κ

- **Example:** change of the volume as a result of the change of the pressure
- Isothermal compressibility: $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \rightarrow -\frac{1}{v\kappa} = \left(\frac{\partial P}{\partial v} \right)_T$



- **Slope of the isotherms in the Pv-diagram:**

$$\left(\frac{\partial P}{\partial v} \right)_T = -\frac{1}{v\kappa}$$

- $v \rightarrow 0$ then $-\frac{1}{v\kappa} \rightarrow -\infty$
- $v \rightarrow \infty$ then $-\frac{1}{v\kappa} \rightarrow -0$
- - sign, negative slope

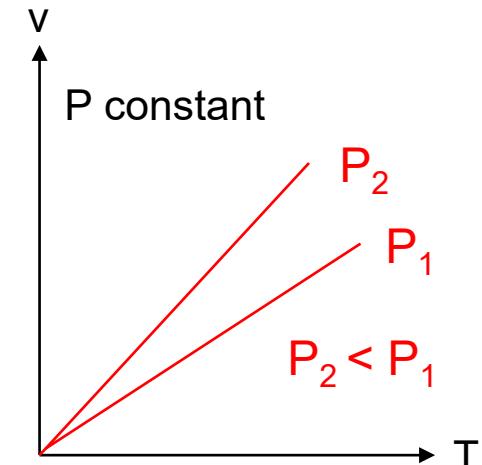
β and κ for ideal gas and liquid

- Thermal expansion: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$
- Isothermal compressibility: $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$
- Ideal gas: $Pv = RT \rightarrow v = RT/P$

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{v} \frac{R}{P} = \frac{1}{T}$$

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = -\frac{1}{v} \left(-\frac{RT}{P^2} \right) = \frac{1}{v} \frac{v}{P} = \frac{1}{P}$$

$$\left(\frac{\partial v}{\partial T} \right)_P = \frac{R}{P}$$



Isobars for an ideal gas in a Tv -diagram

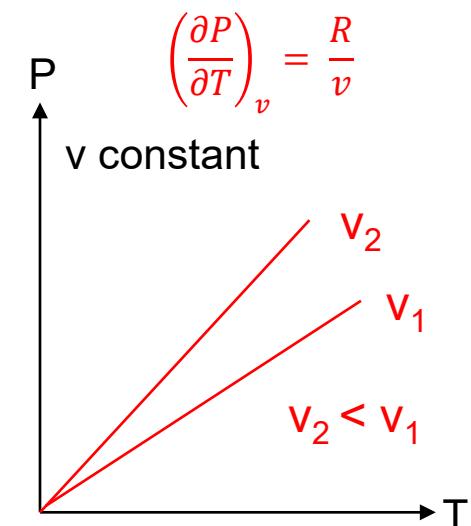
- Liquid, if the liquid is assumed to be incompressible: $dv = 0$

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = 0$$

$$\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = 0$$

Isochoric pressure coefficient, α

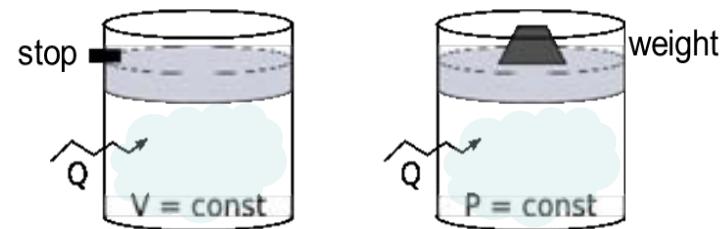
- Thermal expansion: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$
- Isothermal compressibility: $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$
- Both coefficients can be measured easily
- A third partial derivative follows from variables P, T, v
- Percentage pressure change at a temperature change with constant volume
- Isochoric pressure coefficient: $\alpha = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_v$
- For an ideal gas: $\alpha = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_v = \frac{1}{P} \left(\frac{\partial \left(\frac{RT}{v} \right)}{\partial T} \right)_v = \frac{1}{P} \frac{R}{v} = \frac{1}{T}$
- A disadvantage of this coefficient is that it is not easy to measure, but α can be expressed in β and κ using the minus 1 rule: $\alpha = \frac{1}{P} \frac{\beta}{\kappa}$ (see WaTT exercise 7.1c)



Isochors for an ideal gas in a PT-diagram

Class 9: Specific Heat

- The **specific heat** is the amount of heat needed to raise the temperature of 1 kg of a substance by one degree in a specified way
- It depends on the **substance** and the **process** involved
- Which process cost more energy?



1. Heating at constant pressure \rightarrow v as well as T will increase
 2. Heating at constant volume \rightarrow P as well as T will increase
- Specific heat capacity (c_v) for **constant volume** process: $c_v = \left(\frac{\partial u}{\partial T}\right)_v$
 - Specific heat capacity (c_p) for **constant pressure** process: $c_p = \left(\frac{\partial h}{\partial T}\right)_p$
 - Generally, $c_p > c_v$ as extra energy (work) is needed to expand the volume in order to keep the pressure constant ($\delta w = Pdv$):
 - $c_p - c_v = R$ for an ideal gas (see WaTT exercise 7.2d)

Specific Heat at Constant Volume

- Specific heat capacity (c_v) for constant volume process: $c_v = \left(\frac{\partial u}{\partial T}\right)_v$
- Isochoric process, $v = \text{constant} \rightarrow dv = 0$
- Total differential of the internal energy as a function of entropy and volume, $u(s, v)$:

$$du(s, v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv \xrightarrow[0]{dv} = Tds - Pdv \xrightarrow[0]{dv}$$

which, for an isochoric process, reduces to: $du(s, v) = Tds$

- Take partial derivative to T with constant volume: $\left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$
- Therefore: $c_v = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$

$$\text{Specific heat at constant volume: } c_v = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$$

Specific Heat at Constant Pressure

- Specific heat capacity (c_p) for **constant pressure** process: $c_p = \left(\frac{\partial h}{\partial T}\right)_p$
- Isobaric process, $P = \text{constant} \rightarrow dP = 0$
- Total differential of the enthalpy as a function of entropy and pressure, $h(s, P)$:

$$dh(s, P) = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP \xrightarrow[0]{dP} = Tds + v dP \xrightarrow[0]{dP}$$

which, for an isobaric process, reduces to: $dh(s, P) = Tds$

- Take partial derivative to T with constant volume: $\left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$
- Therefore: $c_P = \left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$

$$\text{Specific heat at constant pressure: } c_P = \left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$$

Nernst-Lindemann or Mayer Relation

- The specific heat at constant volume, c_v , is difficult to measure
- The specific heat at constant pressure, c_P is more easy to measure
- However, c_v can be expressed in c_P , β and κ , quantities that are relatively easy to measure

$$c_v = c_P - \frac{Tv\beta^2}{\kappa} \quad \rightarrow \quad c_P - c_v = \frac{Tv\beta^2}{\kappa}$$

(derivation see WaTT exercise 7.6)

- This relation is called the **Mayer relation** in honor of the German physician and physicist J.R. Mayer (1814-1878), also the name **Nernst-Lindemann relation** is used
- **For an ideal gas:** $\frac{Tv\beta^2}{\kappa} = R$ which results in the (well) known relation between c_P and c_v for an ideal gas: $c_P - c_v = R$ (see next slide)
- **For an incompressible substance:** $\frac{Tv\beta^2}{\kappa} = 0$ which results in $c_P = c_v$ in agreement with the theory as seen before

Nernst-Lindemann / Mayer Relation Ideal Gas

EXAMPLE 12–9 The Specific Heat Difference of an Ideal Gas

Show that $c_p - c_v = R$ for an ideal gas.

Solution It is to be shown that the specific heat difference for an ideal gas is equal to its gas constant.

Analysis This relation is easily proved by showing that the right-hand side of Eq. 12–46 is equivalent to the gas constant R of the ideal gas:

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$$

$$\kappa = - \frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$$

$$c_p - c_v = \frac{T v \beta^2}{\kappa} \rightarrow c_p - c_v = -T \left(\frac{\partial v}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial v} \right)_T$$

$$P = \frac{RT}{v} \rightarrow \left(\frac{\partial P}{\partial v} \right)_T = -\frac{RT}{v^2} = \frac{P}{v}$$

$$v = \frac{RT}{P} \rightarrow \left(\frac{\partial v}{\partial T} \right)_P^2 = \left(\frac{R}{P} \right)^2$$

Substituting,

$$-T \left(\frac{\partial v}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial v} \right)_T = -T \left(\frac{R}{P} \right)^2 \left(-\frac{P}{v} \right) = R$$

Therefore,

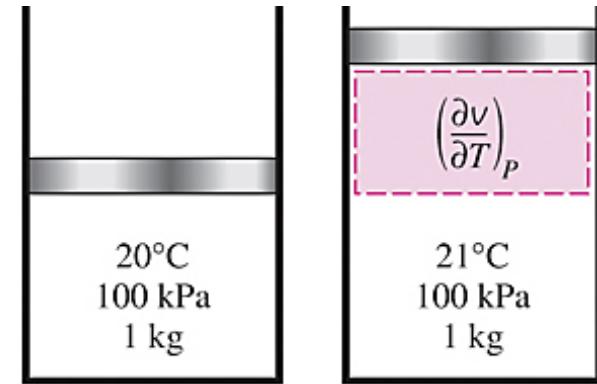
$$c_p - c_v = R$$

Nernst-Lindemann or Mayer Relation

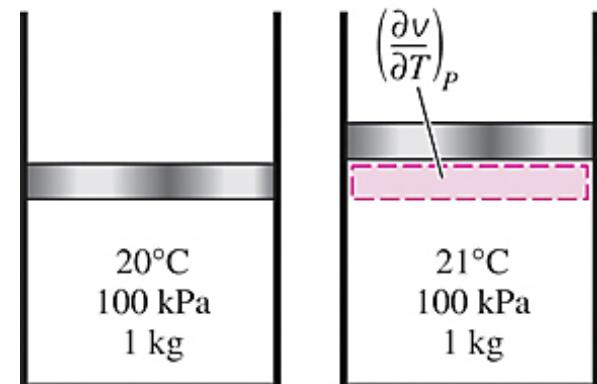
- Mayer relation or Nernst–Lindemann relation:

$$c_p - c_v = \frac{T v \beta^2}{\kappa}$$

- The right-hand side of the equation is always greater than or equal to zero. Therefore, it can be concluded that: $c_p \geq c_v$, this is because of the extra work needed to expand to volume compared to a constant volume process
- The difference between c_p and c_v approaches zero as the absolute temperature approaches zero
- The two specific heats are identical for incompressible substances since $v = \text{constant}$. The difference between the two specific heats is very small and is usually disregarded for substances that are nearly incompressible, such as liquids and solids



(a) A substance with a large β



(b) A substance with a small β

The volume expansivity (also called the *coefficient of volumetric expansion*) is a measure of the change in volume with temperature at constant pressure

What are the tools so far?

- **Remember:** The goal of all this mathematics is to derive general relations for changes (by integration over differential changes) in internal energy, enthalpy and entropy in terms of pressure, specific volume, temperature, and specific heats alone, therefore the partial derivatives should be known or be expressed in properties that are known or easy to measure
- **Partial derivatives that are known or can be measured:**
 - Thermal expansion: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$
 - Isothermal compressibility: $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$
 - Specific heat at constant pressure: $c_P = \left(\frac{\partial h}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P$
 - Isochoric pressure coefficient: $\alpha = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_v = \frac{1}{P} \frac{\beta}{\kappa}$ (Not easy to measure)
 - Specific heat at constant volume: $c_v = \left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v$ (Not easy to measure)
 - Mayer relation or Nernst–Lindemann relation: $c_P - c_v = \frac{T v \beta^2}{\kappa}$
 - Note: α and c_v are not easy to measure but can be expressed in c_P , β and κ

What are the tools so far?

- More partial derivatives that are known and relations that can be used to express partial derivatives into other properties
- Thermodynamic energies (state functions / exact differentials)**

Energy	Symbol, variables	Total differential	Partial Derivatives
Internal energy	$u(s, v)$	$du = Tds - Pdv$	$T = \left(\frac{\partial u}{\partial s}\right)_v$ and $-P = \left(\frac{\partial u}{\partial v}\right)_s$
Enthalpy	$h(s, P) = u + Pv$	$dh = Tds + vdp$	$T = \left(\frac{\partial h}{\partial s}\right)_P$ and $v = \left(\frac{\partial h}{\partial P}\right)_s$
Helmholtz energy	$a(T, v) = u - Ts$	$da = -sdT - Pdv$	$-s = \left(\frac{\partial a}{\partial T}\right)_v$ and $-P = \left(\frac{\partial a}{\partial v}\right)_T$
Gibbs energy	$g(T, P) = u + Pv - Ts$	$dg = -sdT + vdp$	$-s = \left(\frac{\partial g}{\partial T}\right)_P$ and $v = \left(\frac{\partial g}{\partial P}\right)_T$

• Maxwell relations

First (u)	$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$
Second (h)	$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$
Third (a)	$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$
Fourth (g)	$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$

• Relations between partial derivatives

- Reciprocity relation: $\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1$
- Cyclic relation (or -1 rule / minus one rule):

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$
- Chain rule: $\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y = \left(\frac{\partial x}{\partial w}\right)_y / \left(\frac{\partial z}{\partial w}\right)_y$
- Combined derivatives: $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$

Evaluation of unknown Partial Derivatives

- **Goal:** To find a systematic method to evaluate the partial derivatives that are not known or not easy to measure
- This method uses the tools that were derived before to express this unknown derivatives into know of measurable ones
- **Systematic evaluation of partial derivatives**
 1. Put energies (u , h , a , g) into the numerator
 2. Eliminate the energy term using the differential expression for the energy
 3. Rewrite the partial derivatives that are left into partial derivatives that are equal to β , κ , c_p , (c_v, α) using the Maxwell relations and/or the relations between partial derivatives
 4. Replace the isochoric pressure coefficient α by: $\alpha = \frac{1}{P} \frac{\beta}{\kappa}$ and replace the specific heat at constant volume c_v with: $c_v = c_p - \frac{Tv\beta^2}{\kappa}$
- Not always all steps have to be done

Evaluation of unknown Partial Derivatives

- **Example:** consider the change of pressure as a function of the change in enthalpy at constant temperature, this is described by the partial derivative $\left(\frac{\partial P}{\partial h}\right)_T$, an expression for $\left(\frac{\partial P}{\partial h}\right)_T$ in terms of P, v, T, s, β , κ , c_p needs to be found
- **Systematic evaluation of partial derivatives**

1. Put energies (u, h, a, g) into the numerator

Applying the reciprocity relation gives:

$$\left(\frac{\partial P}{\partial h}\right)_T = \frac{1}{\left(\frac{\partial h}{\partial P}\right)_T} = \left(\frac{\partial h}{\partial P}\right)_T^{-1}$$

2. Eliminate the energy term using the differential expression for the energy

Consider the total derivative of h: $dh = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP = Tds + vdP$

$$\left(\frac{\partial P}{\partial h}\right)_T = \left(\frac{\partial h}{\partial P}\right)_T^{-1} = \left[\left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial s}{\partial P}\right)_T + \left(\frac{\partial h}{\partial P}\right)_s \left(\frac{\partial P}{\partial P}\right)_T \right]^{-1} = \left[T \left(\frac{\partial s}{\partial P}\right)_T + v \right]^{-1}$$

$\stackrel{=T}{\approx}$ $\stackrel{=v}{\approx}$ $\stackrel{=1}{\approx}$

Evaluation of unknown Partial Derivatives

- **Example:** give an expression for $\left(\frac{\partial P}{\partial h}\right)_T$ in terms of P, v, T, s, β , κ , c_p
3. Rewrite the partial derivatives that are left into partial derivatives that are equal to β , κ , c_p , (c_v , α) using the Maxwell relations and/or the relations between partial derivatives

Using the fourth Maxwell relation: $\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial v}{\partial T}\right)_P$ and $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$

$$\left(\frac{\partial P}{\partial h}\right)_T = \left[T \left(\frac{\partial s}{\partial P}\right)_T + v \right]^{-1} = \quad \text{Work out yourself}$$

Evaluation of unknown Partial Derivatives

- **Example:** give an expression for $\left(\frac{\partial P}{\partial h}\right)_T$ in terms of P, v, T, s, β , κ , c_p
3. Rewrite the partial derivatives that are left into partial derivatives that are equal to β , κ , c_p , (c_v , α) using the Maxwell relations and/or the relations between partial derivatives

Using the fourth Maxwell relation: $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$ and $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$

$$\left(\frac{\partial P}{\partial h}\right)_T = \left[T \left(\frac{\partial s}{\partial P}\right)_T + v \right]^{-1} = \left[-T \left(\frac{\partial v}{\partial T}\right)_P + v \right]^{-1} = [v - T v \beta]^{-1} = \frac{1}{v(1 - T \beta)}$$

4. Replace the isochoric pressure coefficient α by: $\alpha = \frac{1}{P} \frac{\beta}{\kappa}$ and replace the specific heat at constant volume c_v with: $c_v = c_p - \frac{T v \beta^2}{\kappa}$

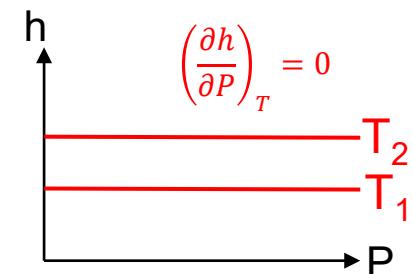
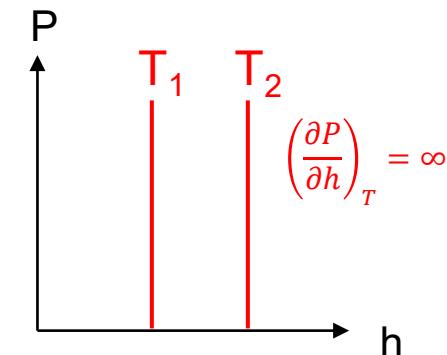
In this case this step is not necessary

Evaluation of unknown Partial Derivatives

- **Example:** give an expression for $\left(\frac{\partial P}{\partial h}\right)_T$ in terms of P, v, T, s, β , κ , c_p
- **Answer:**
$$\left(\frac{\partial P}{\partial h}\right)_T = \frac{1}{v(1-T\beta)}$$
- **What does this mean?**
- To answer this, the value of β is important, this value can be determined / measured
- Consider different substances:
 - Ideal gas
 - Incompressible liquid

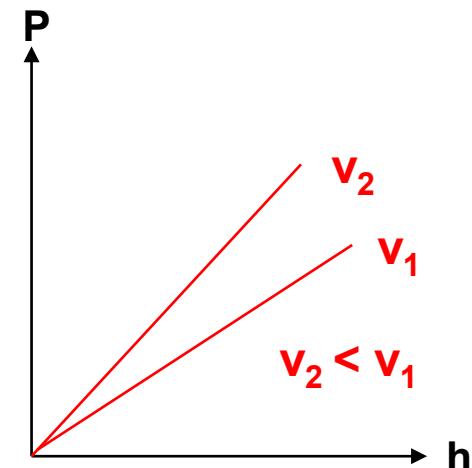
Evaluation of unknown Partial Derivatives

- What does $\left(\frac{\partial P}{\partial h}\right)_T = \frac{1}{v(1-T\beta)}$ mean?
- Evaluate the value of β for an ideal gas:
- Ideal gas: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{T} \rightarrow \left(\frac{\partial P}{\partial h}\right)_T = \frac{1}{v(1-T\beta)} = \frac{1}{0} = \infty$
- This implies that for an ideal gas at a constant T the pressure can change dramatically even if the enthalpy does not change (P is independent of h)
- This is right as the for an ideal gas h does not depend on pressure, but only on temperature ($dh=c_p dT$)



Evaluation of unknown Partial Derivatives

- What does $\left(\frac{\partial P}{\partial h}\right)_T = \frac{1}{v(1-T\beta)}$ mean?
- Evaluate the value of β for an incompressible liquid:
- Incompressible substance: $v = \text{constant} \rightarrow dv = 0$
$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P = 0 \rightarrow \left(\frac{\partial P}{\partial h}\right)_T = \frac{1}{v(1-T\beta)} = \frac{1}{v} = \text{constant}$$
- This implies that if that for an incompressible substance the slope of the isotherm is constant
- There is a linear relation between P and h
- The smaller the volume, the steeper the slope



Internal Energy Changes

- How does the internal energy depend on pressure and temperature?
- Differential change of the internal energy as a function of P and T:

$$du(P, T) = \left(\frac{\partial u}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T dP$$

- Expressions for $\left(\frac{\partial u}{\partial T}\right)_P$ and $\left(\frac{\partial u}{\partial P}\right)_T$ must be found in terms of the measurable properties P, v, T, β , K, c_p

1. First, analyze first partial derivative: $\left(\frac{\partial u}{\partial T}\right)_P$

- Known is $u(s, v)$: $du(s, v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv = Tds - Pdv$
- Therefore: $\left(\frac{\partial u}{\partial T}\right)_P = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_P + \left(\frac{\partial u}{\partial v}\right)_s \left(\frac{\partial v}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P - P \left(\frac{\partial v}{\partial T}\right)_P = c_P - vP\beta$
as $\left(\frac{\partial v}{\partial T}\right)_P = v\beta$ ↑
and $\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_P}{T}$ ↑
 ↑
 -P
 ↑
 $\frac{c_P}{T}$
 ↑
 $v\beta$

Thus: $\left(\frac{\partial u}{\partial T}\right)_P = c_P - vP\beta$

Internal Energy Changes

- How does the internal energy depend on pressure and temperature?
- Differential change of the internal energy as a function of P and T:

$$du(P, T) = \left(\frac{\partial u}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T dP$$

- Expressions for $\left(\frac{\partial u}{\partial T}\right)_P$ and $\left(\frac{\partial u}{\partial P}\right)_T$ must be found in terms of the measurable properties P, v, T, β , κ , c_p (first one is done)

2. Second, analyze second partial derivative: $\left(\frac{\partial u}{\partial P}\right)_T$

- Known is $u(s, v)$: $du(s, v) = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv = Tds - Pdv$
 - Therefore: $\left(\frac{\partial u}{\partial P}\right)_T = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial P}\right)_T + \left(\frac{\partial u}{\partial v}\right)_s \left(\frac{\partial v}{\partial P}\right)_T = T \left(\frac{\partial s}{\partial P}\right)_T - P \left(\frac{\partial v}{\partial P}\right)_T = v(P\kappa - \beta T)$
- as $\left(\frac{\partial v}{\partial P}\right)_T = -v\kappa$ ↑
 ↑
 -P
 ↑
 -vβ
 ↑
 -vκ
- and $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P = -v\beta$
 ↑
 Maxwell

Thus: $\left(\frac{\partial u}{\partial P}\right)_T = v(P\kappa - \beta T)$

Internal Energy Changes

- How does the internal energy depend on pressure and temperature?
- Differential of the internal energy as a function of P and T:

$$du(P, T) = \left(\frac{\partial u}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T dP$$

- Found: $\left(\frac{\partial u}{\partial T}\right)_P = c_P - vP\beta$ and: $\left(\frac{\partial u}{\partial P}\right)_T = v(P\kappa - \beta T)$ filling in, in the differential yields:

$$du(P, T) = (c_P - vP\beta)dT + v(P\kappa - \beta T)dP$$

- This is the general expression for the change of the **internal energy** as a function of the **pressure** and the **temperature** for **any** substance
- Changes of the internal energy can be found by integration of this expression between the upper and lower limits of pressure and temperature $\int_{(P_1, T_1)}^{(P_2, T_2)} du(P, T)$
- All quantities in this expression can be measured, if they are measured the change of the internal energy can be found
- Similar expressions can be found for enthalpy, entropy, Helmholtz and Gibbs energy

General Expressions for Changes in u , h and s

- How do the internal energy, enthalpy and entropy in general depend on pressure and temperature?

- General expression for internal energy change as a function of pressure and temperature

$$du(P, T) = (c_P - vP\beta)dT + v(P\kappa - \beta T)dP$$

- General expression for enthalpy change as a function of pressure and temperature
(see WaTT exercise 8.2)

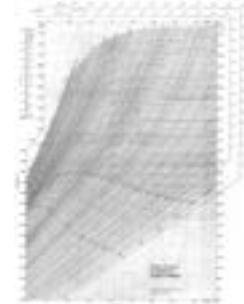
$$dh(P, T) = c_P dT + \nu(1 - \beta T) dP$$

- General expression for entropy change as a function of pressure and temperature

$$ds(P, T) = \frac{c_P}{T} dT - v\beta dP$$

- Integration yields expressions for changes in u , h and s and together with measurements changes in u , h and s can be determined

- These relations are used to make tables and diagrams



Temp (°C)	Press (bar)	Specific volume (m³/kg)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (kJ/kg)
T	P	v ₁ , v ₂	s ₁ , s ₂	h ₁ , h ₂	s ₁ , s ₂
120	1.000	1.023 / 1.019	503.00 / 502.93	503.77 / 502.93	0.4776 / 0.4776
100	2.001	1.000 / 0.9865	544.02 / 539.94	546.01 / 539.94	0.5000 / 0.4994
90	2.013	1.070 / 0.9900	581.14 / 569.00	583.13 / 569.00	0.5247 / 0.5131
80	4.004	1.000 / 0.9500	631.00 / 611.00	633.00 / 611.00	0.5518 / 0.5418
70	6.078	1.023 / 0.9301	684.00 / 656.00	696.27 / 656.00	0.5783 / 0.5647
60	9.179	1.052 / 0.8900	747.00 / 707.00	769.27 / 707.00	0.6047 / 0.5870
50	13.957	1.070 / 0.8400	819.00 / 759.00	841.27 / 759.00	0.6303 / 0.5993
40	20.626	1.074 / 0.7800	899.00 / 709.00	921.27 / 709.00	0.6553 / 0.5993

Internal Energy Changes of an Ideal Gas

- How does the internal energy depend on pressure and temperature for an ideal gas?
- General expression for internal energy change as a function of pressure and temperature

$$du(P, T) = (c_P - vP\beta)dT + v(P\kappa - \beta T)dP$$

- For an **ideal gas** the equation of state is: $Pv = RT \rightarrow v = RT/P$

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{T} \quad \text{and} \quad \kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = \frac{1}{P}$$

- Substitution of this result in the general relation yields:

$$du(P, T) = \left(c_P - \frac{vP}{T} \right) dT + v \left(P \frac{1}{P} - \frac{1}{T} T \right) dP = (c_P - R)dT + v(1 - 1)dP = c_v dT$$

- LOOK GOOD AT THIS ANSWER, LET IT COME TO YOU AND ENJOY IT !! ☺ ☺
- We DERIVED and PROVED what we already used before: $du = c_v dT$, the internal energy of an ideal gas is a function of temperature only and not of pressure
- Similar follows for the enthalpy $dh = c_p dT$ (also used before without prove)

Int. Energy Changes of Incompressible Substance

- How does the internal energy depend on pressure and temperature for an incompressible substance?
- General expression for internal energy change as a function of pressure and temperature

$$du(P, T) = (c_P - vP\beta)dT + v(P\kappa - \beta T)dP$$

- For an **incompressible substance**: $v = \text{constant} \rightarrow dv = 0$

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = 0 \quad \text{and} \quad \kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = 0$$

- Substitution of this result in the general relation yields:

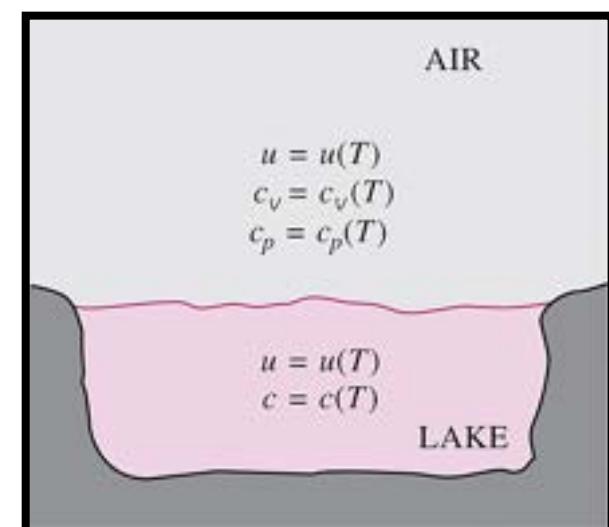
$$du(P, T) = c_P dT = c_v dT$$

- ENJOY THIS ANSWER !!

- Also, this was already known but is proven now

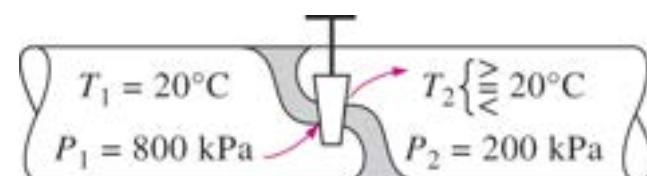
An important fact in thermodynamics is derived and proven:

The internal energies and specific heats of ideal gases and incompressible substances depend on temperature only



Joule Thomson Effect / Throttling

- A **throttling process or Joule–Thomson process** is the process where a gas or liquid is forced through a valve or porous plug while kept insulated so that no heat is exchanged with the environment
- During such a process no work is performed, and no heat is transferred therefore the enthalpy does not change ($dh = 0$) (remember from first law: $q_{in} + w_{in} + h_{in} = q_{out} + w_{out} + h_{out} \rightarrow h_{in} = h_{out} \rightarrow dh = 0$)
- In thermodynamics this is called, **the Joule–Thomson effect or Joule–Kelvin effect or Kelvin–Joule effect or Joule–Thomson expansion**
- At room temperature, all gases except hydrogen, helium and neon cool upon expansion by the Joule–Thomson process
- The effect is named after James Prescott Joule and William Thomson, 1st Baron Kelvin, who discovered it in 1852
- It followed upon earlier work by Joule, on Joule expansion, in which a gas undergoes free expansion in a vacuum and the temperature is unchanged, if the gas is ideal
- A video about Joule Thompson Throttling / Adiabatic Cooling of Adam Beatty <https://www.youtube.com/watch?v=FpE5FgK3zWk>



Generally, the temperature of a fluid may increase, decrease, or remain constant during a throttling process.

Joule Thomson Effect / Throttling

- The throttling process is of the highest technical importance
- It is at the heart of thermal machines such as refrigerators, air conditioners, heat pumps and liquefiers
- Throttling is a fundamentally irreversible process
- The throttling due to the flow resistance in supply lines, heat exchangers, regenerators, and other components of (thermal) machines is a source of losses that limits the performance
- We met throttling in the refrigeration and heat pump cycles, examples:



Refrigerator



Air conditioning



Snow cannon



Aerosol

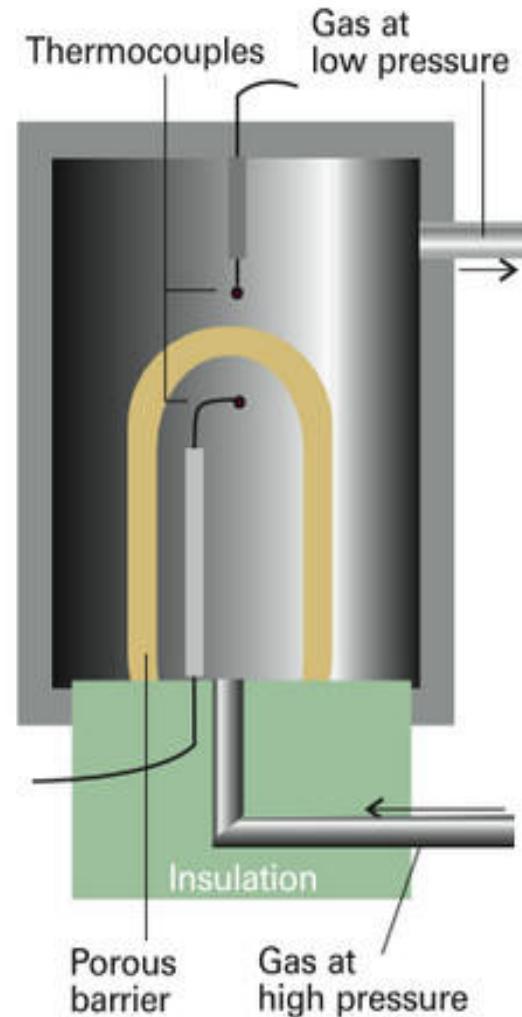
Joule Thomson Effect in Snow Cannon

- Example Joule Thomson effect: Snow cannon
- Small droplets of water are mixed with compressed air
- This mixture expands in a throttling valve
- The gas cools down and the water droplets turn into ice



Measuring the Joule Thomson Effect

- Measuring the Joule Thomson effect
- Apparatus used for measuring the Joule – Thomson effect
- The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated
- This arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy)
- Whether the expansion results in a heating or a cooling of the gas depends on the conditions



Joule Thomson Coefficient

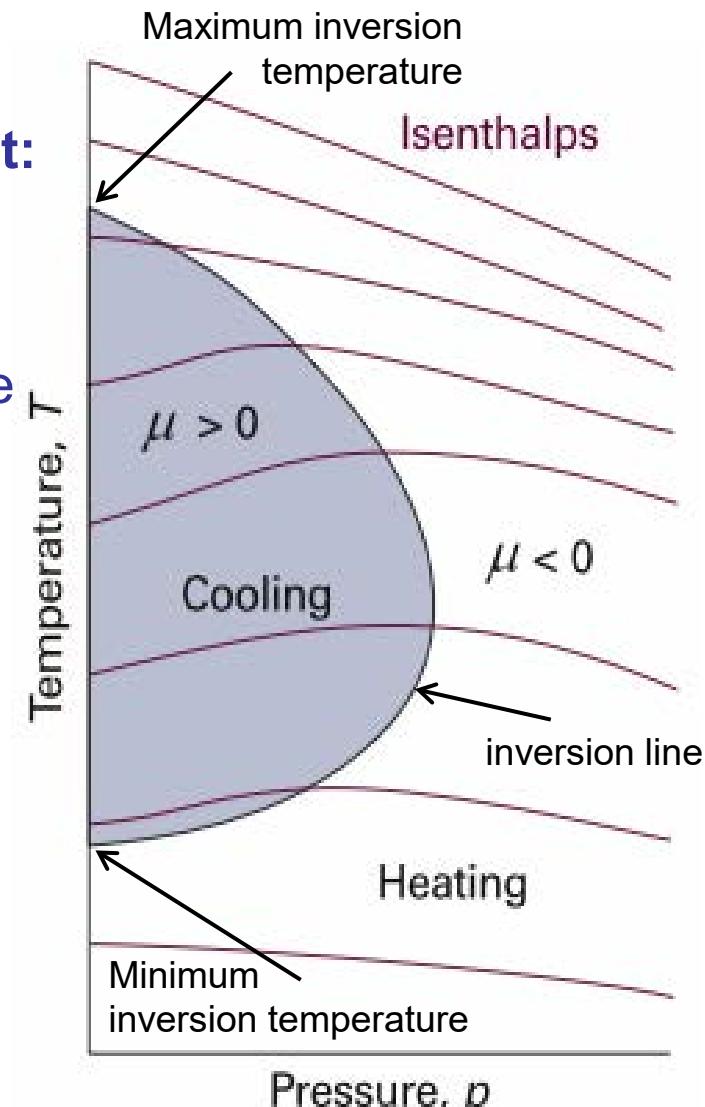
- The temperature behavior of a fluid during a throttling ($h = \text{constant}$, $dh = 0$) process is described by the **Joule-Thomson coefficient**:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

- The Joule-Thomson coefficient represents the slope of $h = \text{constant}$ lines on a T-P diagram
- The slope can be positive, negative or 0:

$$\mu_{JT} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

- The line that passes through the points with $\mu_{JT} = 0$ is called the inversion line
- The temperature at that point is called the inversion temperature



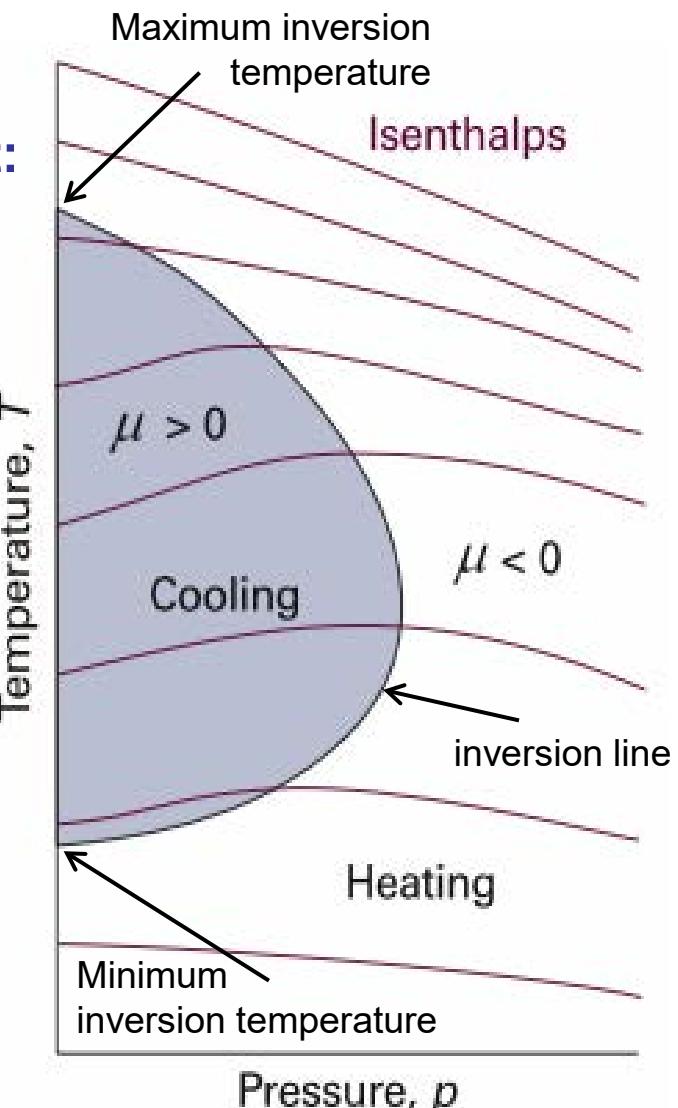
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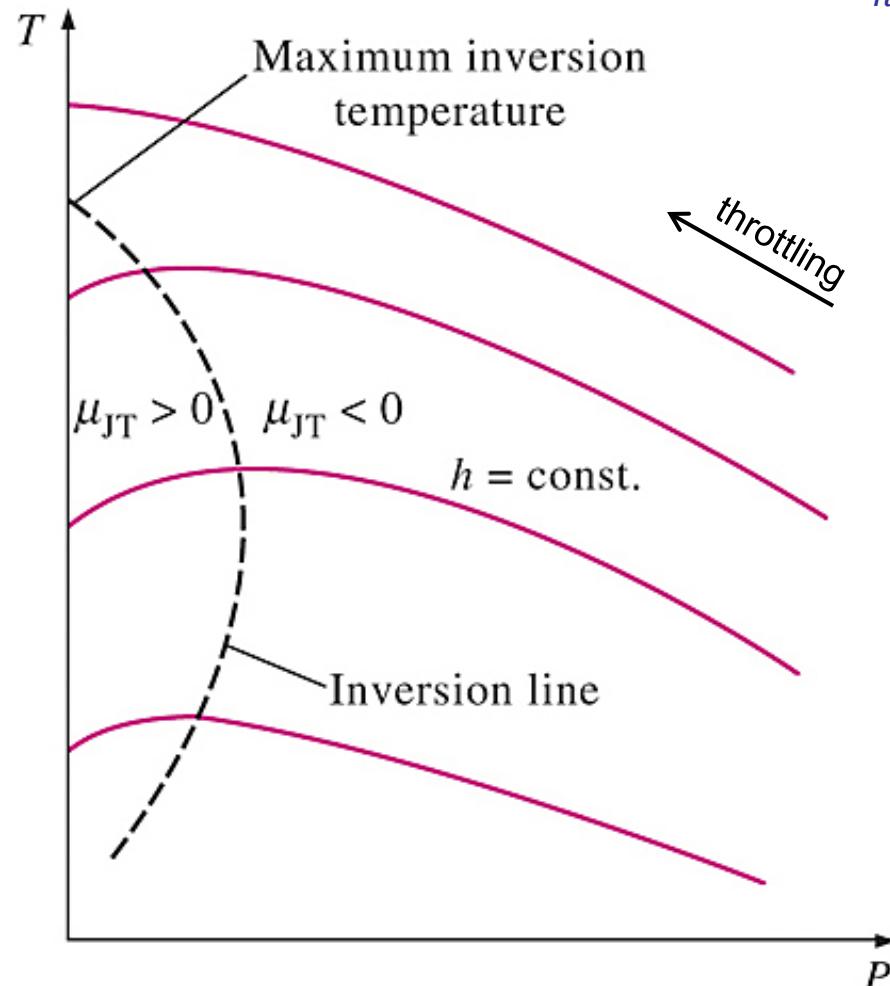
- The Joule-Thomson coefficient is a measure of the change in temperature during a constant enthalpy throttling process
- During a throttling process (decreasing pressure, expansion), the coefficient can be positive, negative or 0 (for ideal gas only):

$$\mu_{JT} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature constant} \\ > 0 & \text{temperature decreases} \end{cases}$$



Joule Thomson Coefficient

Joule Thomson coefficient: $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$



Constant-enthalpy lines of a substance
on a T - P diagram

- A throttling process proceeds along a constant-enthalpy line in the direction of decreasing pressure (from right to left)
- Therefore, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line
- However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line
- It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature
- This presents a problem for substances whose maximum inversion temperature is well below room temperature

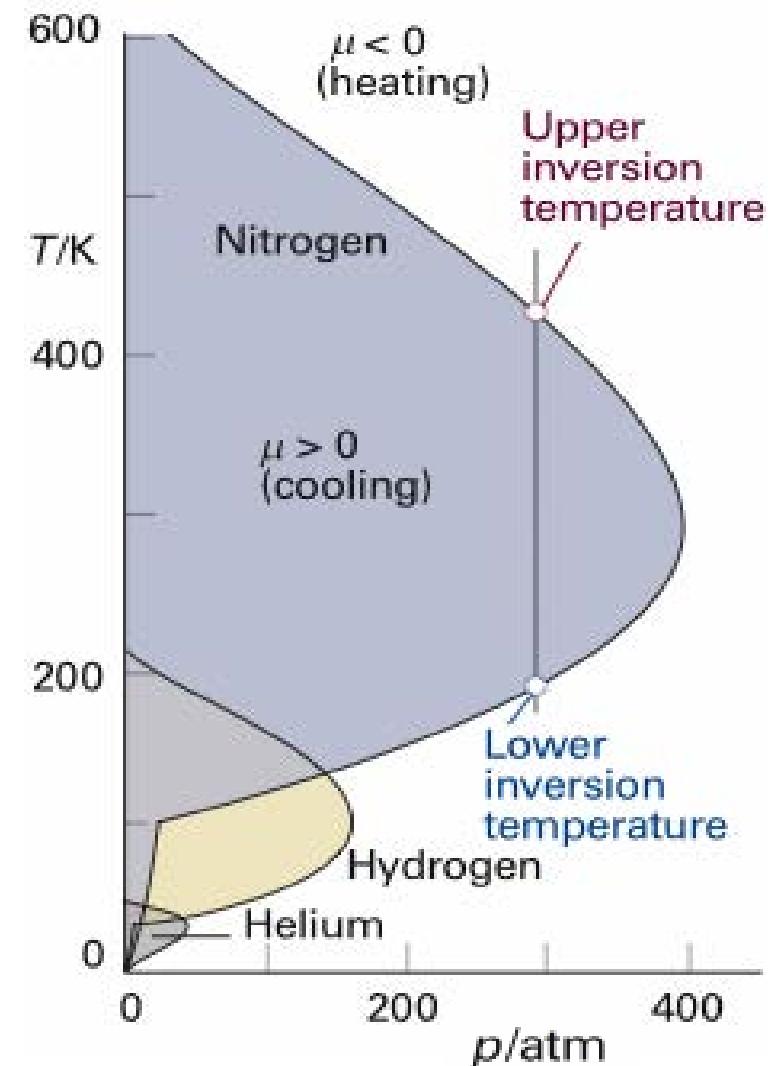
Joule Thomson Coefficient

- Joule-Thomson coefficient: $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$

- During a throttling process (decreasing pressure, expansion):

$$\mu_{JT} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

- **Helium:** only in a small area close to the absolute zero $\mu_{JT} > 0$. Therefore, cooling during expansion of helium takes place close to zero only → helium heats during expansion at environmental pressure
- **Nitrogen:** the area in which $\mu_{JT} > 0$ is large and the inversion temperature at environmental pressure is far above room temperature → nitrogen cools during expansion at environmental pressure



Joule Thomson Coefficient

- Find an expression for the Joule Thomson coefficient $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$ in terms of measurable quantities: P, v, T, s, β, κ, c_p
- Follow the method of systematic evaluation of partial derivatives**

1. Put energies (u, h, a, g) into the numerator

Applying the -1 rule and the reciprocity relation gives:

$$\left(\frac{\partial T}{\partial P}\right)_h \left(\frac{\partial h}{\partial T}\right)_P \left(\frac{\partial P}{\partial h}\right)_T = -1 \rightarrow \mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = \frac{-1}{\left(\frac{\partial h}{\partial T}\right)_P \left(\frac{\partial P}{\partial h}\right)_T} = -\frac{\left(\frac{\partial h}{\partial P}\right)_T}{\left(\frac{\partial h}{\partial T}\right)_P}$$

- now we are left with two partial derivatives instead of one ☹, however the energy term h is in the numerator and we can further evaluate both partial derivatives ☺
- We did already (almost) one of them, we found in slide 22 and further:
$$\left(\frac{\partial P}{\partial h}\right)_T = \left(\frac{\partial h}{\partial P}\right)_T^{-1} = \frac{1}{v(1-T\beta)}$$
, so therefore: $\left(\frac{\partial h}{\partial P}\right)_T = v(1 - T\beta)$
- Now we have (only) to do the second partial derivative: $\left(\frac{\partial h}{\partial T}\right)_P$

Joule Thomson Coefficient

- Now we have (only) to do also the second partial derivative: $\left(\frac{\partial h}{\partial T}\right)_P$
- Systematic evaluation op partial derivatives**

1. Put energies (u, h, a, g) into the numerator

The energy is already in the numerator, this step can be skipped

2. Eliminate the energy term using the differential expression for the energy

Consider the total derivative of h : $dh = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_S dP = Tds + vdP$

$$\left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial s}{\partial T}\right)_P + \left(\frac{\partial h}{\partial P}\right)_S \left(\frac{\partial P}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P + v \cdot 0$$

$\Rightarrow T$ $\Rightarrow v$ $\Rightarrow 0$

3. Rewrite the partial derivatives that are left into partial derivatives that are equal to β , κ , c_p , (c_v , α) using the Maxwell relations and/or the relations between partial derivatives

$$\left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P = c_P \quad \text{as is defined: } c_P = \left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$$

Joule Thomson Coefficient

- Find an expression for the Joule Thomson $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$ in terms of measurable quantities: P, v, T, s, β , κ , c_p
- **Following the method of systematic evaluation op partial derivatives we found:**

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = - \frac{\left(\frac{\partial h}{\partial P}\right)_T}{\left(\frac{\partial h}{\partial T}\right)_P}$$

- We analyzed both partial derivatives and found:

$$\left(\frac{\partial h}{\partial P}\right)_T = v(1 - T\beta) \quad \text{and} \quad \left(\frac{\partial h}{\partial T}\right)_P = c_P$$

- Combing everything results in: $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = - \frac{\left(\frac{\partial h}{\partial P}\right)_T}{\left(\frac{\partial h}{\partial T}\right)_P} = \frac{v(T\beta - 1)}{c_P}$
- So, the Joule-Thomson coefficient can be determined from c_P and the knowledge of the behavior of P, T and v of a substance
- The other way around it is also possible to determine c_P by measuring the Joule-Thomson coefficient together with the P, T and v data of a substance

Joule Thomson Coefficient of Ideal Gas

- What is the value of the Joule–Thomson coefficient for an ideal gas?
- The general expression for the Joule–Thomson coefficient:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h = \frac{v(T\beta - 1)}{c_P}$$

- For an **ideal gas** the equation of state is: $Pv = RT \rightarrow v = RT/P$

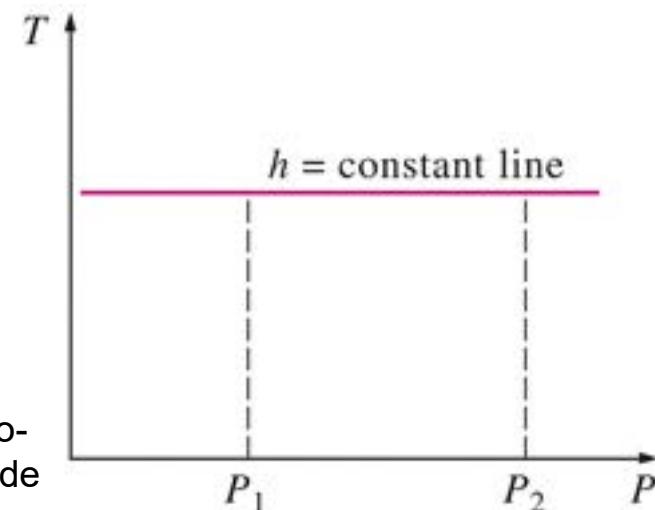
$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{T}$$

- Substitution of this result in the general relation yields:

$$\mu_{JT, \text{ideal gas}} = \left(\frac{\partial T}{\partial P} \right)_h = \frac{v(T/T-1)}{c_P} = 0$$

- Thus, the Joule-Thomson coefficient of an ideal gas is zero and during throttling the temperature of an ideal gas does not change

The temperature of an ideal gas remains constant during a throttling process since $h = \text{constant}$ and $T = \text{constant}$ lines on a $T-P$ diagram coincide



Recapitulate Class 17

- **Thermodynamic coefficients**
 - Thermal expansion: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$
 - Isothermal compressibility: $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$
 - Isochoric pressure coefficient: $\alpha = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_v = \frac{1}{P} \frac{\beta}{\kappa}$ (Not easy to measure)
 - Joule Thomson coefficient: $\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$
 - Specific heat at constant pressure: $c_P = \left(\frac{\partial h}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P$
 - Specific heat at constant volume: $c_v = \left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v$ (Not easy to measure)
 - Mayer relation or Nernst–Lindemann relation: $c_P - c_v = \frac{T v \beta^2}{\kappa}$
- Note: α and c_v are not easy to measure but can be expressed in c_P , β and κ
- **Systematic evaluation of partial derivatives** to express quantities which are difficult to measure in terms of readily measured quantities as much as possible (the goal of all this Math)
- Applied to internal energy: $du(P, T) = (c_P - vP\beta)dT + v(P\kappa - \beta T)dP$, which for an ideal gas reduces to: $du(P, T) = c_v dT$ (U for ideal gas only depends on T !)

WaTT Summarized

- The state postulate states that two independent properties are enough to find all other thermodynamic data, it is obvious to choose for those two quantities two that are easy to measure (e.g., P, T, v)
- To this end, we want to write changes in quantities (e.g., energies, entropy) as a function of two other (easily measurable) quantities → partial differentials play an important role and properties are written as total differential with two variables
- To be able to calculate values for e.g., energy changes it is important to find an expression for the partial differentials which also consists of properties that can be measured
- The value of a few partial differentials is known, others must be rewritten into known or measurable quantities
- Different relationships are available for this, such as the Maxwell relations and calculation rules for differentials
- Via (sometimes long) descriptions an expression can be found for the differential of the quantity to be determined
Integrating the differential leads to the desired change of a property as energy or entropy
- These relationships are behind the values in tables and diagrams

Formulas (WaTT)

- Most important relations summarized on one page
- Formula form is supplied at the exam
- For the test also remember that you understand what the partial differential physically represents (slope in a diagram) and you can draw them in a diagram, so you know whether the line increases or decreases and whether it is linear
- E.g., $\left(\frac{\partial h}{\partial s}\right)_P = T$ is the slope of an isobar in a Mollier – diagram (hs)
- The slope of the line is therefore equal to the temperature, T, so in the two-phase zone where the temperature is constant, the isobar is linearly rising, in the superheated vapor zone it is becoming steeper as T increases

Differential expressions for thermodynamic energies

Energy	Symbol, variables	Differential
Internal energy	$u(s, v)$	$du = Tds - Pdv$
Enthalpy	$h(s, P) = u + Pv$	$dh = Tds + vdP$
Helmholtz energy	$a(T, v) = u - Ts$	$da = -sdT - Pdv$
Gibbs energy	$g(T, P) = u - Ts + Pv$	$dg = -sdT + vdP$

Maxwell relations

$$\left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$\left(\frac{\partial v}{\partial T}\right)_P = - \left(\frac{\partial s}{\partial P}\right)_T$$

Thermodynamic coefficients

Isothermal compressibility coefficient: $\kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T$

Thermal expansion coefficient: $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$

Joule-Thomson coefficient: $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$

Specific heat for a constant volume process: $c_v = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$

Specific heat for a constant pressure process: $c_p = \left(\frac{\partial h}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P$

Nernst-Lindeman Relation: $c_v = c_P - \frac{T v \beta^2}{\kappa}$

Clapeyron relation: $\left(\frac{dP}{dT}\right)_{sat} = \left(\frac{h_{12}}{T v_{12}}\right)$

Clausius-Clapeyron relation: $\left(\frac{dP}{T}\right)_{sat} = \frac{h_{1v}}{R} \left(\frac{dT}{T^2}\right)_{sat}$ of $\left(\frac{d(\ln P)}{dT}\right)_{sat} = \frac{h_{1v}}{RT_{sat}^2}$