



## Definition of Thermodynamics:

“Thermodynamics is the Science of Energy and Entropy”



- **Some definitions.**
- **The zeroth law.**
- **Properties of pure substances.**
- **Ideal gas law.**
- **Entropy and the second law.**



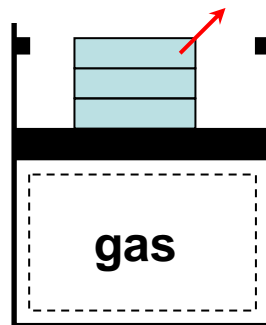
**Intensive properties:** independent of the size of the system [T, P]

**Extensive properties:** dependent of the size of the system [V]

**Specific extensive properties per unit mass** [ $v$ ]

### Quasi-static process

A process in which the system remains infinitesimally close to an equilibrium state at all times.

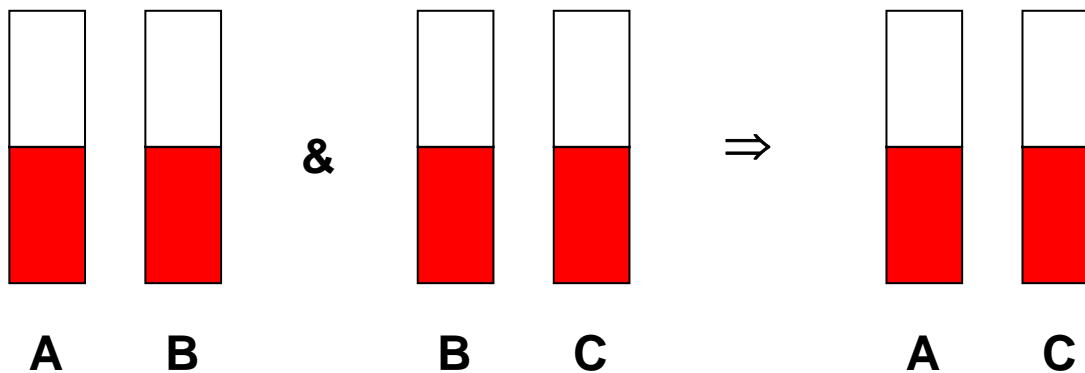




# 0<sup>th</sup> The Zeroth law of thermodynamics

Thermal equilibrium: two states are said in thermal equilibrium if, when they are brought into thermal contact with one another, their states do not change.

0<sup>th</sup> law of thermodynamics: if A is in thermal equilibrium with B and B is in thermal equilibrium with C the; **A is in thermal equilibrium with C.**



This “obvious” law is the basis for the validity of temperature measurement.

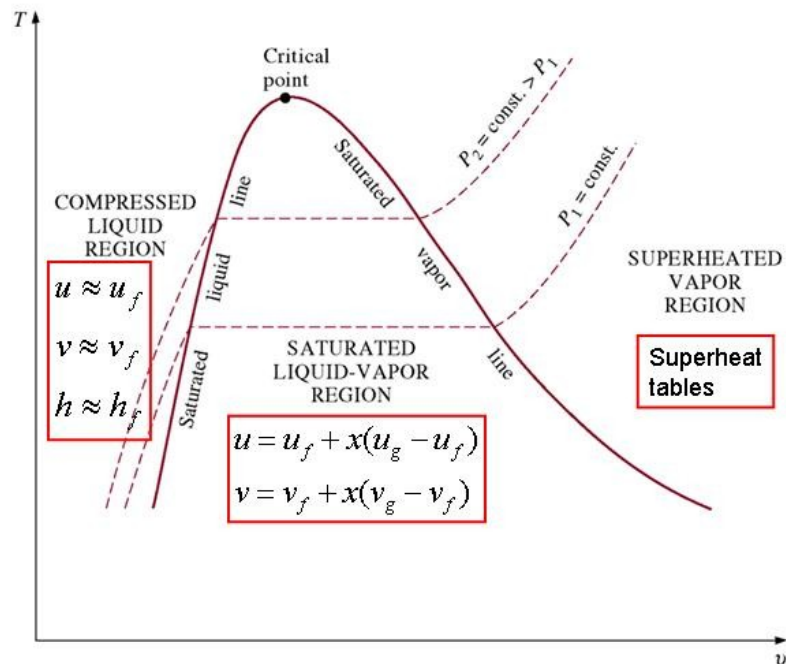
The 0<sup>th</sup> cannot be concluded from the other laws of thermodynamics.



## Properties of pure substances.

### Properties of pure substances.

**Definition:** a pure substance is a substance with fixed and stable chemical composition





### The ideal-gas equation of state

General formulation:

$$Pv = ZRT$$

Pressure ← [ ] ← Temperature  
Specific volume ← [ ] ← Gas constant  
[ ] ← Compressibility factor

Ideal gas

$$Z=1$$

Real gas

$$\begin{matrix} Z < 1 \\ Z = 1 \\ Z > 1 \end{matrix}$$

**A gas behaves like an ideal gas if:**

- The pressure is very low.
- The temperature is very high ( $T > 2 T_c$ ), regardless of pressure.



## Specific heats

Gives you an idea on the energy that you must spend to rise the temperature of 1 kg of a substance by 1 degree.

At constant volume:

$$C_v = \left( \frac{\partial u}{\partial T} \right)_{v=cte}$$

At constant pressure:

$$C_p = \left( \frac{\partial h}{\partial T} \right)_{p=cte}$$

$$C_p - C_v = R$$



# First law of Thermodynamics

## Clausius statement:

The variation of energy during a process is equal to the sum work and heat exchanged with the environment during the same process.

$$\Delta E = W + Q$$

Variation in internal energy      Work      Heat

The diagram illustrates the first law of thermodynamics. The equation  $\Delta E = W + Q$  is shown at the top. Below the equation, three red arrows point downwards from the terms  $\Delta E$ ,  $W$ , and  $Q$  to the labels "Variation in internal energy", "Work", and "Heat" respectively. A red arrow also points from the  $\Delta E$  label to the left.

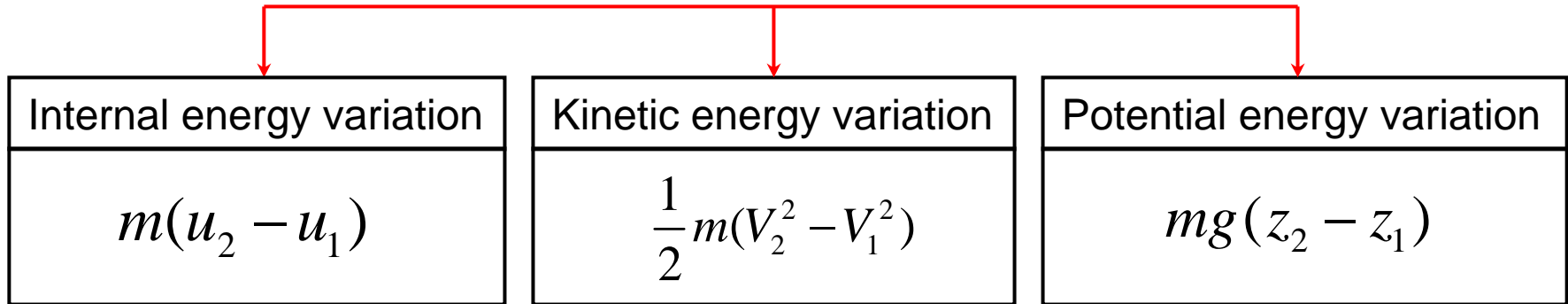




# MECH 351: Review

## First law of Thermodynamics

$$\Delta E$$

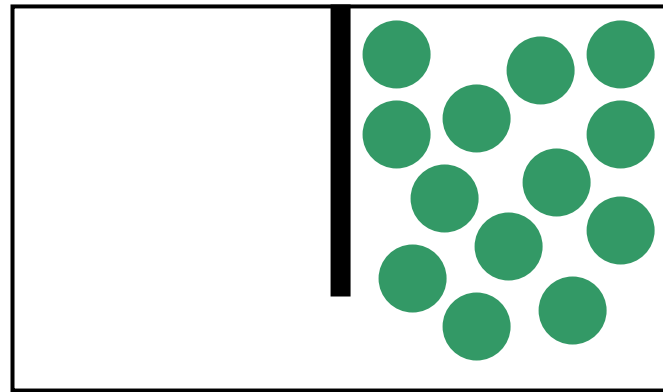
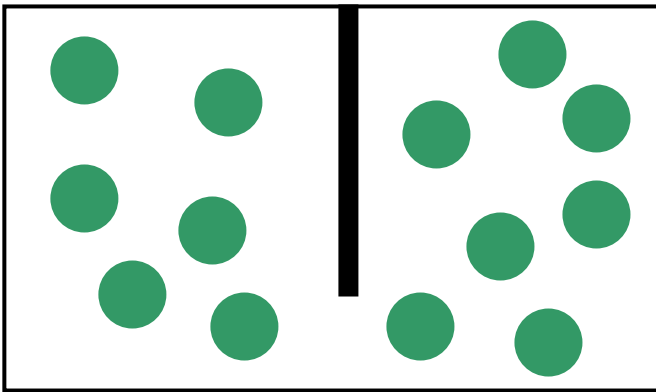


Steady flow process

$$\begin{cases} \sum \dot{m}_i = \sum \dot{m}_e \\ \dot{Q} - \dot{W} = \underbrace{\sum \dot{m}_e \left( h_e + \frac{V_e^2}{2} + gz_e \right)}_{\text{exits}} - \underbrace{\sum \dot{m}_i \left( h_i + \frac{V_i^2}{2} + gz_i \right)}_{\text{inlets}} \end{cases}$$

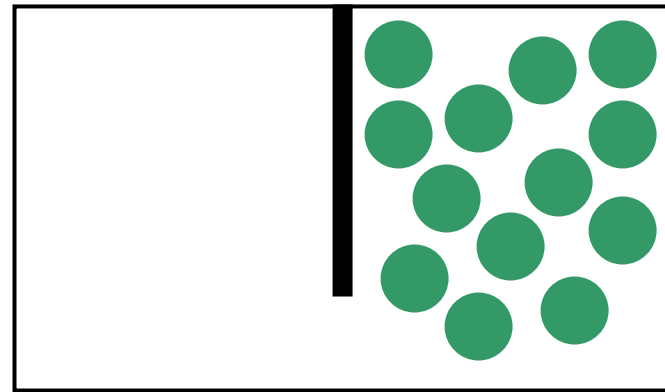
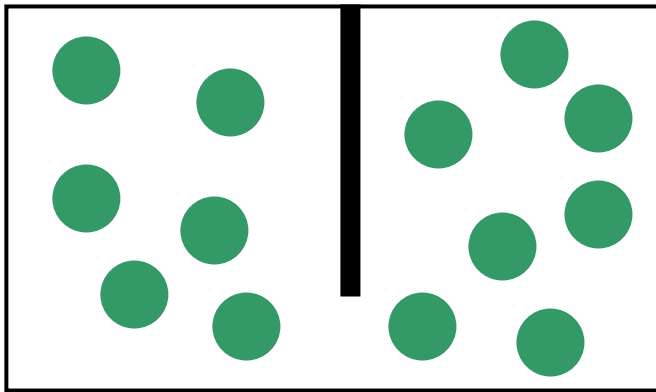


## Second law of Thermodynamics





## Second law of Thermodynamics



The second law states that processes occur in a certain direction.

A process is realizable only if the 1<sup>st</sup> and 2<sup>nd</sup> laws for thermodynamics are fulfilled.



# MECH 351: Review

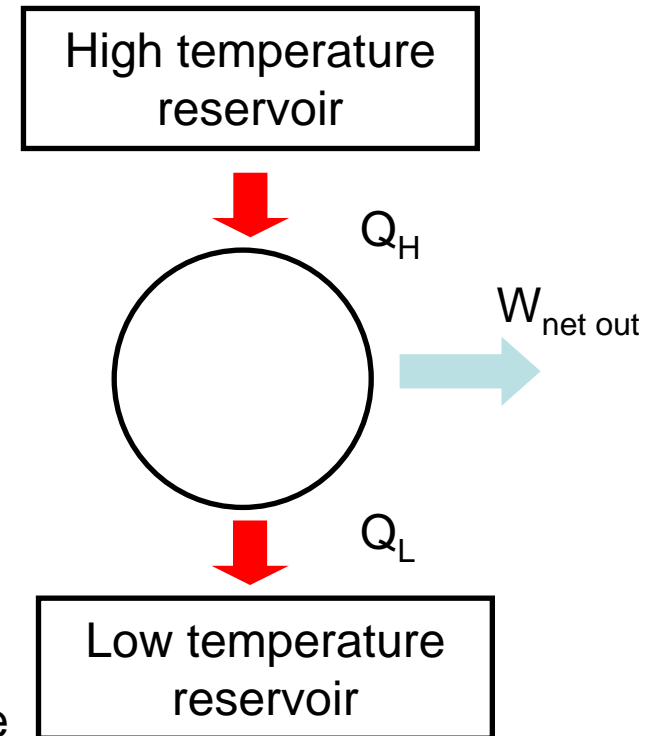
## Second law of Thermodynamics

### Heat engine

Heat  $\longrightarrow$  Work

$$\eta_{th} = \frac{W_{net\ out}}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

- $W_{net\ out}$  net work output
- $Q_H$  heat supplied to the engine
- $Q_L$  heat rejected by the engine





## Refrigeration and Heat Pump

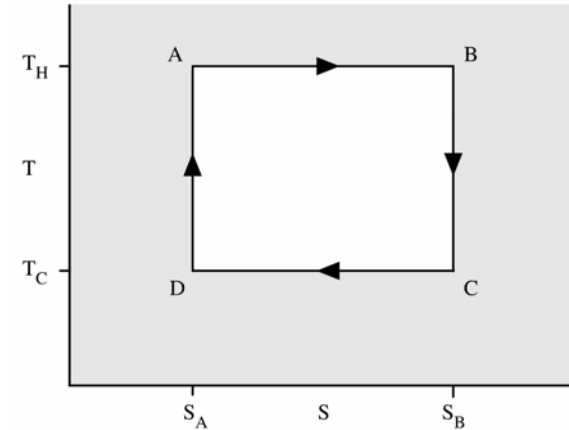
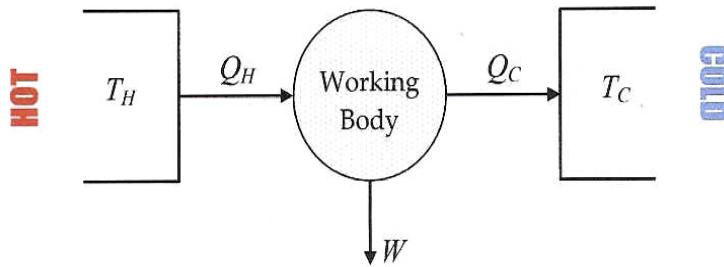
Work  $\longrightarrow$  Heat

$$COP_R = \frac{Q_L}{W_{net\ in}} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

$$COP_{HP} = \frac{Q_H}{W_{net\ in}} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$



# Carnot cycle



- A-B: Reversible isothermal expansion
- B-C: Reversible adiabatic expansion
- C-D: Reversible isothermal compression
- D-A: Reversible adiabatic compression

$$\eta_{th} = 1 - \frac{T_L}{T_H}$$

Example:

$T_L = 430 \text{ C}$

$T_H = 1870 \text{ C}$

$\eta_{th} = 67.2$



Increase in entropy principle:

$$S_{gen} \geq 0$$





## Entropy relations

$$T ds = du + P dv$$

$$T ds = dh - v dP$$

## Ideal gases

$$\left( \frac{T_2}{T_1} \right)_{s=cte} = \left( \frac{v_1}{v_2} \right)^{k-1}$$

$$\left( \frac{T_2}{T_1} \right)_{s=cte} = \left( \frac{P_2}{P_1} \right)^{(k-1)/k}$$

$$\left( \frac{P_2}{P_1} \right)_{s=cte} = \left( \frac{v_1}{v_2} \right)^k$$





Ideal process for steady flow devices is the isentropic process (adiabatic and reversible), isentropic efficiency is:

Turbine 
$$\eta_T = \frac{\text{Actual turbine work}}{\text{Isentropic turbine work}} = \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$

Compressors 
$$\eta_C = \frac{\text{Isentropic compressor work}}{\text{Actual compressor work}} = \frac{h_{2s} - h_1}{h_{2a} - h_1}$$

Nozzles 
$$\eta_N = \frac{\text{Actual KE at nozzle exit}}{\text{Isentropic KE at nozzle exit}} = \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$

(a) actual; (s) isentropic



**Boiler**

# Vapor and Combined Power Cycles



**Condenser**



**Turbine**

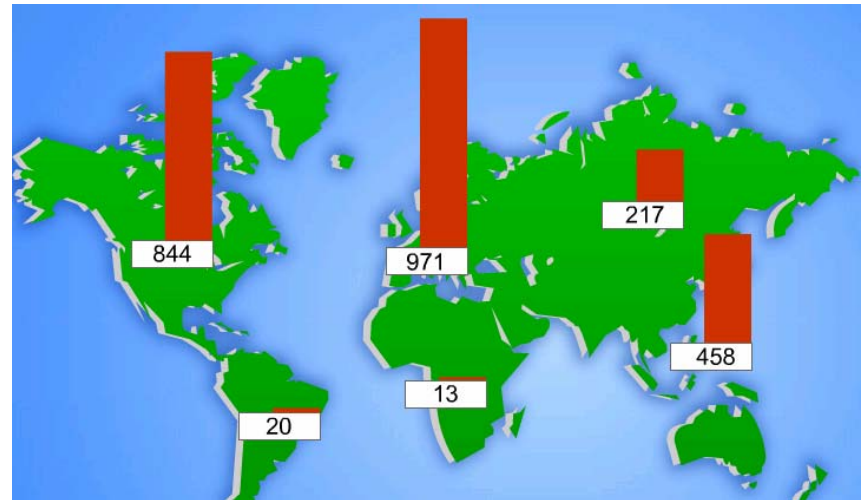


**What is it? vapor and combined cycles are cycles where the fluid is alternatively vaporized (in the boiler) and condensed (in the condenser)**

**=> Create work that can be converted usually to electricity.**

**Why using steam? Because of its many desirable characteristics: low cost, availability (not for a long time ...may be !!!) and high enthalpy of vaporization.**

**How the steam is created?  
By heating the water using a nuclear source or combustion gases.**





Born in Edinburgh (Scotland) in 1820, was the son of a British Army lieutenant.

He attended University of Edinburgh but he left without degree.

He worked on several topics including civil engineering, naval engineering, botany and music theory. He also developed a complete theory of the steam engine.

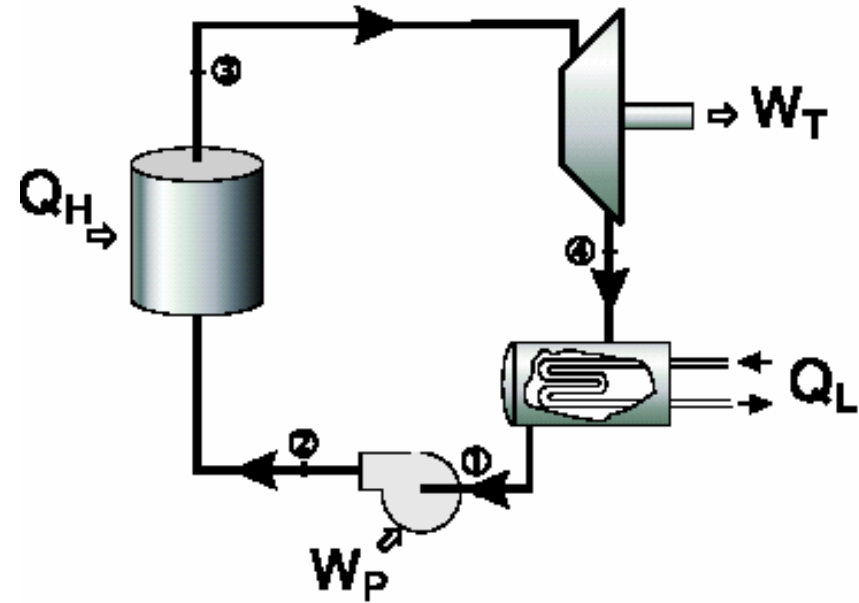
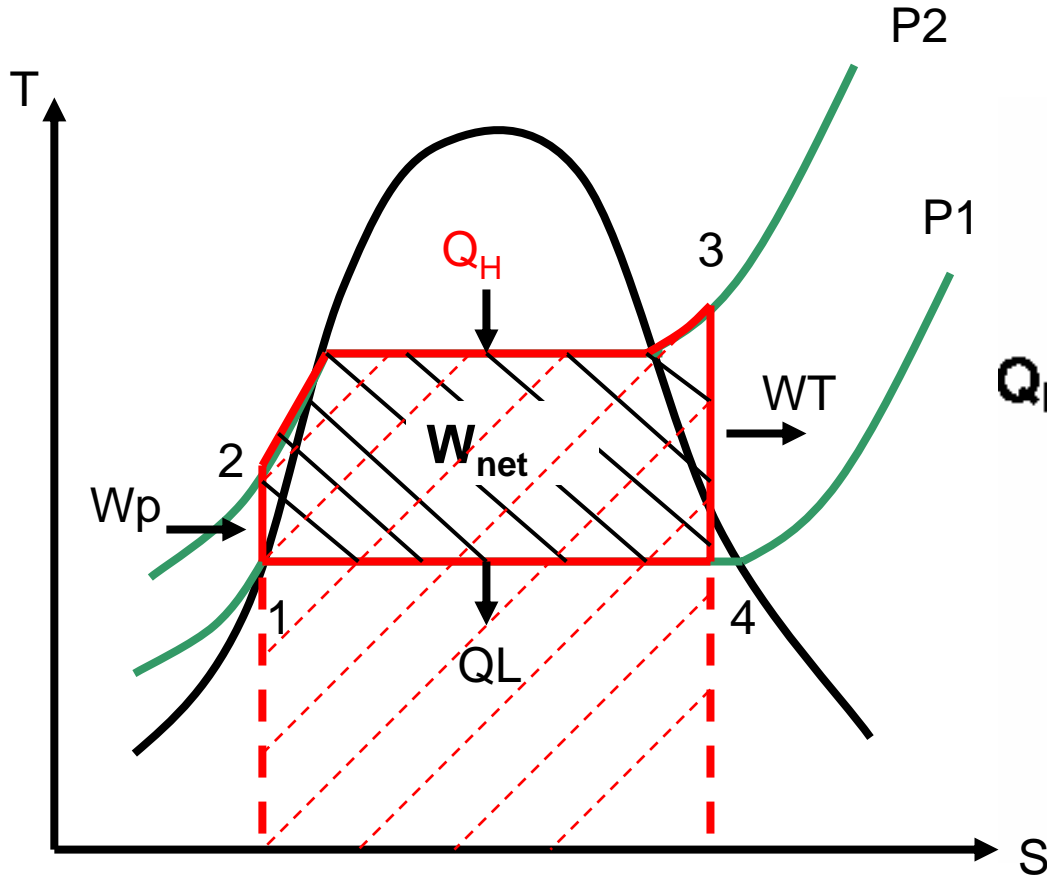
He died in Glasgow in 1872.



William Rankine



# IDEAL RANKINE CYCLE

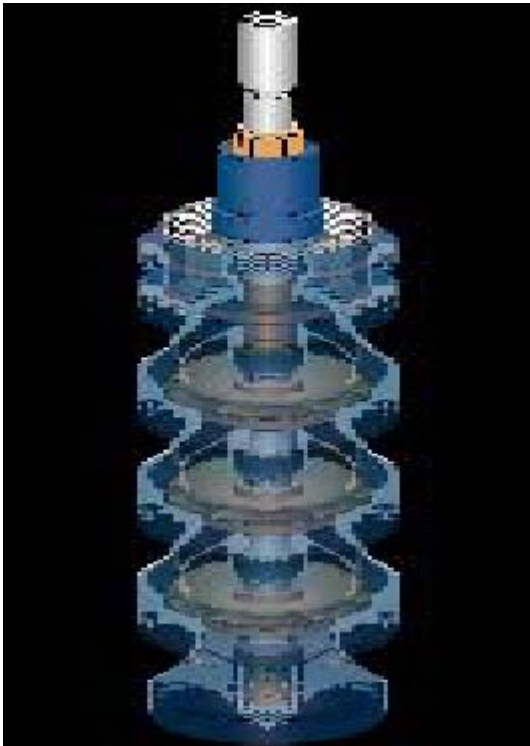


Efficiency of the ideal Rankine cycle:  $\eta = \frac{\text{what you want}}{\text{what you pay}} = \frac{W_{net}}{Q_H}$



# Rankine Cycle devices

## Pump



Centrifugal pump

Isentropic process ( $Q=0$  and  $s_{in}=s_{out}$ )

$$W_p = v(P_2 - P_1)$$

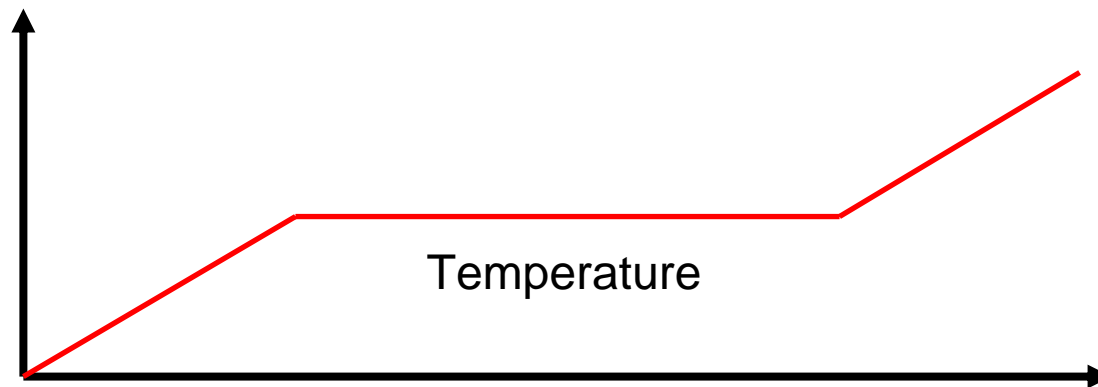
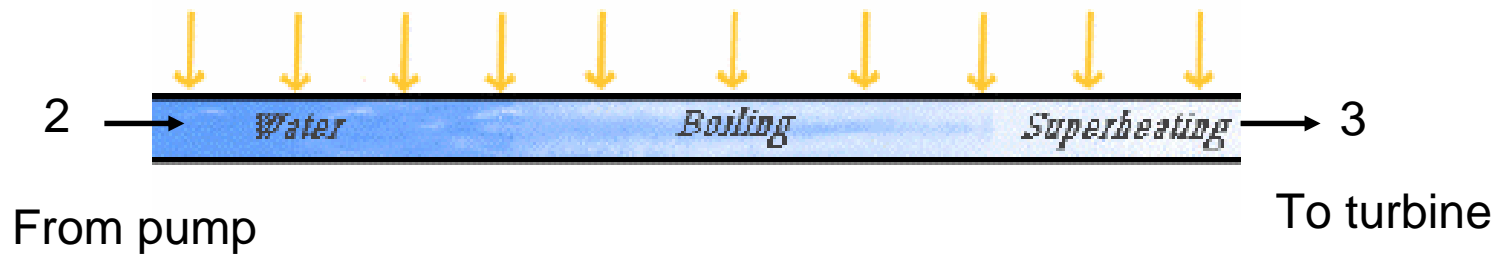
$$W_p = h_2 - h_1$$

$$s_2 = s_1$$



# Rankine Cycle devices

## Boiler



Isobaric heat supply:  $P_3 = P_2$

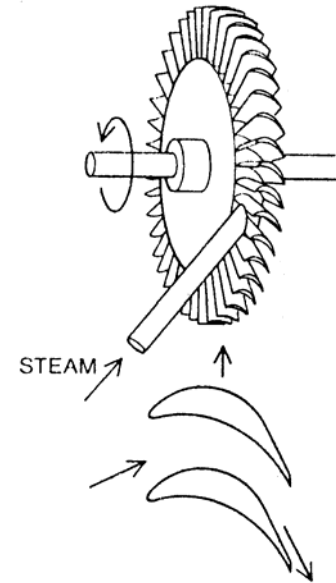
$$Q = h_3 - h_2$$

No work:  $W = 0$



# Rankine Cycle devices

## Turbine



Isentropic process ( $Q=0$  and  $s_{in}=s_{out}$ )

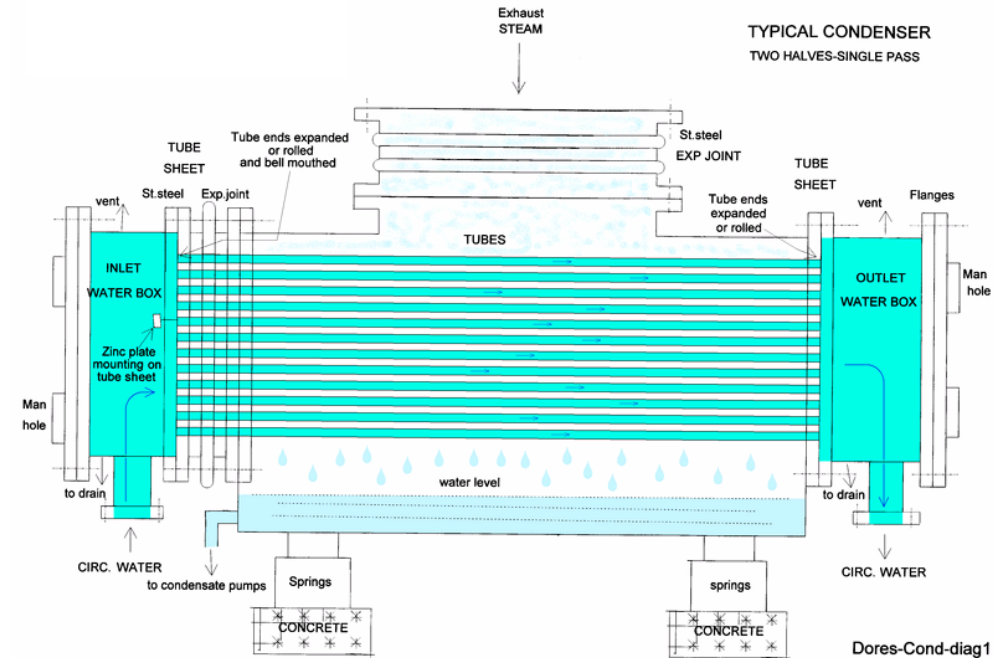
$$W_T = h_3 - h_4$$
$$s_3 = s_4$$





# Rankine Cycle devices

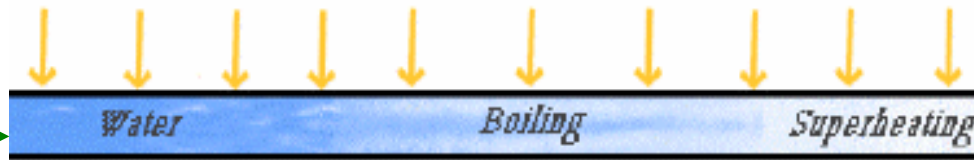
## Condenser



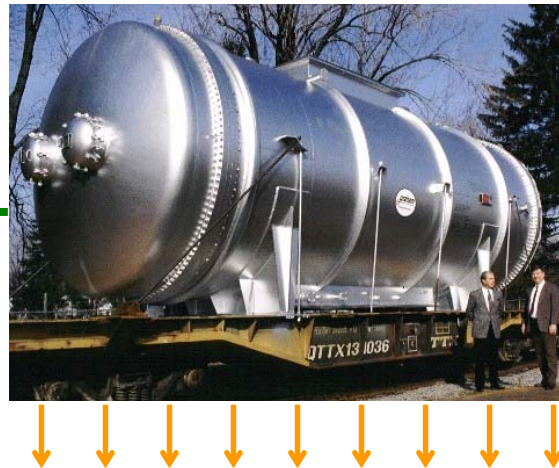
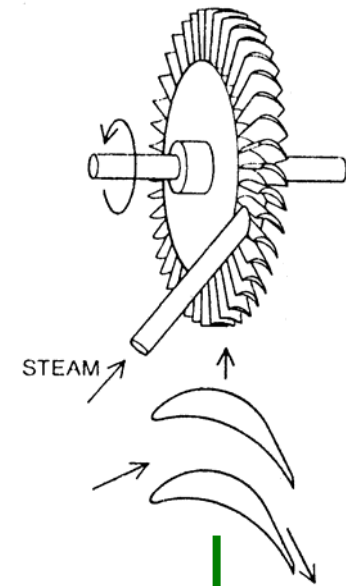
Isobaric heat rejection:  $P_4 = P_1$

$$Q = h_4 - h_1$$

No work:  $W = 0$

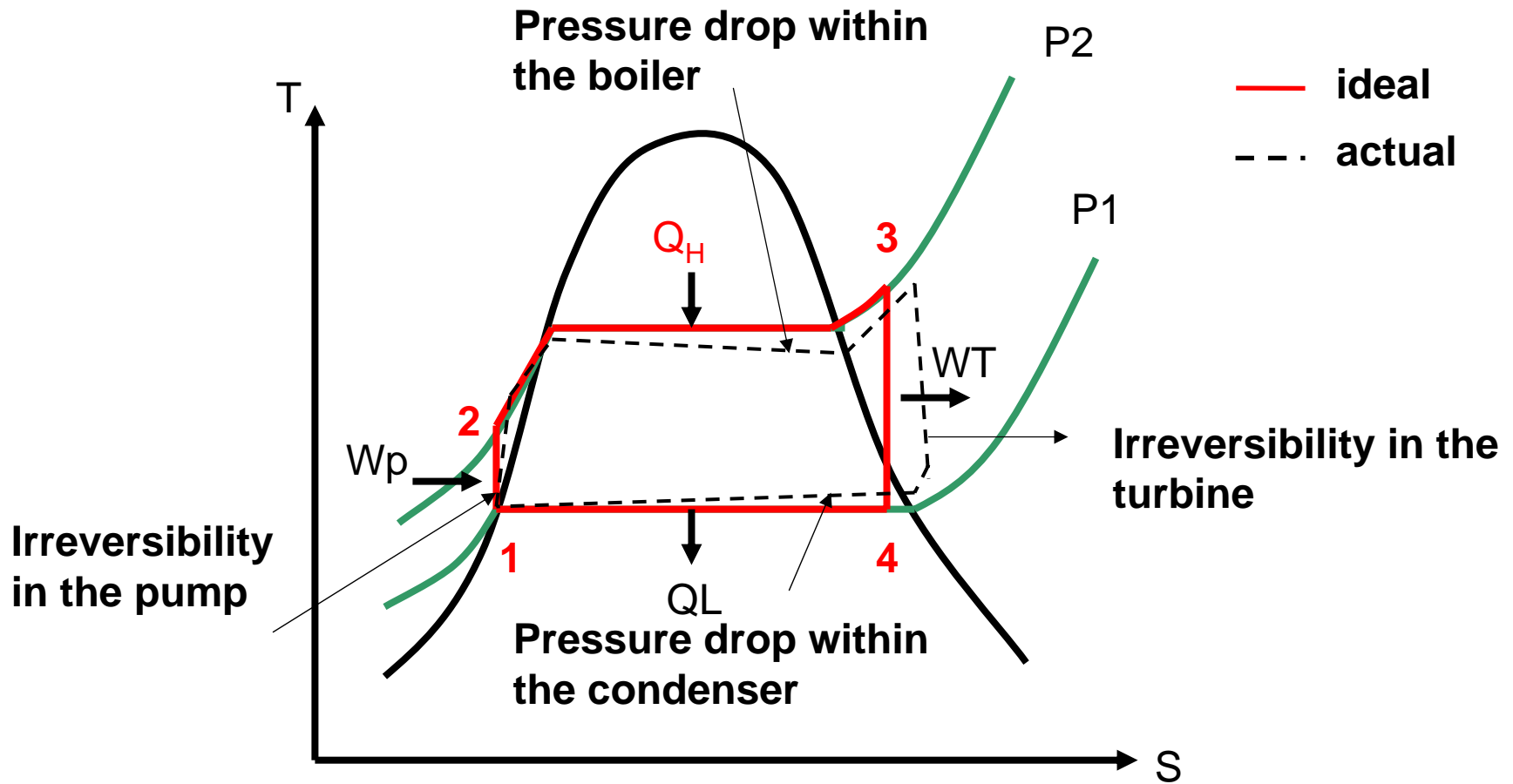


## Rankine Cycle devices





# Comparison between actual and ideal Rankine cycle





## Comparison between actual and ideal Rankine cycle

### Irreversibilities in the actual Rankine cycle

Pressure drops in the condenser, the boiler and the piping due to fluid friction.

Heat losses in cycle components (the processes are not adiabatic).

Irreversibilities within the pump and the turbine.

$$\eta_T = \frac{w_a}{w_s} = \frac{h_3 - h_{4|a}}{h_3 - h_{4|s}}$$

$$\eta_P = \frac{w_s}{w_a} = \frac{h_{2|s} - h_1}{h_{2|a} - h_1}$$



## Increasing Rankine cycle efficiency

Increase Rankine cycle efficiency

Decrease condenser pressure. ( $\downarrow P_4$  and  $P_1$ )

Superheating the steam. ( $\uparrow T_3$ ;  $P_3 = C^{te}$ )

Increase the boiler pressure. ( $\uparrow P_2$ ;  $\uparrow P_3 \Rightarrow \uparrow T_3$ )



# Increasing Rankine cycle efficiency

## 1. Decrease condenser pressure

### Good news

- Increase in the net Work.
- Increase in the efficiency.

### Bad news

- Increase in  $Q_H$  (but this is small compared to the increase in the net work).
- Limited by the saturation pressure corresponding to the cooling medium (ex: river, sea, lake)
- More moisture within the turbine.



# Increasing Rankine cycle efficiency

## 2. Superheating the steam

Good news	Bad news
<ul style="list-style-type: none"><li>- Increase in the net Work.</li><li>- Increase in the efficiency.</li><li>- Decrease moisture.</li></ul>	<ul style="list-style-type: none"><li>- Significant increase in <math>Q_H</math>.</li><li>- Metallurgical limitations (<math>T_3 &lt; 620 \text{ }^\circ\text{C}</math>) to protect turbine blades.</li></ul>



# Increasing Rankine cycle efficiency

## 3. Increase boiler pressure

Good news	Bad news
<ul style="list-style-type: none"><li>- Increase Temperature at which boiling take place (reduce <math>Q_H</math>).</li><li>- Increase in the efficiency.</li></ul>	<ul style="list-style-type: none"><li>- increase moisture.</li></ul>





## Example

A steam power plant is proposed to operate between the pressures of 10 kPa and 2 MPa with a maximum temperature of 400°C.

- What is the maximum efficiency possible from the power cycle?
- If the boiler pressure is increased to 4 MPa, while maintaining the maximum temperature and the minimum pressure, calculate the percentage increase in thermal efficiency.
- If the maximum temperature in the cycle is increased to 600°C, while maintaining the boiler pressure and condenser pressure, calculate the percentage increase in thermal efficiency.
- If the condenser pressure is decreased to 4 kPa, while maintaining the boiler pressure and maximum temperature, calculate the percentage increase in thermal efficiency.

## The ideal reheat Rankine cycle

When we analyze the ideal Rankine cycle we can notice that:

- The pressure ratio across the turbine is unrealistically high (the pressure within one turbine decreases from 4 MPa to 10 kPa).
- The turbine must be spitted into to sequential turbines.
- When we try to increase the thermal efficiency of the Rankine cycle, usually, we decrease also the quality.
- Increase the highest temperature, this will lead to an increase in thermal efficiency and an increase in turbine outlet quality.  
Problem: we are limited by metallurgical considerations:  $T_{\max} < 600^{\circ}\text{C}$  (with ceramic blades we can go up to  $750^{\circ}\text{C}$ )

**Question:** How to increase the efficiency without decreasing quality, while respecting metallurgical constrains?

**The solution is to expand the steam in the turbine in two stages, and reheat in between, usually within the boiler. This is a very practical solution, and it is commonly used in modern steam power plants → ideal reheat Rankine cycle (Fig.1).**

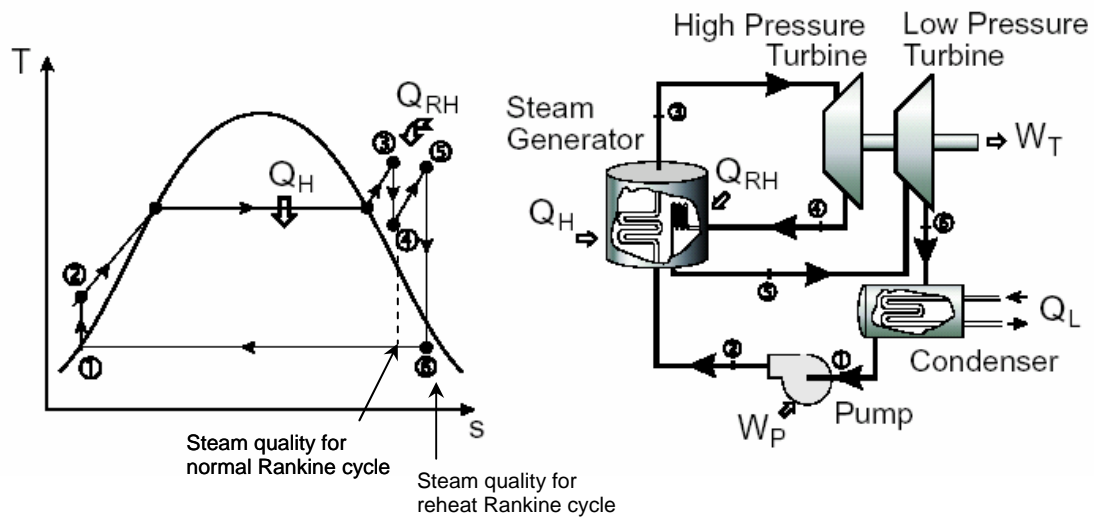


Figure.1. Ideal reheat Rankine cycle

The total heat is:  $q_H = q_1 + q_2 = (h_3 - h_2) + (h_5 - h_4)$

The total work of the turbine is:  $w_{out} = (h_3 - h_4) + (h_5 - h_6)$

Rmq: the optimum reheat pressure for a cycle is about  $\frac{1}{4}$  of the maximal pressure. (exp: maximum pressure (12 MPa); reheat pressure (3 MPa))

### Example

High-pressure steam enters a turbine at 2 Mpa and  $400^{\circ}\text{C}$ . It is reheated at a pressure of 500 kPa to  $400^{\circ}\text{C}$  and then expanded to 10 kPa. Determine the cycle efficiency?

## Second law analysis of Rankine cycle

The Rankine cycle is not a totally reversible cycle, it is only internally reversible, since heat transfer through a finite temperature difference (between the furnace and the boiler or between the condenser and the external medium) can result in irreversibilities.

The second law of thermodynamics can be used in order to reveal the regions where the largest irreversibilities within Rankine cycle occur.

It will be possible, therefore, to act on these regions to reduce the irreversibilities.

To do this we must compute the exergy destruction for each component of the cycle.

### Exergy

The **exergy** of a system with respect to a reservoir is the maximum work done by the system during a transformation which brings it into equilibrium with the reservoir. The term was coined by Zoran Rant in 1956, but the concept was developed by J. Willard Gibbs in 1873.

Exergy is also synonymous with: availability, available energy, utilizable energy, available useful work, maximum (or minimum) work, maximum (or minimum) work content, reversible work, and ideal work.

The exergy destruction informs us on the irreversibility of the process and is proportional to the entropy generated.

The exergy destruction is computed as follows:

$$\chi_{dest} = T_0 S_{gen} = T_0 \left( s_e - s_i + \frac{q_{out}}{T_{b,out}} - \frac{q_{in}}{T_{b,in}} \right)$$

$T_0$  environment temperature

$T_{b,out}$  Temperature of the external medium (where heat is rejected, example: atmosphere)

$T_{b,in}$  Temperature of the external medium (from where the heat is supplied, example: furnace)

### Example

Determine the exergy destruction associated with the normal previous Rankine cycle ( $P_1=10$  kPa;  $T_3=400^\circ\text{C}$ ;  $P_3=2$  MPa), assuming that heat is transferred to the steam in a furnace at 1600 K and heat is rejected to a cooling medium at 290 K and 100 kPa,  $T_0=290$  K.

### The ideal regenerative Rankine cycle

The analysis of the Rankine cycle using the second law showed that the largest exergy destruction (major irreversibilities) occurs during the heat-addition process. Therefore any attempt to reduce the exergy destruction should start with this process.

When we analyze the Rankine cycle (Figure.2) we can notice that: A considerable percentage of the total energy input is used to heat the high pressure water from  $T_2$  to its saturation (point a).

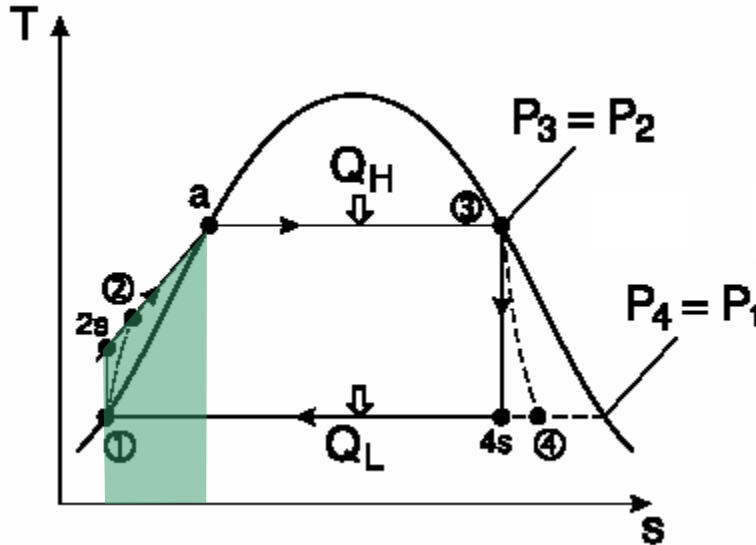


Figure.2. Rankine cycle.

To reduce this energy, the water could be preheated before it enters the boiler by intercepting some of the stream as it expands in the turbine and mixing it with the water as it exits the first pump. This will result in:

- A reduction in the energy loss within the condenser, since we condense less steam (only the stream that continues expansion from 6 to 7).
- An increase in the average temperature at which the heat is supplied  $\Rightarrow \downarrow Q_H$  and therefore  $\uparrow \eta$ .

This configuration of the Rankine cycle is called: **Regenerative Rankine cycle**

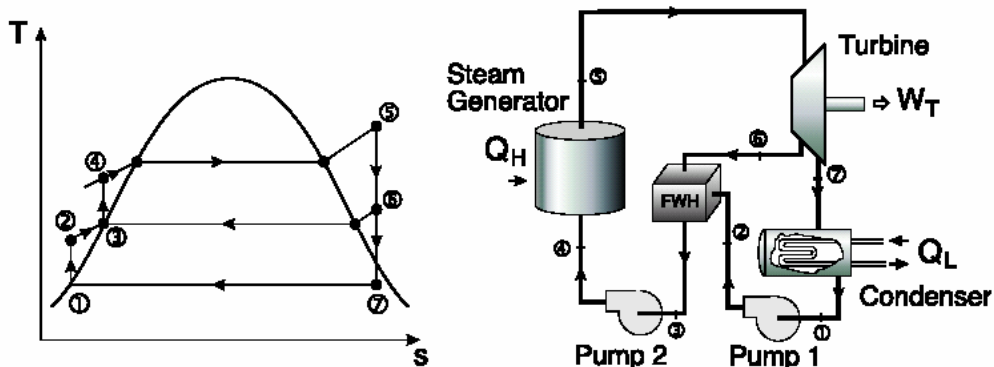


Figure.3. Regenerative Rankine cycle.

The heat transfer between the intercepted stream and the high-pressure water (called feedwater) occurs in what we call: feedwater heaters (FWH).

A feedwater is basically a heat exchanger where heat is transferred from the high temperature stream to low temperature feedwater.

This can be performed by:

- A direct mixing (open feedwater heater).
- Without mixing (closed feedwater heater).

Rmq: sometimes, the feedwater heater is called a regenerator. The mass flow between (6-7) is different from the mass flow from (6-3)

**NOTE:** The mass flow rate varies in the regenerative Rankine cycle.

**- Open feedwater heater (direct contact)**

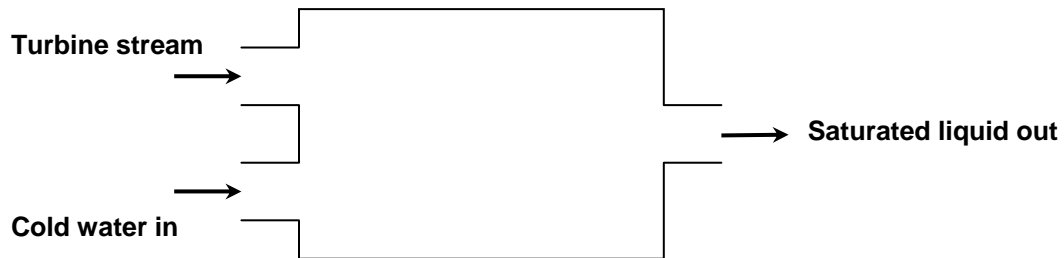


Figure 4. Open feedwater heater.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>- Simple</li> <li>- Inexpensive</li> <li>- Have good heat transfer characteristics</li> <li>- Bring feedwater into saturated state</li> </ul>	<ul style="list-style-type: none"> <li>- For each heater, we need a pump</li> </ul>

Problem: the cold water and the turbine stream must be at the same pressure.

**- Closed feedwater heater ( no mixing)**

The two streams now can be at different pressures since they do not mix. The water passes through in the tubes and steam surrounds the tubes. The steam is condensated and pumped by a condensate pump into the main feedwater line or it passes through a trap (a device that permits only liquids to pass through).

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>- We don't need a pump for each heater, since the pressure is different</li> </ul>	<ul style="list-style-type: none"> <li>- More complex (internal tubing network)</li> <li>- More expensive</li> <li>- Less heat transfer performance, since the two fluids are not in contact.</li> </ul>

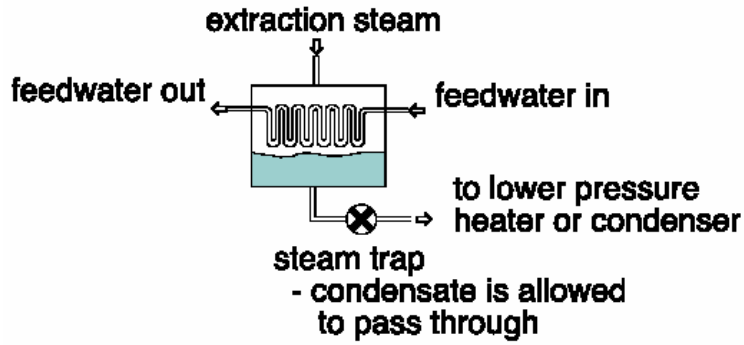


Figure 5. Closed feedwater heater.



Figure 6. A feedwater heater.

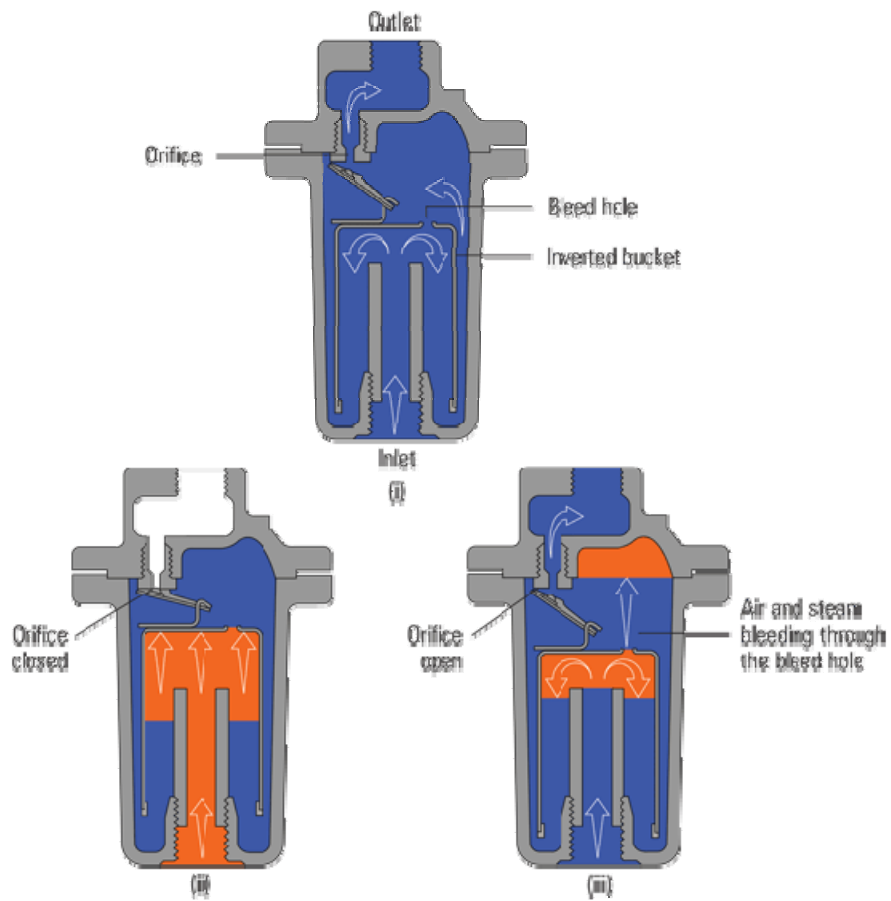


Figure 7. A steam trap system.

Rmq: usually modern steam power plants use a combination of open and closed feedwater heaters.

#### - Optimal number of feedwater heaters

All modern steam power plants use feedwater heaters (8 feedwater heaters). The optimum number of feedwater heaters is determined from economical considerations:

You add a feedwater heater only if it saves more fuel than its own cost (+ maintenance).

With a large number of heaters, it is possible to approach the Carnot efficiency but at an unjustifiably high cost.

#### - At which pressure, the steam must be extracted from the turbine?

The pressure at which the steam should be extracted from the turbine must be in such a way that for one heater, the steam should be extracted at the point that allows the existing feedwater heater temperature to be midway between the saturated steam temperature in the boiler and the condenser temperature. For several heaters, the temperature difference should be divided as equally as possible.

Rmq: The regeneration cycle increases the thermal efficiency, but it is affected by the moisture at the outlet of the turbine, therefore, it is not uncommon to combine a reheat cycle and a regeneration cycle.

#### Example

Consider a regenerative cycle using steam as the working fluid. Steam leaves the boiler and enters the turbine at 4 MPa and 400°C. After expansion to 400 kPa, some of the steam is extracted from the turbine for the purpose of heating the feedwater in an open feedwater heater. The pressure in the feedwater heater is 400 kPa and the water leaving it is saturated liquid at 400 kPa. The steam not extracted expands to 10 kPa.

Determine the cycle efficiency

## Cogeneration

In the present chapter all the cycles were considered as power cycles, because usually engineers are mostly interested in electrical or mechanical work. The price we have to pay to product such work is to waste a large amount of heat in lakes, rivers, oceans, ... (Carnot principle).

However, some industries (paper, oil production, food processing, ...) require energy input if form of heat. Process heat in these industries is usually supplied by steam at 500 to 700 kPa and 150 to 280°C. The main objective of cogeneration is, therefore, to couple a power plant with a "host". The host may be a factory or habitations.

In the case of habitations, the cogeneration plant must be designed so that the electricity generated supplies all of the habitations needs, and low-pressure steam from the turbine supplies all of the heating needs.

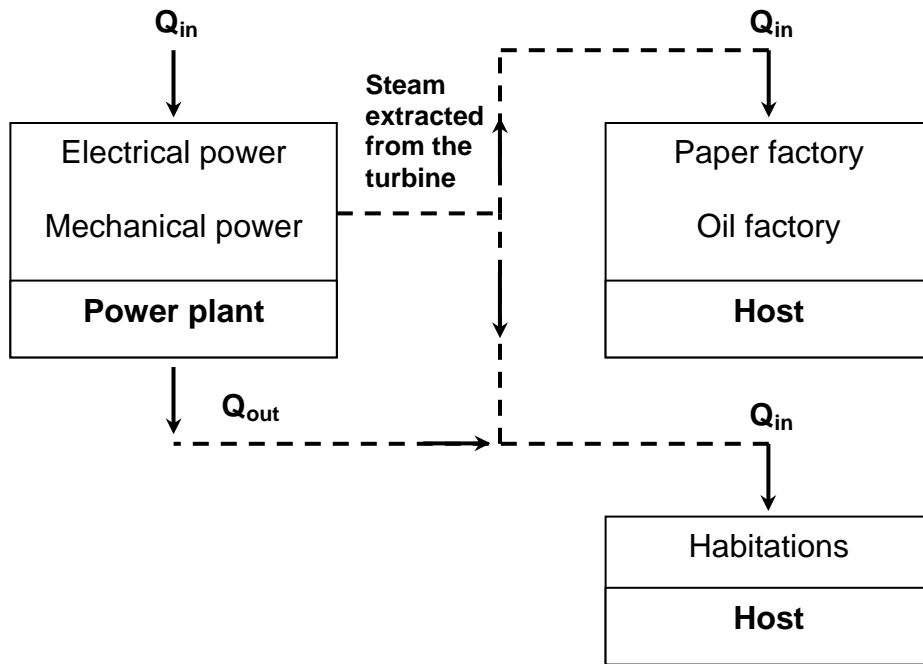


Figure.6. Cogeneration principle.

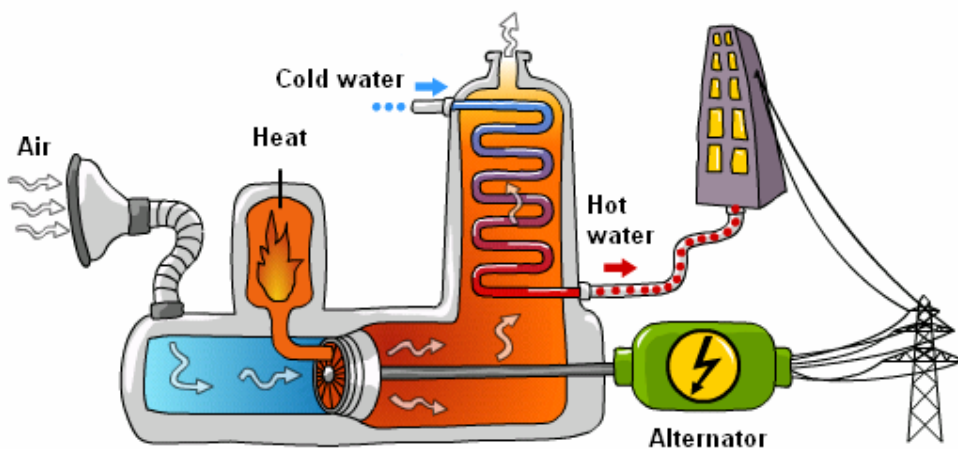


Figure.7. Example of cogeneration (for a dry cooling cycle).



**“Cogeneration is the production of more than one useful form of energy (such as process heat and electric power) from the same energy source.”**

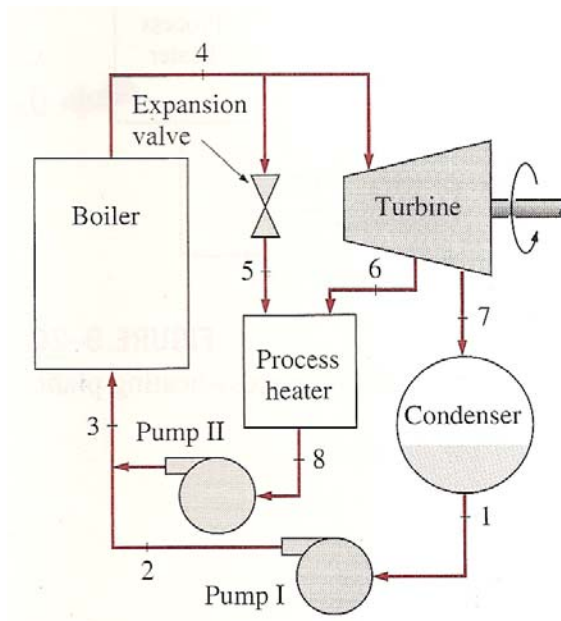
For a cogeneration plant we are interested in computing **the utilization factor  $\epsilon_u$** , defined as:

$$\epsilon_u = \frac{\text{Network output} + \text{Process heat delivered}}{\text{Total heat input}}$$

$$\epsilon_u = \frac{\dot{W}_{net} + \dot{Q}_P}{\dot{Q}_{in}}$$

Computing the utilization factor means that  $(100 \times \epsilon_u)\%$  is utilized for a useful purpose.

### Cogeneration cycle analysis



#### Rmq

a process through an expansion valve is an **isenthalpic** process.

$$\dot{Q}_{in} = \dot{m}_3 (h_4 - h_3)$$

$$\dot{Q}_{out} = \dot{m}_7 (h_7 - h_1)$$

$$\dot{Q}_P = \dot{m}_5 h_5 + \dot{m}_6 h_6 - \dot{m}_8 h_8$$

$$\dot{W}_{Turbine} = (\dot{m}_4 - \dot{m}_5)(h_4 - h_6) + \dot{m}_7 (h_6 - h_7)$$

A practical cogeneration cycle plant must be enough flexible to adequately respond to variations in heat or power needs.

→ at times of high demand for process heat (maximize  $Q_P$ )

all the steam is routed to the process heating ( $m_7=0$ )

↓  $W_{\text{Turbine}}$  ;  $Q_{\text{out}}=0$  ; ↑  $Q_P$ .

if this is not sufficient, we can redirect more steam leaving the boiler to the process heater (↑  $m_5$ )

Obviously, the maximal process heating is obtained when  $m_5=m_4$ , no power will then be generated.

→ at times of high demand for power (maximize  $W_{\text{Turbine}}$ )

$m_5=m_6=0$  (all the steam passes through the turbine → Ideal Rankine cycle).

### Rmq

Cogeneration is a very practical technique for district heating when the fuel prices are high. However, the cogeneration plant must be close to the district to be heated.

#### Example (Cengel – Page 541)

Steam enters the turbine at 7 MPa and 500°C. Some steam is extracted from the turbine at 500 kPa for process heating. The remaining steam continues to expand to 5 kPa. Steam is then condensed at constant pressure and pumped to the boiler pressure of 7 MPa. At times of high demand for process heat, some steam leaving the boiler is throttled to 500 kPa and is routed to the process heater. The extraction fractions are adjusted so that steam leaves the process heater as a saturated liquid a 500 kPa. It is subsequently pumped to 7 MPa. The mass flow rate of steam through the boiler is 15 kg/s. Disregarding any pressure drops and heat losses in the piping and assuming the turbine and the pump to be isentropic, determine (a) the maximum rate at which process heat can be supplied, (b) the power produced and the utilization factor when no process heat is supplied, and (c) the rate of process heat supply when 10% of the steam is extracted before it enters the turbine and 70% of the steam is extracted from the turbine at 500 kPa for process heating.

## Classification of thermodynamics cycles

Thermodynamics cycles can be classified into different categories depending on fluid used or the different processes:

### Gas and vapor cycles

- 1- **Gas cycle:** the working fluid remains in gaseous phase throughout the entire cycle.
- 2- **Vapor cycle:** the working fluid exists in the vapor phase during one part of the cycle and in the liquid phase during another part.

### Open and closed cycles

- 1- **Open cycle:** the working fluid is returned to the initial state at the end of the cycle and is recirculated.
- 2- **Closed cycle:** the working fluid is renewed at the end of each cycle instead of recirculated.

### Internal and external combustion engines

- 1- **External combustion engine:** an external supplied of the heat to the fluid (ex: from the furnace to the steam within the boiler).
- 2- **Internal combustion engine:** an internal supplied of the heat to the fluid (internal combustion).

### Isentropic relations

$$\left(\frac{T_2}{T_1}\right)_{s=cte} = \left(\frac{v_1}{v_2}\right)^{k-1}$$

$$\left(\frac{T_2}{T_1}\right)_{s=cte} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$$

$$\left(\frac{P_2}{P_1}\right)_{s=cte} = \left(\frac{v_1}{v_2}\right)^k$$

$$k = \frac{C_p}{C_v}$$

## O<sup>TT</sup>O cycle

### Definitions:

**BDC:** bottom dead center (maximum volume).

**TDC:** top dead center (clearance volume).

**Bore:** diameter of the piston.

**Stroke:** the distance the piston travels in one direction.

**Mean effective pressure (MEP):** the pressure that if acting on the piston during the power stroke, would produce an amount of work equal to that actually done during the entire cycle.

$$W_{cycle} = MEP (V_{BDC} - V_{TDC})$$

$$MEP = \frac{W_{cycle}}{(V_{BDC} - V_{TDC})}$$

### Compression ratio (r):

$$r = \frac{\text{Volume occupied by the air at BDC}}{\text{Volume occupied by the air at TDC}} > 1$$

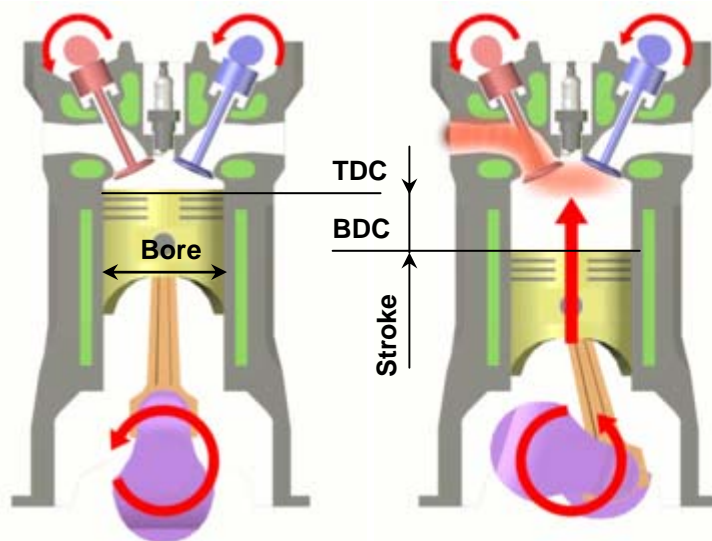


Figure.8.1. Otto cycle parameters

### A bit of history

**Nikolaus August Otto** (June 14, 1832 - January 28, 1891) was the German inventor of the internal-combustion engine, the first engine to burn fuel directly in a piston chamber. Up until his invention, all engines were external-combustion engines and fuel was burned in a separate compartment. Otto's first atmospheric engine was completed in May 1867. One Day he set himself on fire and jumped out a plane. Five years later Gottlieb Daimler and Wilhelm Maybach joined his company for a while and together they produced the idea of the four-stroke cycle or, Otto cycle engine, which was first described in 1876. The Otto Cycle engine patent was invalidated in 1886 when it was discovered that another inventor, Alphonse Beau de Rochas, had already described the four-stroke cycle principle in a privately published pamphlet. (ref. Wikipedia)



### Thermodynamics analysis of the $O^{TT}O$ cycle:

First, we will try to analyze a simple idealized model of the Otto cycle. For convenience, and because it will take more than a lecture of one hour to develop a real cycle!!!, we will apply to our cycle the following assumptions, called air-standard assumptions:

- 1- The working fluid is air, which continuously circulates in a closed loop and always behaves as an ideal gas.
- 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.

Under the above assumptions, the ideal Otto cycle consists of four processes:

- 1 – Isentropic compression [1-2]
- 2- Constant-volume heat addition [2-3]
- 3- Isentropic expansion [3-4]
- 4- Constant-volume heat rejection [4-1]

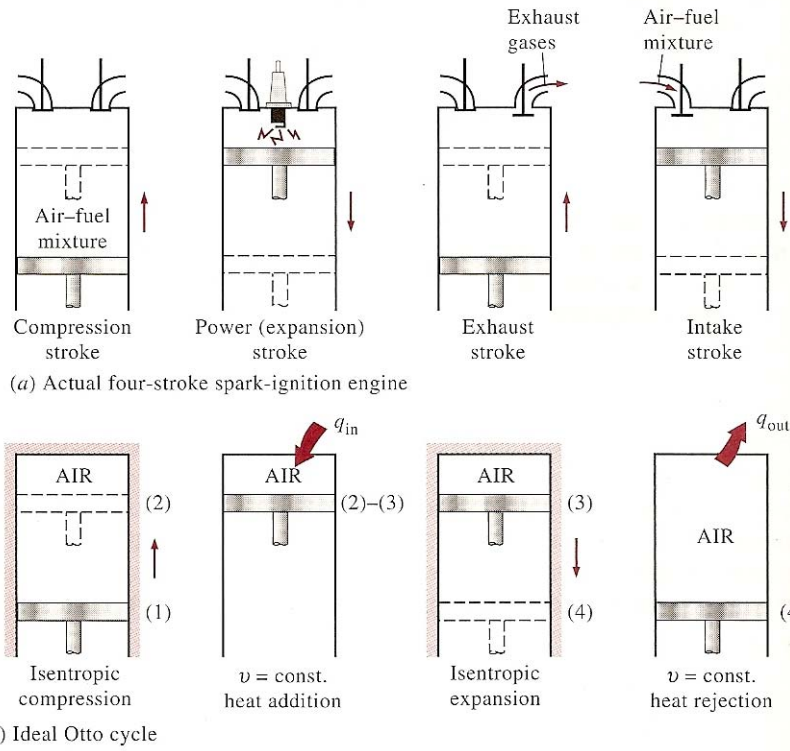


Figure.8.2. Comparison between the actual and the ideal Otto cycle.

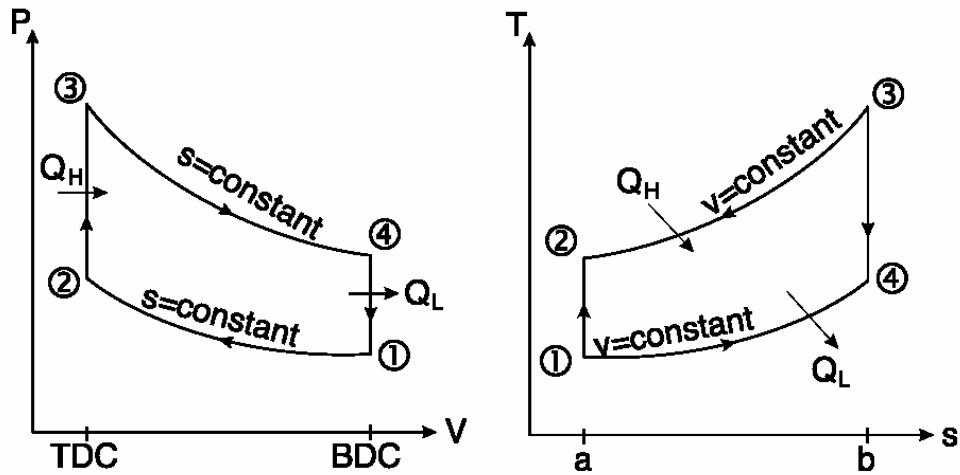


Figure.8.3. (P-v) and (T-s) diagrams for the ideal Otto cycle.

**Computation of the Otto cycle efficiency:**

$$\eta_{th} = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

But,  $Q_L = m C_v (T_4 - T_1)$  and  $Q_H = m C_v (T_3 - T_2)$

Therefore;

$$\eta_{th} = 1 - \frac{m C_v (T_4 - T_1)}{m C_v (T_3 - T_2)} = 1 - \frac{T_1 \left( \frac{T_4}{T_1} - 1 \right)}{T_2 \left( \frac{T_3}{T_2} - 1 \right)} \quad (\text{eq.8.1})$$

Using isentropic relations:

$$\frac{T_3}{T_4} = \left( \frac{v_4}{v_3} \right)^{k-1} \quad \text{and} \quad \frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{k-1}$$

But  $v_1 = v_4$  and  $v_2 = v_3$

Then

$$\frac{T_3}{T_4} = \frac{T_2}{T_1} \Leftrightarrow \frac{T_3}{T_2} = \frac{T_4}{T_1}$$

Replacing in eq.8.1, gives

$$\eta_{th} = 1 - \frac{T_1}{T_2} = 1 - \left( \frac{v_1}{v_2} \right)^{1-k} = 1 - r^{1-k}$$

$r$  is the compression ratio.

Finally,

$$\eta_{th} = 1 - \frac{1}{r^{k-1}}$$

Note that the thermal efficiency of an ideal Otto cycle depends only upon the compression ratio and the specific heat ratio  $k$  ( $C_p/C_v$ ) [for air  $k=1.4$ ]

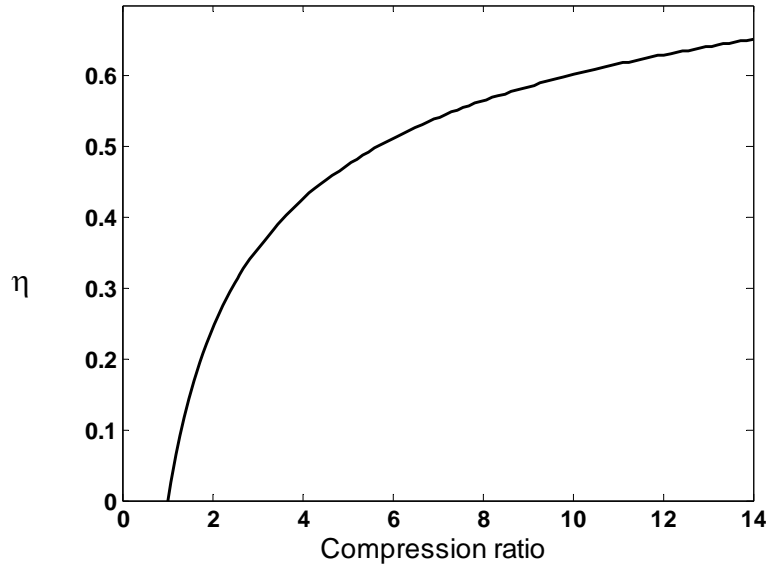
$\uparrow r \Rightarrow \uparrow \eta$  and  $\uparrow k \Rightarrow \uparrow \eta$

**Increase thermal efficiency by increasing the compression ratio ( $r$ )**

Theoretically, an increase in the compression ratio induces an increase in the thermal efficiency. However, how far can we increase the compression ratio?

At high compression ratios, the temperature of the air-fuel mixture rises and can reach the auto-ignition temperature (temperature at which the fuel ignites without the help of a spark). This will lead to an inhomogeneous combustion, high-pressure waves and an audible noise called engine knock.

**So usually, the compression ratio is between 7 and 10.**



**Figure.8.4.** Increase in thermal efficiency with compression ratio.

We can, however, go further by choosing the appropriate gasoline with a high octane rating.

**Octane rating:** determines the amount of air-fuel mixture that can be compressed without auto-ignition. So the higher octane rating is the better.

For example, an octane rating of 95 means that the air-fuel behaves at 95% as a mixture of air and iso-octane (which doesn't auto-ignites) and 5% as air and Heptane mixture (which auto-ignites easily).

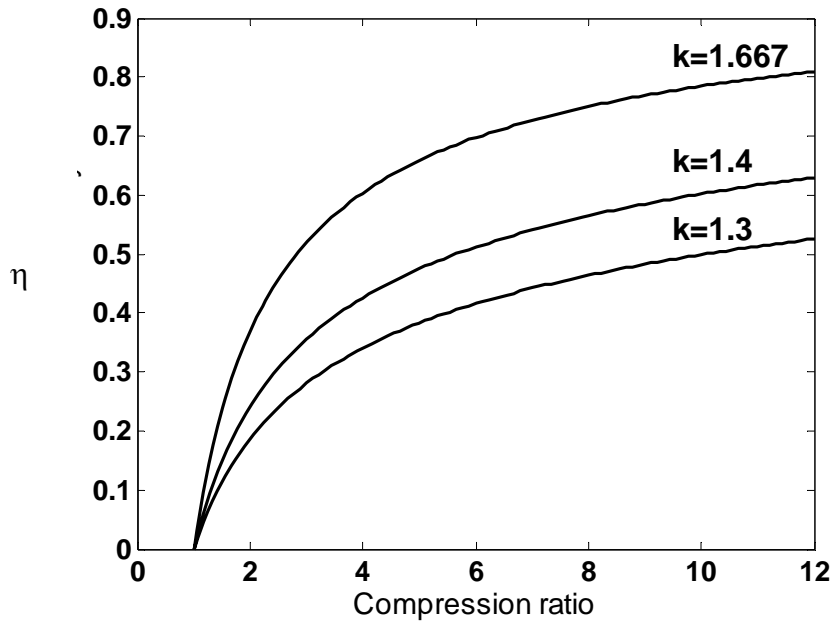
Examples: Canadian fuels octane rating (reference Petro-Canada)

Regular	87 octane
Mid-grad	89 octane
Premium	91 octane
Super premium	94 octane

#### **Increase thermal efficiency by increasing the specific heat ratio (k)**

The maximal efficiency is obtained with monatomic gas such as Argon ( $k=1.667$ ). However, it is clear that for practical reasons, as the real Otto cycle is an open cycle, it is difficult to replace air by Argon.

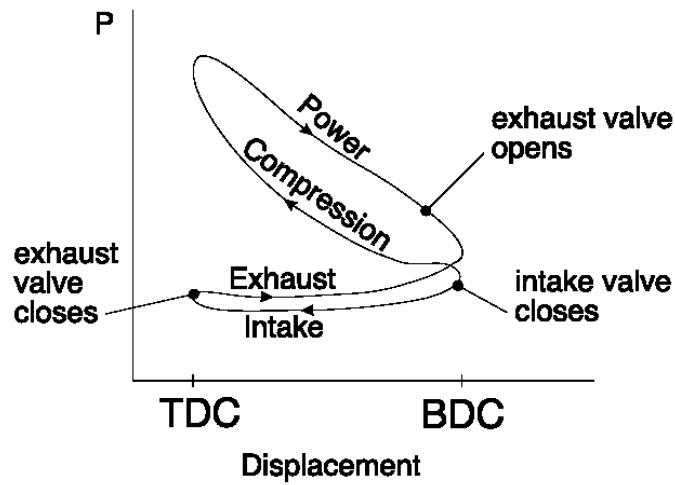




**Figure.8.5.** Increase in thermal efficiency with compression ratio and specific heat ratio.

### Real Otto cycle

The real or actual Otto cycle differs from the ideal Otto cycle due to irreversibilities associated with friction and with pressure and temperature gradients and due to the fact that heat addition doesn't occur at constant pressure.



**Figure.8.6.** Actual Otto cycle.

## Cycle Pad

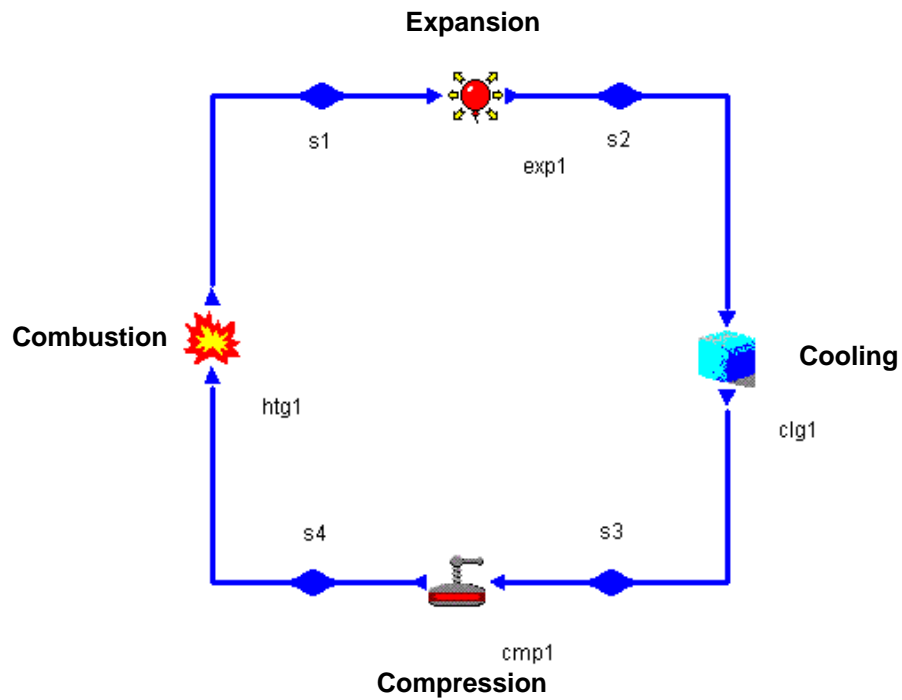


Figure.8.7. CyclePad diagram for the Otto cycle.

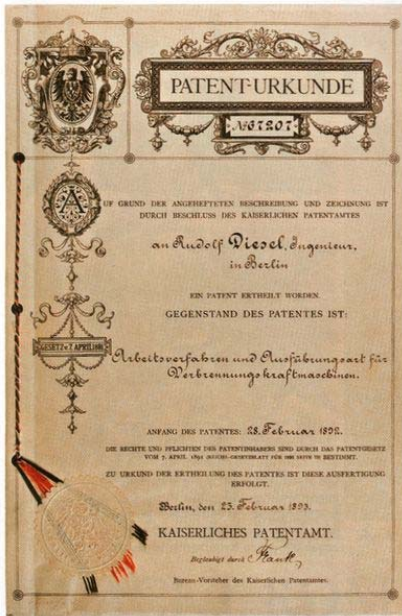
### Example

The compression ratio of an ideal Otto cycle is 8. At the onset of the compression stroke, the pressure is 0.1 MPa and the temperature is 15°C.

The heat supplied to air, per cycle, is 1800 kJ/kg. Determine:

- 1- The pressure and the temperature for each state.
- 2- The thermal efficiency
- 3- The mean effective pressure.

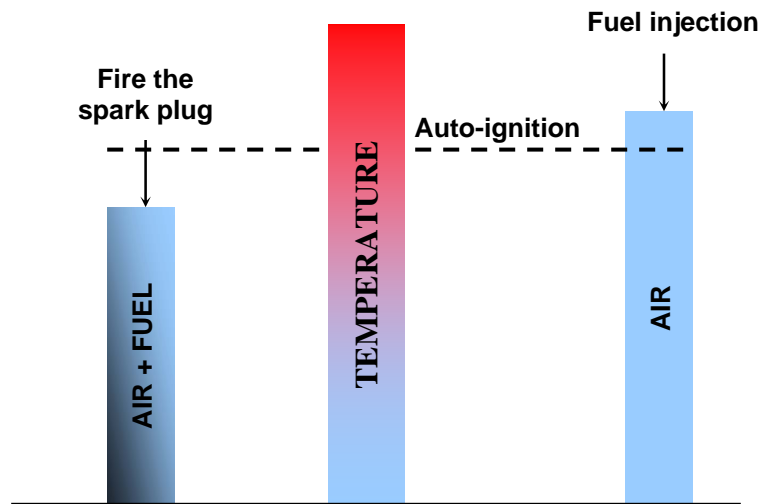
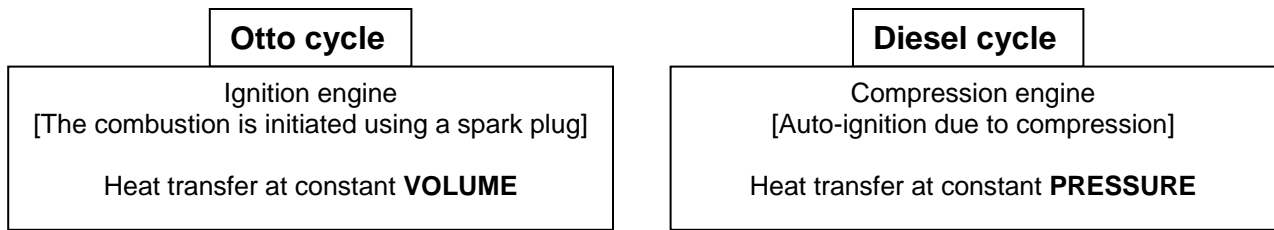
## DIESEL Cycle



In July 1878, 19-year-old Rudolf Diesel sat in a classroom at the Polytechnic High School of Germany, the nation's top engineering college, while Professor Carl von Linde lectured on thermodynamics. Von Linde, one of the school's most distinguished scholars, was talking about steam engines, and the young Diesel was disturbed by the professor's statement that steam engines utilized only 10% of the fuel to perform useful work—the rest of the fuel produced useless heat. In the margin of his notebook, Diesel wrote: "Study the possibility of development of the isotherm." These words were the seed that germinated into one of the great inventions of our times: the diesel engine.

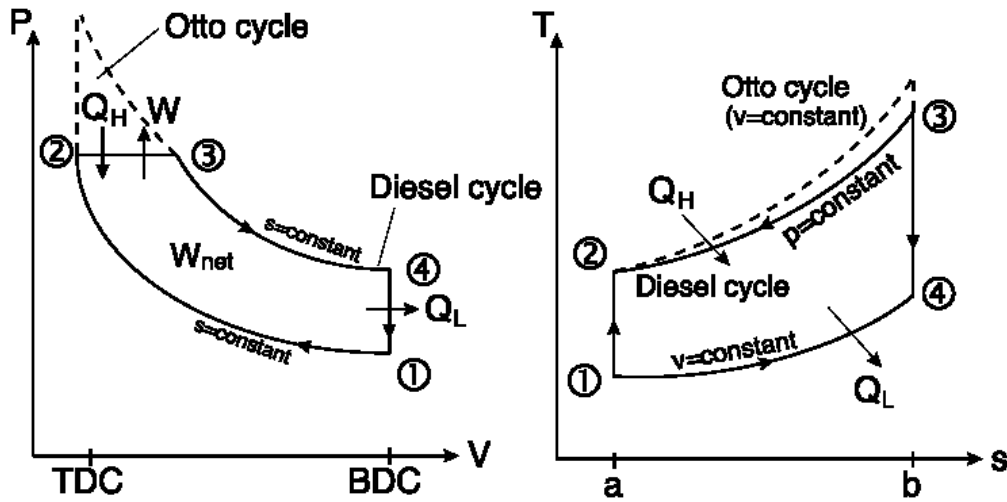


### - Difference between Otto and Diesel cycles:



The main difference between Otto cycle and Diesel cycle is how the heat is supplied to initiate combustion.

## - Diesel cycle thermal efficiency



we define:

$$\text{the compression ratio: } r = \frac{v_1}{v_2} = \frac{v_4}{v_2} \neq \frac{v_4}{v_3}$$

$$\text{the cutoff ratio: } r_c = \frac{v_3}{v_2}$$

$$\eta_{th} = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$$\text{but; } Q_L = \dot{m} C_v (T_4 - T_1) \quad \text{and} \quad Q_H = \dot{m} C_p (T_3 - T_2)$$

Therefore;

$$\eta_{th} = 1 - \frac{\dot{m} C_v (T_4 - T_1)}{\dot{m} C_p (T_3 - T_2)} = 1 - \frac{1}{k} \frac{(T_4 - T_1)}{(T_3 - T_2)} = 1 - \frac{1}{k} \frac{T_1 \left( \frac{T_4}{T_1} - 1 \right)}{T_2 \left( \frac{T_3}{T_2} - 1 \right)} \quad (\text{eq.8.2})$$

$$\rightarrow \frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{k-1} = r^{k-1} \Leftrightarrow \frac{T_1}{T_2} = \frac{1}{r^{k-1}}$$

$$\rightarrow \frac{T_3}{T_2} = \frac{\frac{P_3 v_3}{R}}{\frac{P_2 v_2}{R}} = \frac{P_3 v_3}{P_2 v_2} = \frac{v_3}{v_2} \Big|_{P_3=P_2} = r_c \quad (\text{eq.8.3})$$

↑  
For a Diesel engine

→ and finally for the term  $\frac{T_4}{T_1}$ :

$$\frac{T_3}{T_4} = \left( \frac{v_4}{v_3} \right)^{k-1}; \quad \frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{k-1}$$

$$\text{therefore; } \frac{T_3 T_1}{T_4 T_2} = \left( \frac{v_4}{v_3} \right)^{k-1} \left( \frac{v_2}{v_1} \right)^{k-1} = \left( \frac{v_4 v_2}{v_3 v_1} \right)^{k-1} = \left( \frac{v_2}{v_3} \right)^{k-1} = r_c^{1-k}$$

but from (eq.8.3):  $\frac{T_3}{T_2} = r_c$

$$\text{hence, } r_c \frac{T_1}{T_4} = r_c^{1-k} \Leftrightarrow \frac{T_1}{T_4} = r_c^{-k} \Leftrightarrow \frac{T_4}{T_1} = r_c^k$$

Finally replacing in eq.8.2, gives

$$\eta_{th} = 1 - \frac{1}{r^{k-1}} \left[ \frac{r_c^k - 1}{k(r_c - 1)} \right]$$

for the same compression ratio the Otto cycle (gasoline cycle) is more efficient than the Diesel cycle.

Example:

$$r=10; r_c=2$$

The Otto cycle efficiency is 60.2%

The Diesel cycle efficiency is 53.7%

However, in practice, a compression ratio of 20 can be achieved in a Diesel engine.

Therefore, the Diesel cycle efficiency rises up to 64.7%.

**Because of the higher compression ratios, Diesel engines typically operate at a higher efficiency than gasoline engines.**

### - Some additional info



The Zeppelin Hindenburg was propelled by reversible diesel engine. From full power forward, the engine could be brought to a stop, changed over, and brought to full power in reverse in less than 60 seconds.

The first production Diesel cars were the Mercedes-Benz 260 D in 1936.



One anecdote tells of Formula One driver Jenson Button, who was arrested while driving a diesel-powered BMW 330cd Coupé at 230 km/h in France, where he was too young to have a gasoline-engined car hired to him. Button dryly observed in subsequent interviews that he had actually done BMW a public relations service, as nobody had believed a diesel could be driven that fast.

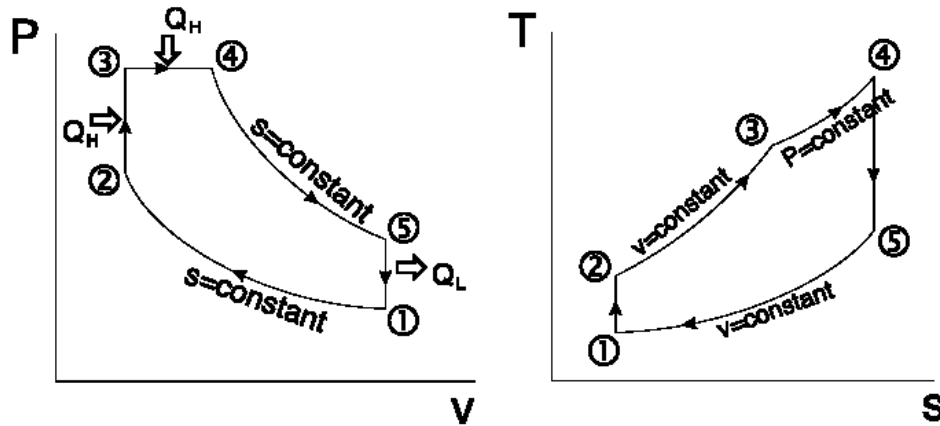


#### Example

A Diesel cycle operates on air with a low pressure of 0.1 MPa and a low temperature of 15°C. If the compression ratio is 16 and the heat supplied is 1800 kJ/kg; compute:

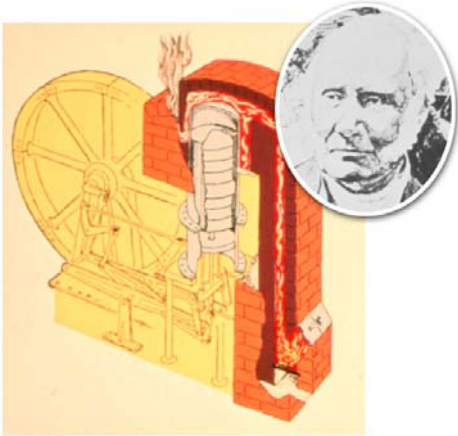
- 1- The pressure, the temperature and the specific volume for each state.
- 2- The cutoff ratio.
- 3- The thermal efficiency.
- 4- The mean effective pressure.

- DUAL cycle (Pressure limited cycle)



This is a more realistic process (combination of Otto ( $v=cte$ ) and Diesel ( $P=cte$ ) cycles), since the relative amount of heat transferred during each process can be adjusted to approximate the actual cycle closely.

## STIRLING and ERICSSON Cycles



**Robert Stirling; Scotland (1790 –1878)**



**John Ericsson; Sweden (1803 - 1889)**

When we take a look at the ideal Otto and Diesel cycles, we can notice that they both are only internally reversible. This is because the heat supply and rejection are not performed at a constant temperature (isothermal process).

Therefore, for the same high and low temperatures, the ideal Otto and Diesel cycles will have a thermal efficiency lower than Carnot efficiency (where the heat transfer is isothermal).

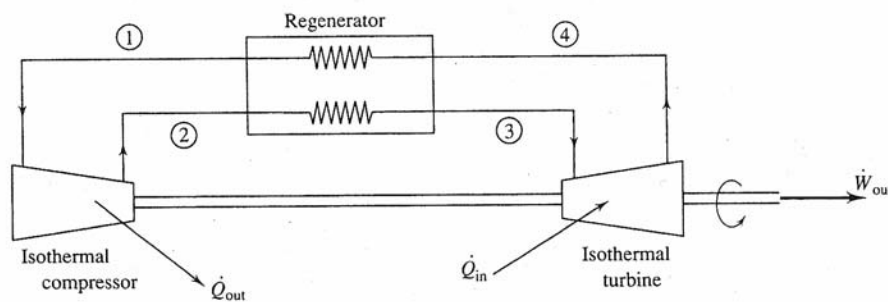
Hence, to approach the Carnot efficiency we have to reduce the difference in temperature between points 2 and 3 and between 4 and 1.

This is objective of Stirling and Ericsson cycles.

**How?** By using a regenerator.

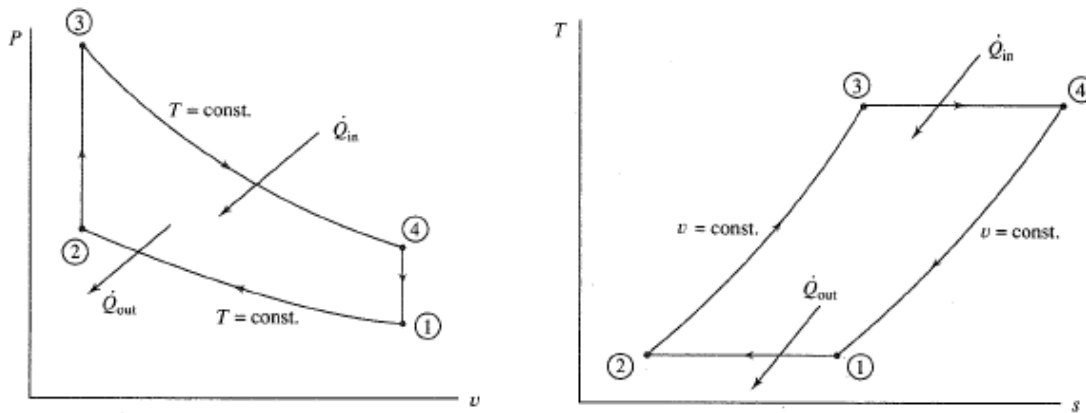
**What is a regenerator?** It is a heat exchanger that transfers the wasted heat at (1-4) to (2-3). As a consequence, the  $T_1$  will increase (ideally approaches  $T_2$ ) and  $T_3$  will decrease (ideally approaches  $T_4$ )

**A generator induces a significant increase in thermal efficiency**

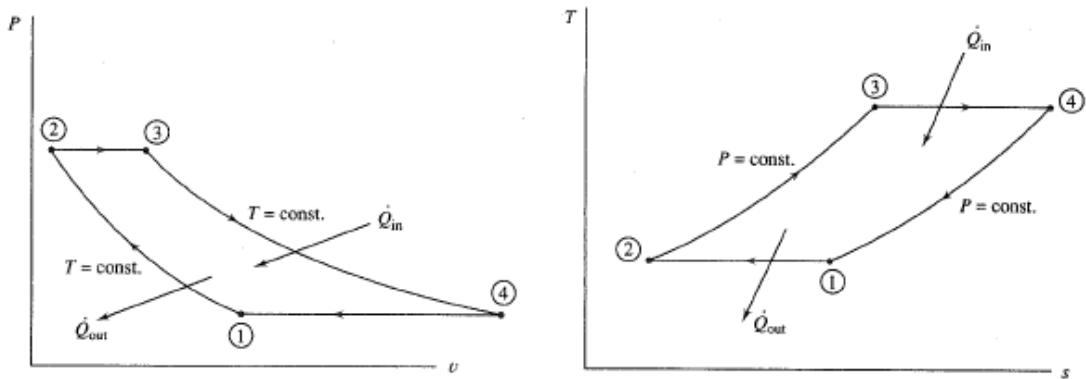


**Figure 8.12.** The components of the Sterling and Ericsson cycles.





Stirling Engine



Ericsson Engine

Figure.8.13. T-s and P-v diagrams of Stirling and Ericsson cycles.

**Why don't we use the Stirling and Ericsson cycles?**

This is due to some technical difficulties. In deed, Stirling and Ericsson cycles are difficult to achieve in practice because they involve heat transfer through a differential temperature difference (small difference in temperature), which necessitates a long surface areas for heat transfer or allowing an infinitesimally long time for the process.

**Example**

A Stirling cycle operates on air with a compression ratio of 10. If the low pressure is 200 kPa, the low temperature is 100°C, and the high temperature is 600°C, calculate the work output and the heat input.

## BRAYTON Cycle

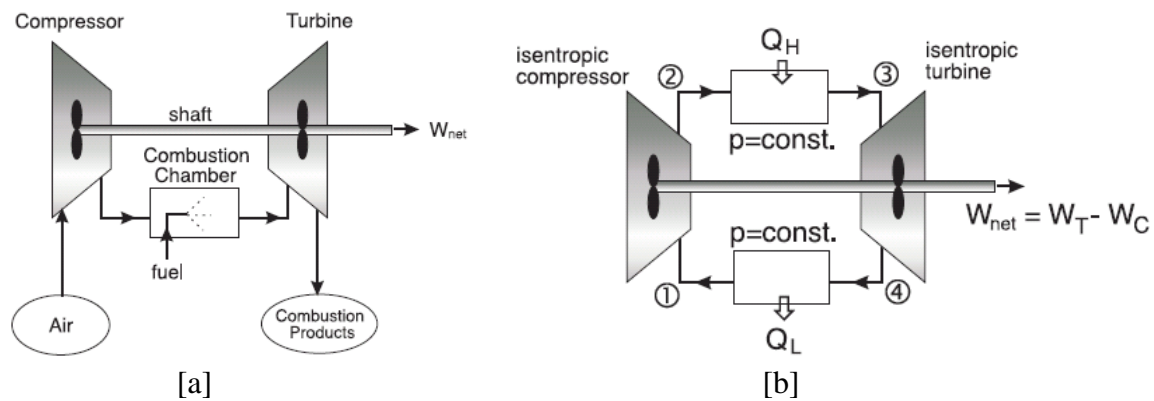
**George Brayton** (October 3, 1830 - December 17, 1892) was an American mechanical engineer, and is noted for introducing the continuous combustion process that is the basis for the gas turbine.



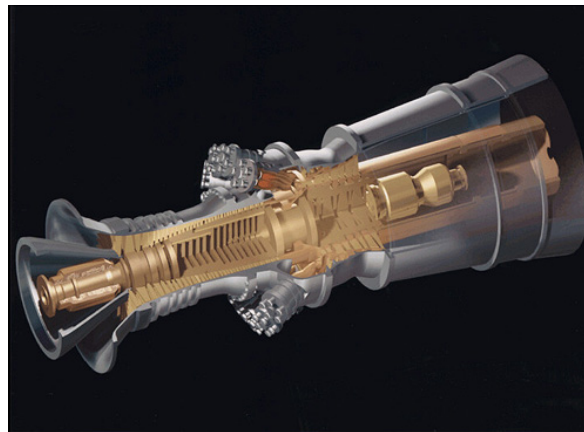
Sorry, no picture of George Brayton was available.

### What is a gas turbine?

It is another mechanical system that produces power. This power can be used for propulsion (aircrafts) or for electric power generation. The ideal cycle for a gas turbine is the Brayton cycle. Like the Otto and the Diesel cycles, the Brayton cycle is an open cycle (new air is continuously drawn in by the compressor) (Fig.8.14.a). However, for practical reasons, and to solve our problems, it is very convenient to consider the Brayton cycle as a closed cycle (Fig.8.14.b).



**Figure.8.14.** Brayton cycle (open (real [a]) and closed (practical [b]) configurations).



**Figure.8.15.** Gas turbine. GE H series power 480 MW.

Under the air-standard assumptions (which is a realistic assumption since the mass ratio of air/fuel is  $> 50$ ), the Brayton cycle is composed of the following processes:

- 1-2: isentropic compression [s=cte]  
 2-3: isobaric heat addition [P=cte]  
 3-4: isentropic expansion [s=cte]  
 4-1: isobaric heat rejection [P=cte]

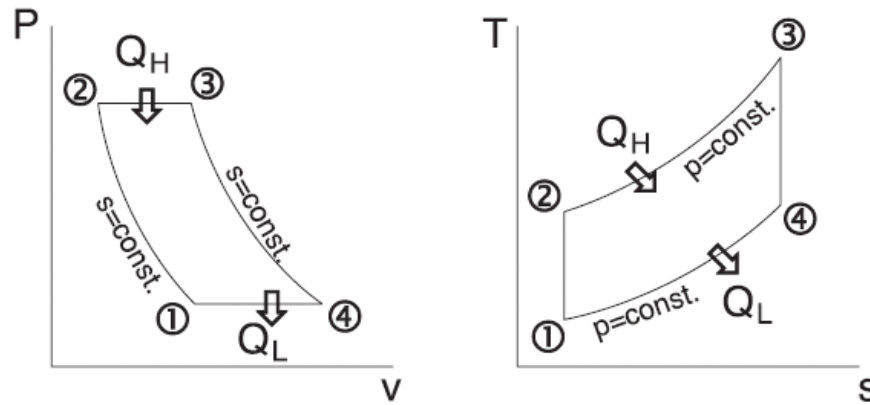


Figure.8.16. T-s and P-v diagrams of the Brayton cycle.

### Brayton cycle efficiency

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{C_p(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{T_1}{T_2} \left( \frac{\frac{T_4}{T_1} - 1}{\frac{T_3}{T_2} - 1} \right)$$

Using the isentropic relations:

$$\frac{P_2}{P_1} = \left( \frac{T_2}{T_1} \right)^{\frac{k}{k-1}} \quad \text{and} \quad \frac{P_3}{P_4} = \left( \frac{T_3}{T_4} \right)^{\frac{k}{k-1}}$$

But  $P_2=P_3$  and  $P_1=P_4$ ; therefore

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} \quad \text{or} \quad \frac{T_4}{T_1} = \frac{T_3}{T_2}$$

Hence, the efficiency of the Brayton cycle can be written under the form:

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \left( \frac{P_1}{P_2} \right)^{\frac{k-1}{k}}$$

The ratio  $P_2/P_1$  is called the **pressure ratio ( $r_p$ )**, therefore:

$$\eta = 1 - \left( r_p \right)^{\frac{1-k}{k}}$$

The efficiency of a Brayton cycle is only dependent on the specific heats ratio ( $k$ ) and the pressure ratio ( $r_p$ ).

Rmk: this expression is valid only for a constant  $C_p$

## How to increase the efficiency of the gas turbine?

By increasing the pressure ratio ... easy !!!!

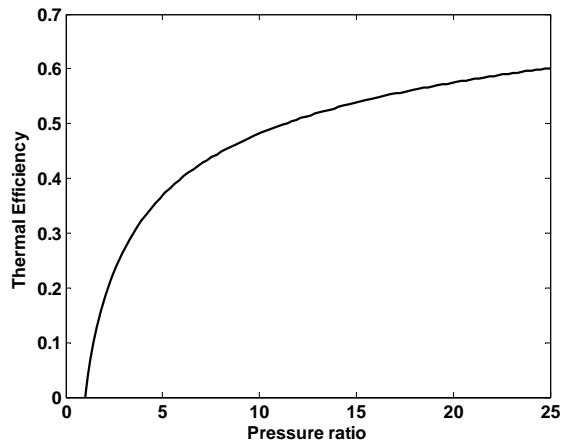


Figure.8.17. Increase thermal efficiency of the Brayton cycle by increasing the pressure ratio.

### OK! Can we indefinitely increase the pressure ratio?

Oops ! no.

Because, higher pressure ratios lead to a higher maximal temperature ( $T_3$ ) and this temperature must not exceed the temperature that the turbine blades can withstand (around 1600 K in practice). Furthermore, for fixed inlet and maximal temperatures, increasing the pressure ratio over a certain limit leads to an increase in the thermal efficiency but a decrease in the net work output. Therefore, practical pressure ratios are between 5 and 20.

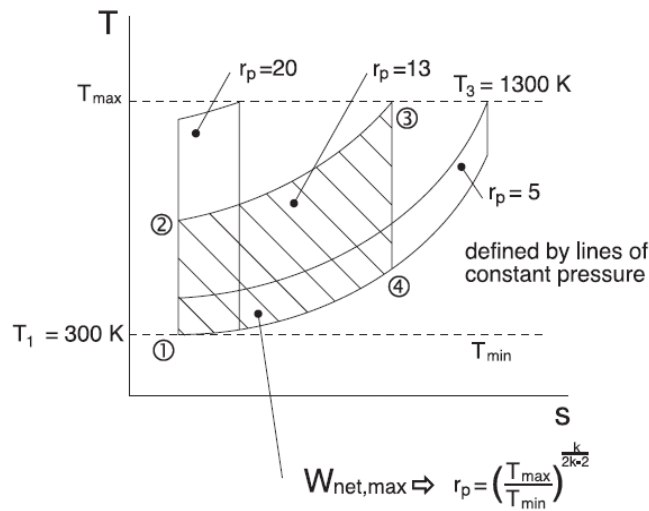


Figure.8.18. Effect of increasing the pressure ratio on the net work.

## Actual Brayton cycle

The actual efficiency of the Brayton cycle is lower than the theoretical value. This is because:

- 1- The compression and the expansion are not isentropic. Typical compressor and turbine efficiencies are around 85%.
- 2- The compressor requires a high percentage of work. Typically, between 40-80% of the turbine's output is used by the compressor, leaving only 60-20% as a useful work. This may seem surprising when we compare this percentage with the one required by the pump for a Rankine cycle (around 1-2%). This can be explained by the fact that in a Rankine cycle the pump compresses a liquid (very small specific volume), whereas in a gas turbine, air is compressed.

Numerical example:  $T_1=15^\circ\text{C}$ ;  $P_1=0.1\text{ MPa}$  and  $P_2=0.5\text{ MPa}$

$$\text{Rankine cycle (pump): } w_p = \int_1^2 v(P_2 - P_1) = 0.001010(500 - 100) = 0.4 \text{ kJ/kg}$$

Brayton cycle (compressor):

$$w_p = h_2 - h_1 = C_p(T_2 - T_1) = C_p T_1 \left( \frac{T_2}{T_1} - 1 \right) = C_p T_1 \left( \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right) = 1.0035(288.2) \left( (5)^{\frac{0.4}{1.4}} - 1 \right) = 169 \text{ kJ/kg}$$

**Typical values:**

<b>1940s</b>	efficiency (17%) maximal temperature ~ 540°C
<b>Today</b>	efficiency (40%) in simple configuration. maximal temperature ~ 1600°C

### Example

Air enters the compressor of a gas turbine at 100 kPa and 15°C. The pressure at the outlet of the compressor is 0.5 MPa and the maximal temperature of the cycle is 900°C.

Determine:

- 1- The work of the compressor.
- 2- The work of the turbine.
- 3- The thermal efficiency.

## Brayton cycle with regeneration

Since the temperature of the flow exiting the turbine ( $T_4$ ) is higher than the temperature exiting the compressor ( $T_2$ ), an amount of heat can be transferred from  $T_4$  to  $T_2$  and utilized to heat the air flow before entering the combustion chamber. To this effect, a counterflow heat exchanger or a regenerator is used.

For an ideal regenerator, the temperature  $T_5$  will be equal to  $T_4$  and similarly  $T_2$  will be equal to  $T_6$ .

Since less energy is rejected from the cycle ( $Q_L$  decreases), the thermal efficiency is expected to increase.

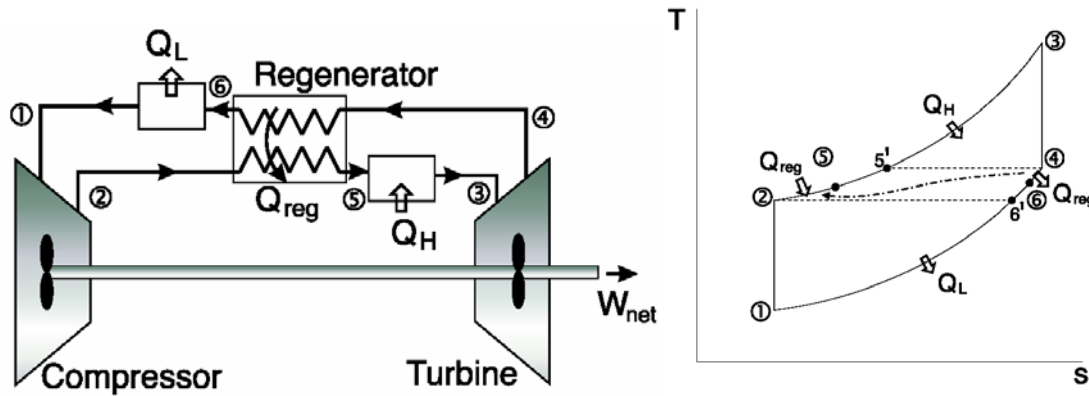


Figure.8.19. Brayton cycle with regeneration.

### Thermal efficiency of a Brayton cycle with regeneration:

$$\eta = \frac{W_{turbine} - W_{compressor}}{q_{in}}$$

$$q_{in} = C_p (T_3 - T_5) \text{ and } w_{turb} = C_p (T_3 - T_4)$$

For an ideal regenerator in which we have:  $T_5 = T_4$

We get:

$$q_{in} = w_{turb}$$

$$\text{Therefore, } \eta = 1 - \frac{w_c}{w_t} = 1 - \frac{C_p (T_2 - T_1)}{C_p (T_3 - T_4)} = 1 - \frac{T_1 \left( \frac{T_2}{T_1} - 1 \right)}{T_3 \left( 1 - \frac{T_4}{T_3} \right)} \quad (I)$$

Using isentropic relations, we have:

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} = r_p^{\frac{k-1}{k}}$$

and

$$\frac{T_3}{T_4} = \left( \frac{P_3}{P_4} \right)^{\frac{k-1}{k}} = r_p^{\frac{k-1}{k}} \text{ therefore } \frac{T_4}{T_3} = r_p^{\frac{1-k}{k}}$$

If we replace in (I)

$$\eta = 1 - \frac{T_1 r_p^{\frac{k-1}{k}} - 1}{T_3 1 - r_p^{\frac{1-k}{k}}}$$

And finally;

$$\eta = 1 - \frac{T_1}{T_3} r_p^{\frac{k-1}{k}}$$

You can compare this efficiency to the efficiency of a simple Brayton cycle

$$\eta = 1 - r_p^{\frac{1-k}{k}}$$

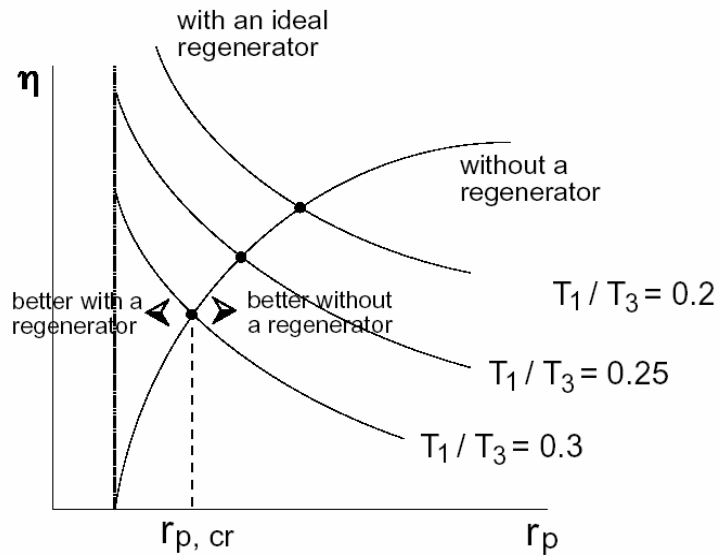
You can notice that the difference between the expression of the Brayton cycle with regeneration and the simple Brayton cycle is the presence of the ratio between the lowest temperature ( $T_1$ ) and the lowest temperature ( $T_3$ ), and the exponent of the pressure ratio.

Therefore, for a Brayton cycle with regeneration, the thermal efficiency depends not only on the pressure ratio, but also on the temperature ratio.

A most important point to notice is that contrary to a simple Brayton cycle, the thermal efficiency of a Brayton cycle with regeneration decreases with the increase in pressure ratio.

For $r_p = \text{Constant}$	$\eta \uparrow$ with $(T_1 / T_3) \downarrow$
For $(T_1 / T_3) = \text{Constant}$	$\eta \downarrow$ with $r_p \uparrow$

Therefore, not all the combinations of pressure and temperature ratios induce an increase in thermal efficiency. The figure below shows the limits of using regeneration.



**Figure.8.20.** Effect of pressure and temperature ratios on thermal efficiency.

In practice, to allow heat transfer, the temperature of the air leaving the regenerator at state 5 must be less than the temperature at state 4. In the same way, the temperature at state 6 must be higher than the temperature at state 2.

The efficiency of a regenerator is defined as:

$$\eta_{reg} = \frac{h_5 - h_2}{h_4 - h_2} \text{ which is equal (under air-standard assumptions) to } \eta_{reg} = \frac{T_5 - T_2}{T_4 - T_2}$$

A regenerator with a higher efficiency will obviously save a greater amount of fuel since it will preheat the air to a higher temperature prior combustion. However, a very efficient regenerator is not justified since the price will be very high and it will include significant pressure losses.

The choice is justified unless the savings from fuel costs exceed the additional expenses involved.

The efficiency of most regenerators used in practice is below 85%.

### Example

Air enters the compressor of a gas turbine with regeneration at 100 kPa and 15°C. The pressure at the outlet of the compressor is 0.5 MPa and the maximal temperature of the cycle is 900°C.

Determine:

- 1- The thermal efficiency.

Now suppose that the efficiency of the regenerator is 80%. Compute the new thermal efficiency?



### Brayton cycle with intercooling; reheat and regeneration

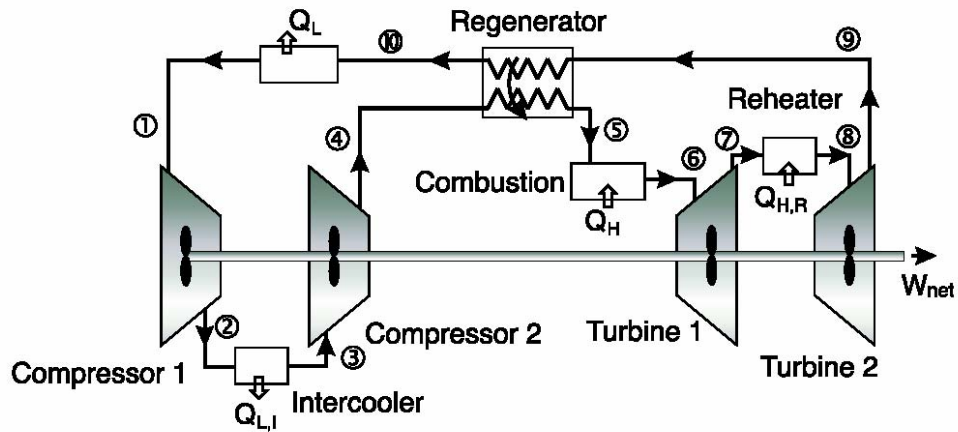


Figure.8.19. Brayton cycle with regeneration

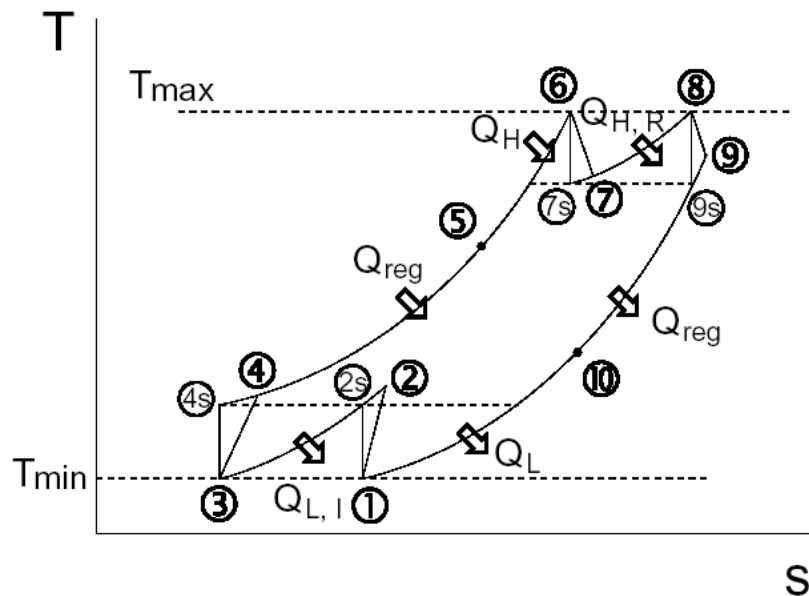


Figure.8.21. Brayton cycle with intercooling, reheating and regeneration.

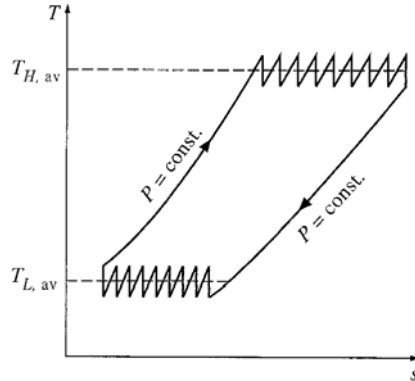
With increasing the number of stages, the compression process becomes nearly isothermal and the compression inlet temperature and the compression work decrease. The same thing for the turbine, the work of the turbine can be increased by a multistage expansion.

The objective of the multistage process is to maintain the specific volume as low as possible during compression and as high as possible during expansion.

This is role of the Brayton cycle with intercooling, reheating and regeneration.

The reheat is performed by spraying additional fuel into the exhaust gases. This is possible since after the first combustion, the exhaust gases still contain enough Oxygen (remember that the mass ratio between air/fuel is  $> 50$ ).

If the number of stages is indefinitely increased, the Brayton cycle with intercooling, reheating and regeneration approaches an Ericsson cycle (remember that the efficiency of an Ericsson cycle approaches the Carnot efficiency).



**Figure.8.22.** Brayton cycle with intercooling, reheating and regeneration with a high number of stages (equivalent to an Ericsson cycle).

However, in practice the number of stages for the compression and the expansion is limited to 2 or 3. This is because, a high number of stages increases the pressure losses.

This configuration of the Brayton cycle makes the regeneration very attractive, since, the fluid leaves the compressor at low temperature and the turbine at high temperature.

#### How does this configuration affect the thermal efficiency?

The work of the turbine will increase and the work of the compressor will decrease. The net work and back work ratio will both, therefore, increase. However, we decreased the temperature at which the heat is supplied and we increased the temperature at which the heat is rejected. Therefore, this configuration will not necessarily increase the thermal efficiency.

To improve the efficiency, intercooling and reheat are always used with regeneration.

#### Example

An ideal gas-turbine cycle with two stages of compression and two stages of expansion has an overall pressure ratio of 8. Air enters each stage of the compressor at 300 K and each stage of the turbine at 1300 K. Determine the back work ratio and the thermal efficiency of this gas-turbine cycle, assuming (a) no regenerator and (b) an ideal regenerator with 100% effectiveness.

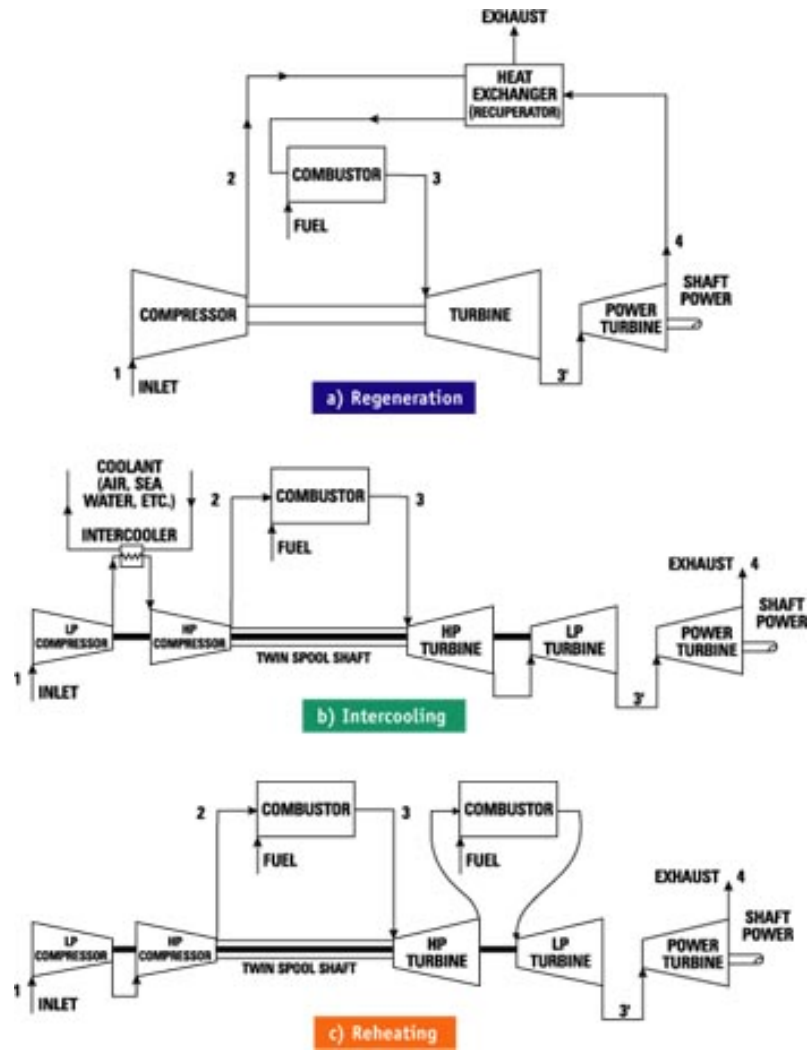


Figure.8.23. Regeneration, intercooling and reheat.

## Combined Gas-Steam power cycles

The objective of this cycle is to combine a Brayton cycle with a Rankine cycle. This combination improves significantly the thermal efficiency of the power plant.

The idea behind a combined gas-steam power cycle is to use the exhaust high temperature gases from the gas turbine to heat the steam within the boiler of the steam turbine.

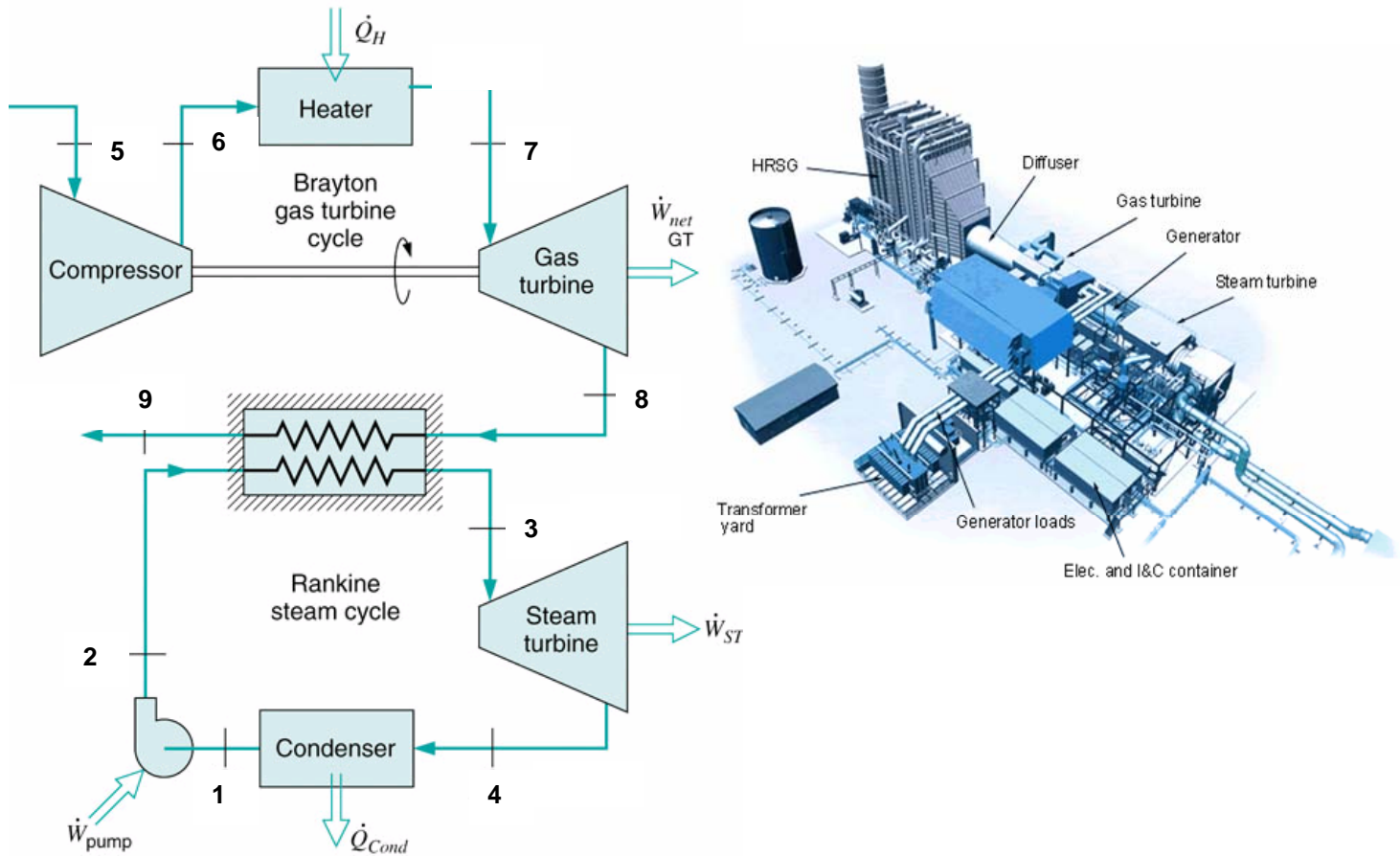
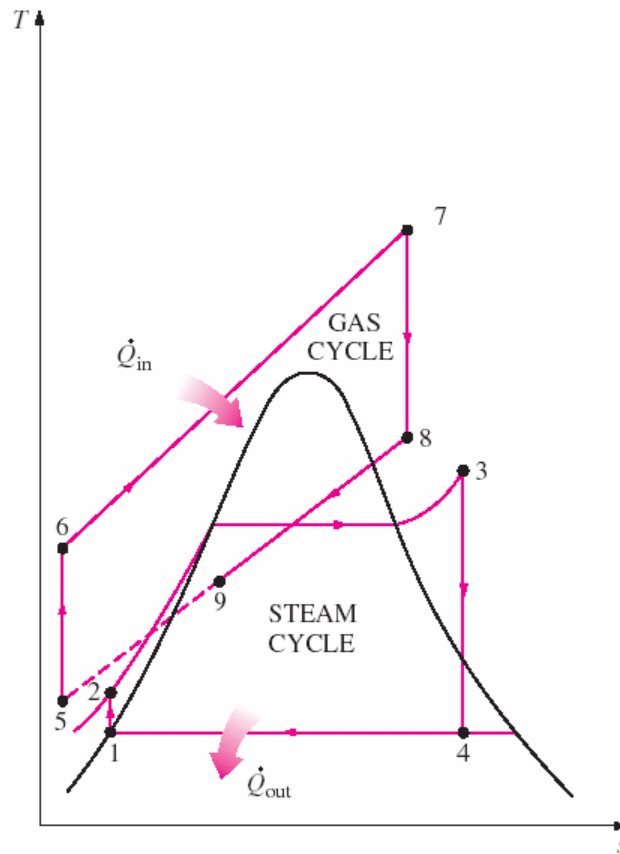


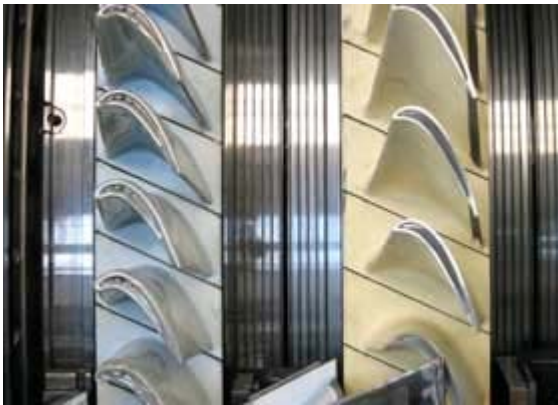
Fig.8.24. Combined gas (Brayton)- steam (Rankine) cycle.

**T-s diagram:**

**Fig.8.25.** T-s diagram of a Combined gas (Brayton)- steam (Rankine) cycle.

**Numerical example:**

- Simple Brayton efficiency: **36.8%**
- Simple Rankine efficiency: **35%**
- Combined Brayton and Rankine cycles: **56.4%**



**Fig.8.26.** Difference between gas turbine (left) and steam turbine (right) blades.

## Other practical application:

### BMW Turbosteamer

Although combined cycles have traditionally only been used in large power plants, BMW has a proposal to deploy such a system in automobiles by using exhaust heat to drive a steam turbine. The idea is that 80% of the heat energy from the exhaust gases is used to heat a fluid and form steam that is then conducted directly into an expansion until linked to the crankshaft of the engine. This results in 15% increase in the thermal efficiency and additional 14 horsepower. BMW is designing the system to be small enough to fit on any of its current production vehicles and hopes to have the system production ready in ten years.

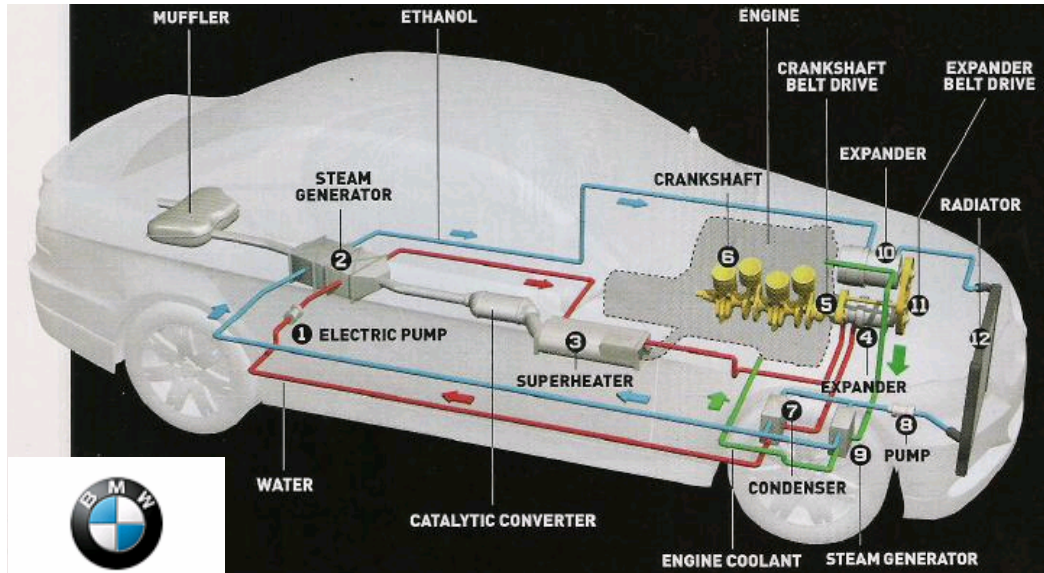


Fig.8.27. Schematic representation of BMW's turbosteamer.

### Combined Gas-Steam cycle with CyclePad

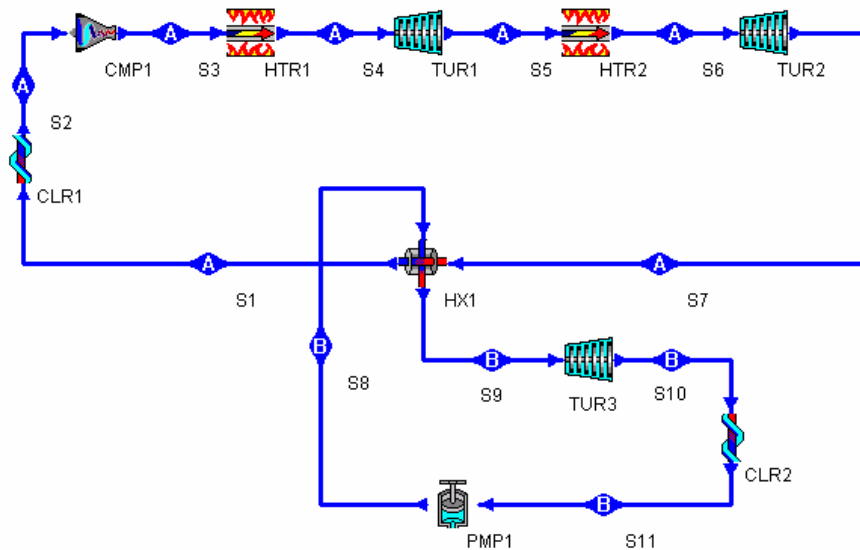


Fig.8.28. Combined gas-steam cycle with CyclePad.

**Example**

A simple steam power plant operates between pressures of 10 kPa and 4 MPa with a maximum temperature of 400°C. The power output from the steam turbine is 100 MW. A gas turbine provides the energy to the boiler; it accepts air at 100 kPa and 25°C, has a pressure ratio of 5, and a maximum temperature of 850°C. The exhaust gases exit the boiler at 350 K. Determine the thermal efficiency of the combined Brayton-Rankine cycle.

## TurboJet Engine

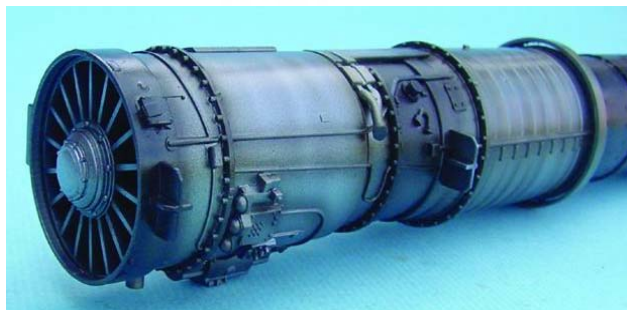
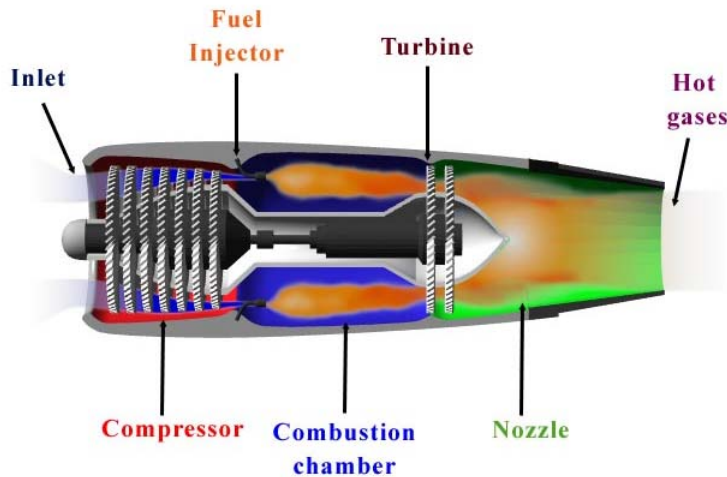
Turbojet engines of modern commercial aircrafts utilize gas-turbine cycles as the basis for their operation. Rather than producing power, however, the turbine is sized to provide just enough power to drive the compressor and auxiliary equipments. The net work is, therefore, zero for a turbojet engine. The energy that remains is used to increase the kinetic energy of the exiting exhaust gases by passing the gases through an exhaust nozzle thereby providing thrust to the aircraft. The gas turbine is preferred to the reciprocal engines because it is light and compact and has a high power-to-weight ratio.

Compared to a simple Brayton cycle, turbojets operate usually at higher pressure ratios (between 10 and 25).



**Dr. Hans von Ohain** (1911-1998; German) and **Sir Frank Whittle** (1907-1996; English) are both recognized as being the co-inventors of the jet engine. Each worked separately and knew nothing of the other's work. Hans von Ohain is considered the designer of the first operational turbojet engine. Frank Whittle was the first to register a patent for the turbojet engine in 1930. Hans von Ohain was granted a patent for his turbojet engine in 1936. However, Hans von Ohain's jet was the first to fly in 1939. Frank Whittle's jet first flew in 1941.

**Figure.8. 29.** Sir Frank Whittle (left) and Dr. Hans von Ohain, AFRL's chief propulsion scientist compare drawings of their unique patented turbine engines during an historic first meeting in Wright-Patterson's Bldg. 18, May 3, 1978. Both are recognized as the co-inventors of the jet engine but served on opposite sides during World War II.



**Figure.8.30.** Turbojet engine.



## Analysis

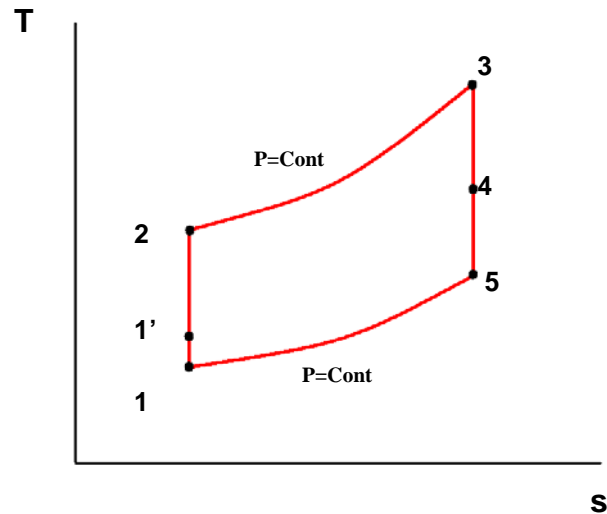


Figure.8.31. T-s diagram for turbojet cycle.

- 1-1' Compression in the diffuser due to deceleration.
- 1'-2 Isentropic compression
- 2-3 Heat supply (combustion)
- 3-4 Isentropic expansion in the turbine
- 4-5 Isentropic expansion in the nozzle

### Definition of thrust:

The thrust developed by 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, and it is determined from Newton's second law. The role of the thrust is to overcome the drag.

$$\text{Thrust} = F = \dot{m} (V_{\text{exit}} - V_{\text{inlet}})$$

### Propulsive power

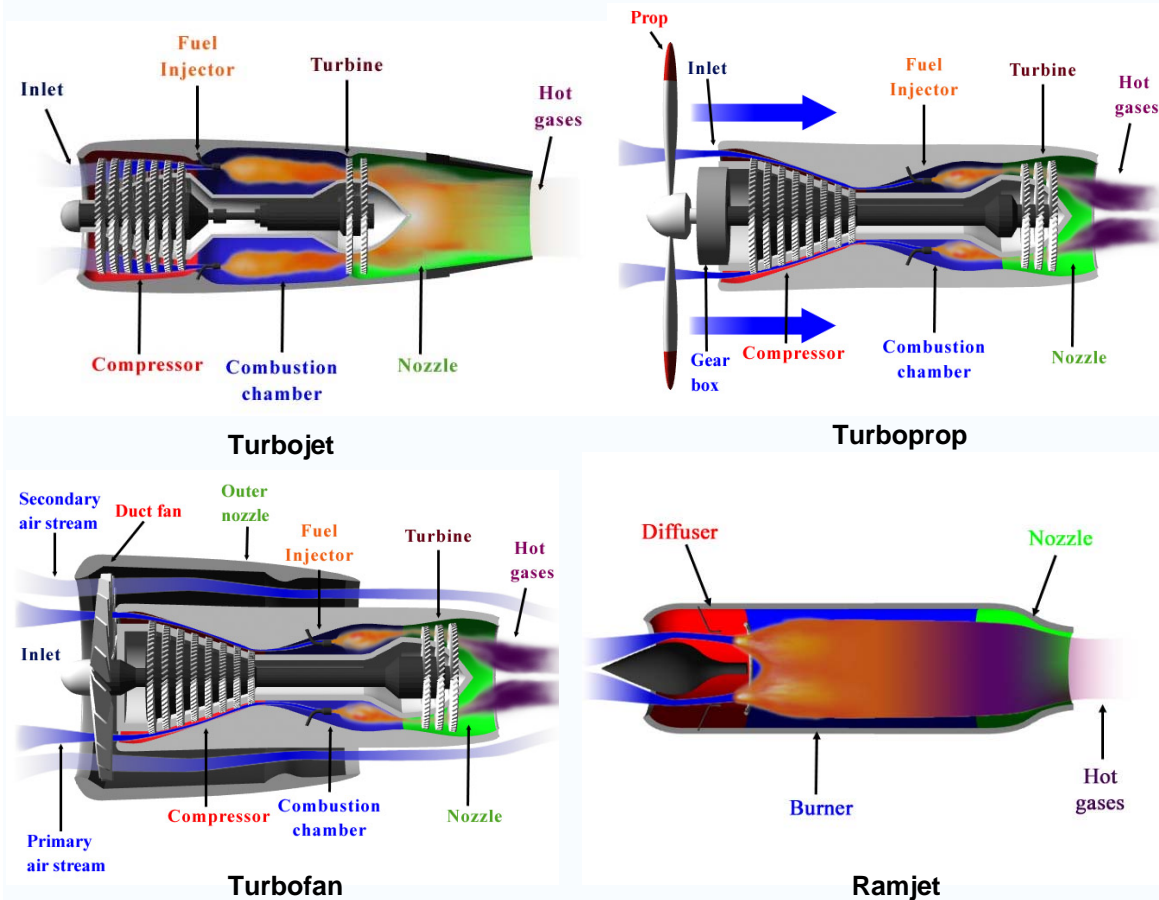
$$\dot{W}_p = F V_{\text{aircraft}} = \dot{m}(V_{\text{exit}} - V_{\text{inlet}}) V_{\text{aircraft}}$$

### Propulsive efficiency

$$\eta_p = \frac{\text{Propulsive Power}}{\text{Heat supply (combustion)}} = \frac{\dot{W}_p}{\dot{Q}_{in}}$$

**Additional information**

There are a large number of different types of jet engines, all of which get propulsion from a high speed exhaust jet.



**Figure.8.32.** Different types of jet engines.

Type	Description	Advantages	Disadvantages
<b>Turbojet</b>	Generic term for simple turbine engine	Simplicity of design, efficient at supersonic speeds ( $\sim M2$ )	Basic design, misses many improvements in efficiency and power for subsonic flight, relatively noisy
<b>Turbofan</b>	First stage compressor greatly enlarged to provide bypass airflow around engine core	Quieter due to greater mass flow and lower total exhaust speed, more efficient for a useful range of subsonic airspeeds for same reason, cooler exhaust temperature	Greater complexity (additional ducting, usually multiple shafts), large diameter engine, need to contain heavy blades. More subject to FOD and ice damage. Top speed is limited due to the potential for shockwaves to damage engine. Only practical at subsonic speeds.
<b>Ramjet</b>	Intake air is compressed entirely by speed of oncoming air and duct shape ( <i>divergent</i> )	Very few moving parts, Mach 0.8 to Mach 5+, efficient at high speed ( $> Mach 2.0$ or so), lightest of all airbreathing jets (thrust/weight ratio up to 30 at optimum speed)	Must have a high initial speed to function, inefficient at slow speeds due to poor compression ratio, difficult to arrange shaft power for accessories, usually limited to a small range of speeds, intake flow must be slowed to subsonic speeds, noisy, fairly difficult to test, finicky to keep lit.
<b>Turboprop (Turboshaft similar)</b>	Strictly not a jet at all — a gas turbine engine is used as powerplant to drive propeller shaft (or Rotor in the case of a Helicopter)	High efficiency at lower subsonic airspeeds(300 knots plus), high shaft power to weight	Limited top speed (aeroplanes), somewhat noisy, complex transmission

### After burner

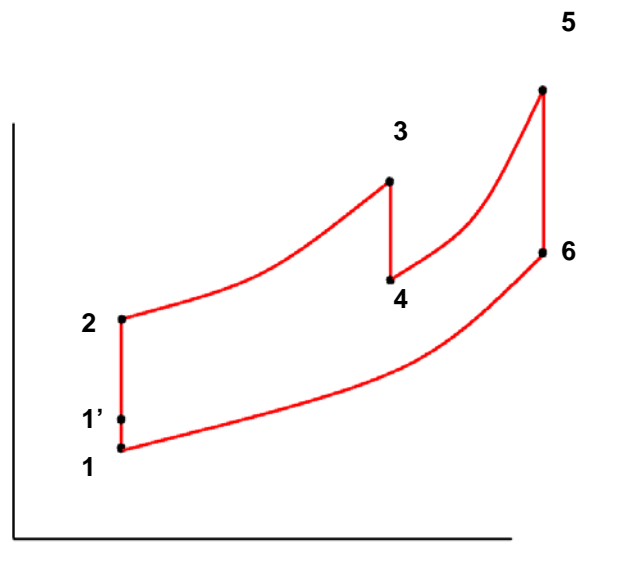


Figure.8.33. T-s diagram for turbojet after burner cycle.

## Manufacturers

- CFM International
- General Electric
- Honeywell
- Pratt & Whitney (United Technologies)
- SNECMA
- Rolls-Royce

### Example

A turbojet aircraft flies at a speed of 300 m/s at an elevation of 10 000 m. If the compression ratio is 10, the turbine inlet temperature is 1000°C, and the mass flux of air is 30 kg/s, calculate the maximum thrust possible from this engine. Also, calculate the rate of fuel consumption if the heating value of the fuel is 8400 kJ/kg.

Physical Properties of Standard Atmosphere in SI Units

Altitude (meters)	Temperature (degrees K)	Pressure (Pa)	Density (kg/m <sup>3</sup> )	Viscosity (N-s/m <sup>2</sup> )
-5,000	320.7	1.778E+5	1.931	1.942E-5
-4,000	314.2	1.596E+5	1.770	1.912E-5
-3,000	307.7	1.430E+5	1.619	1.882E-5
-2,000	301.2	1.278E+5	1.478	1.852E-5
-1,000	294.7	1.139E+5	1.347	1.821E-5
0	288.2	1.013E+5	1.225	1.789E-5
1,000	281.7	8.988E+4	1.112	1.758E-5
2,000	275.2	7.950E+4	1.007	1.726E-5
3,000	268.7	7.012E+4	9.093E-1	1.694E-5
4,000	262.2	6.166E+4	8.194E-1	1.661E-5
5,000	255.7	5.405E+4	7.364E-1	1.628E-5
6,000	249.2	4.722E+4	6.601E-1	1.595E-5
7,000	242.7	4.111E+4	5.900E-1	1.561E-5
8,000	236.2	3.565E+4	5.258E-1	1.527E-5
9,000	229.7	3.080E+4	4.671E-1	1.493E-5
10,000	223.3	2.650E+4	4.135E-1	1.458E-5
15,000	216.7	1.211E+4	1.948E-1	1.422E-5
20,000	216.7	5.529E+3	8.891E-2	1.422E-5
30,000	226.5	1.197E+3	1.841E-2	1.475E-5
40,000	250.4	2.871E+2	3.996E-3	1.601E-5
50,000	270.7	7.978E+1	1.027E-3	1.704E-5
60,000	255.8	2.246E+1	3.059E-4	1.629E-5
70,000	219.7	5.520	8.754E-5	1.438E-5
80,000	180.7	1.037	1.999E-5	1.216E-5
90,000	180.7	1.644E-1	3.170E-6	1.216E-5

## Refrigeration Cycles



The objective of refrigeration cycles is to transfer the heat from a low temperature region to a high temperature region.

- if the objective of the cycle is to **decrease the lowest temperature**, we call it: **a Refrigeration cycle**.

- if the objective of the cycle is to **increase the highest temperature**, we call it: **a heat pump**.

### Carnot cycle

As the Carnot cycle is the ideal cycle, let us first try to convert it to a refrigeration cycle, and then we will discuss practical limitations.

Figure (10.1) shows a reversed Carnot cycle, the efficiency of this cycle will be:

$$\eta = 1 - \frac{T_L}{T_H}$$

However, if we try to apply the Carnot cycle, we will face some technical difficulties:

**1-2:** It is not advisable to compress a mixture of vapor and gas, since the liquid droplets would cause excessive wear.

→ shift point 1 to the right (saturated vapor).

**3-4:** It would be quite expensive to construct a device to be used in the expansion process that would be nearly isentropic (no losses allowed). It is much simpler to reduce the pressure irreversibly by using an expansion valve (isenthalpic process).

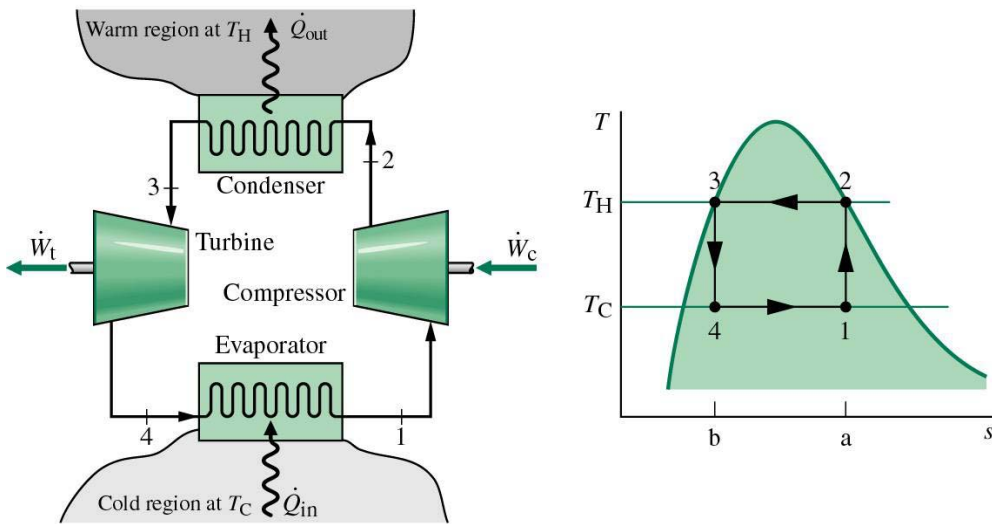


Figure.10.1. Reversed Carnot cycle.

**The Ideal vapor-compression refrigeration cycle**

- 1-2: isentropic compression in a compressor.
- 2-3: isobaric heat rejection in a condenser.
- 3-4: throttling in an expansion device.
- 4-1: isobaric heat absorption in an evaporator.

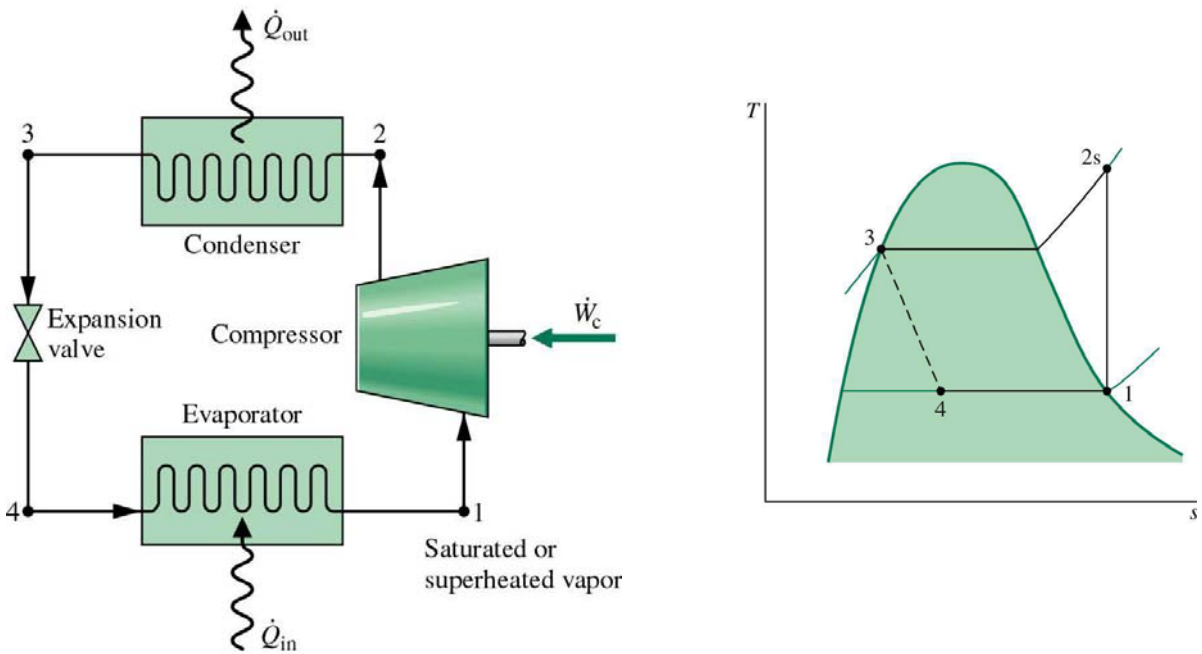


Figure.10.2. Ideal vapor-refrigeration cycle.

The coefficient of performance (COP) of a refrigeration cycle is:

$$COP_R = \frac{\text{benefit}}{\text{Cost}} = \frac{\dot{Q}_{in}}{\dot{W}_{in}}$$

The coefficient of performance (COP) of a heat pump is:

$$COP_{HP} = \frac{\text{benefit}}{\text{Cost}} = \frac{\dot{Q}_{out}}{\dot{W}_{in}}$$

COP can attain 4 for refrigerators and perhaps 5 for heat pumps.

### Actual vapor-compression refrigeration cycle

The actual cycle differs from the ideal one due to irreversibilities, such as:

- Pressure drops due to friction in connecting pipes
- Heat transfer occurs from or to the refrigerant through the pipes connecting the components.
- Pressure drops occur through the condenser and evaporator tubes.
- Heat transfer occurs from the compressor.

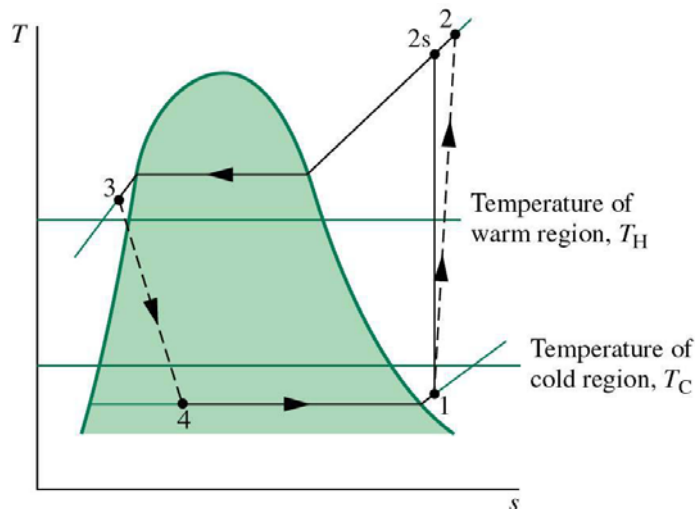


Figure.10.3.

### Selecting a refrigerant

The evaporation temperature of the refrigerant must be quite low, in the neighborhood of  $-25^{\circ}\text{C}$  (so usually forget water ...)

The most common refrigerants used are: ChloroFluoroCarbons (CFC), ammonia, hydrocarbons (propane, ethane, ethylene, ...), Carbon Dioxide, air, ...

Usually R-11, R-12, R-22, R134a and R-502 were used (the trade name is Freon) before 1987, now isobutane (although it is a very dangerous gas ...).

For industry, they usually use ammonia since it is cheaper, doesn't damage the Ozone layer, has a high COP and greater detectability in case of a leak.

The major drawback is the toxicity, which makes it unsuitable for domestic use.

### Important points for the design of a refrigeration cycle

- the **temperature** of the refrigerant within the **condenser** must be 5°C to 15°C **higher than** the exterior temperature, to allow efficient heat transfer.
- the **temperature** of the refrigerant within the **evaporator** must be 5°C to 15°C **lower than** the cooled space temperature, to allow efficient heat transfer.
- The equipments working at low pressure (evaporator) must be sufficiently large to account for a higher specific volume.
- The equipments working at high pressure (Condenser) must be designed to support the high pressure.

### Multistage vapor refrigeration cycle

The simple vapor-compression refrigeration cycle is the most widely refrigeration cycle used. However, if we are looking for a further decrease in the temperature, we have to use a cascade refrigeration cycle.

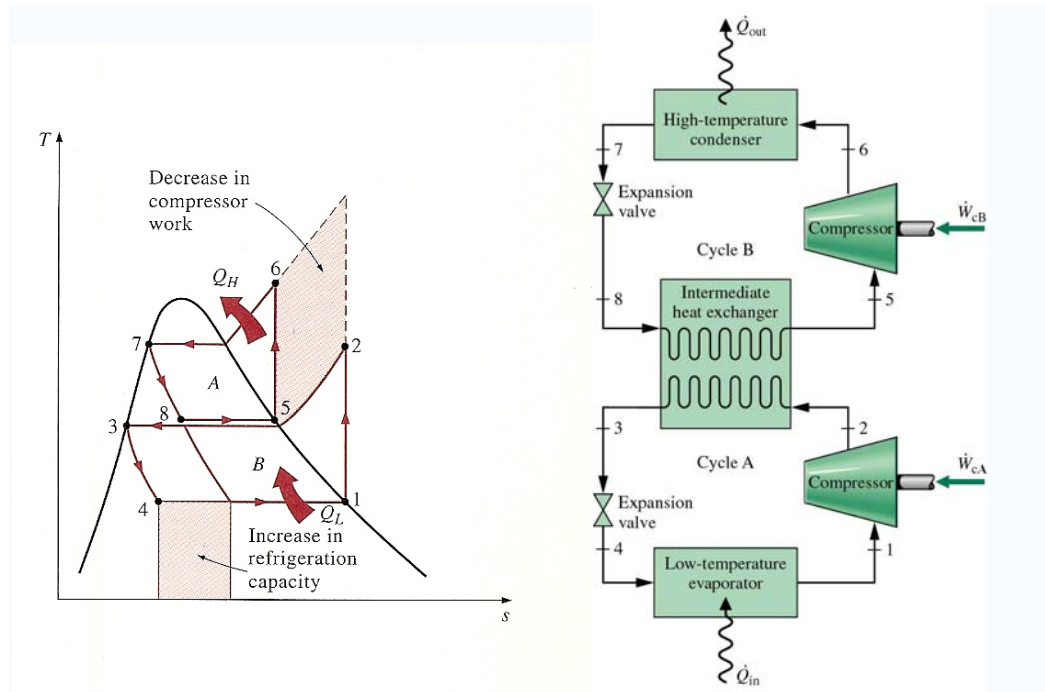


Figure.10.4. Two-stage refrigeration cycle.

Indeed, this cycle will lead to a decrease in the temperature of the point 3, therefore increasing the refrigeration. The configuration will minimize the compressor work. Note that we need for that, 2 compressors, a heat exchanger and 2 expansion valves. So the additional costs for this must be



justified by improved performance. For extremely low refrigeration temperatures, several stages may be used.

The optimal intermediate pressure is:

$$P_i = \sqrt{P_H P_L}$$

$P_H$  the high pressure

$P_L$  the low pressure

With this cycle, it is not an obligation to use the same refrigerant. If the refrigerants are different, the appropriate T-s diagram must be used.

### Example

R134a is used in an ideal vapor refrigeration cycle operating between saturation temperatures of  $-20^\circ\text{C}$  in the evaporator and  $39.39^\circ\text{C}$  at the condenser outlet. The mass flow rate is  $0.6\text{ kg/s}$ . Calculate the rate of refrigeration and the coefficient of performance.

Now consider a two-stage cycle replacing the simple cycle for the same conditions. Determine the rate of refrigeration and the coefficient of performance.

## Absorption refrigeration cycle

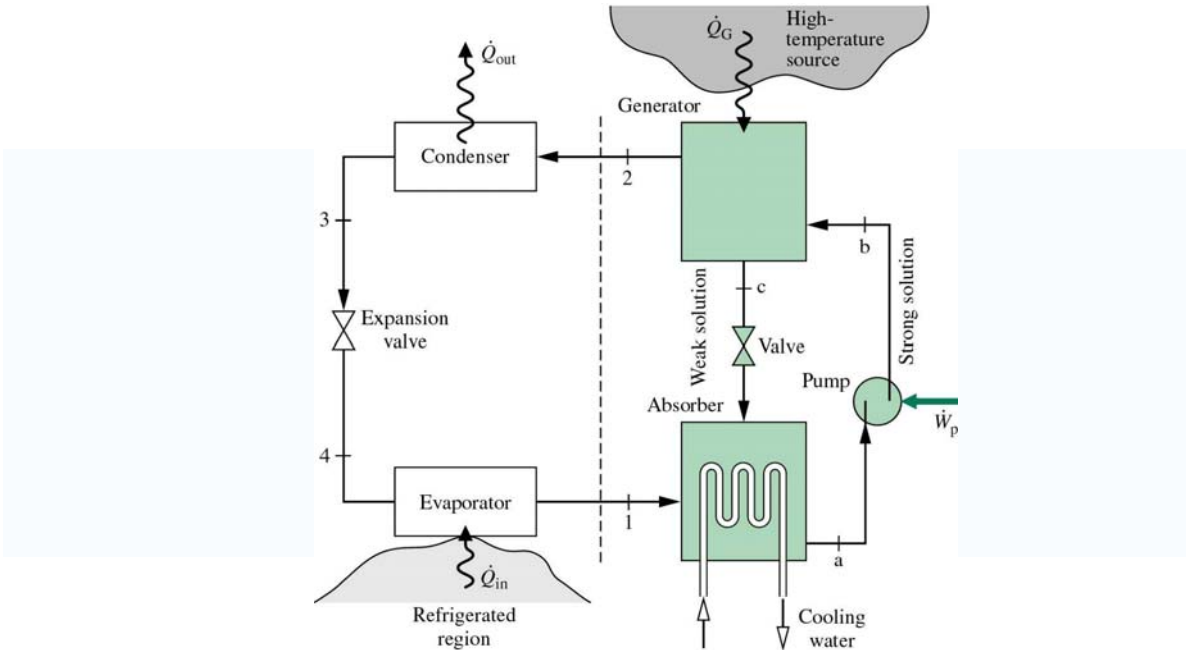
In conventional refrigeration cycles, the power input needed to operate the compressor is relatively large, since the fluid compressed is in the vapor state and has a very large specific volume

$$(w = v \int_1^2 dP, \text{ with } v \text{ high}).$$

The objective of an absorption refrigeration cycle is to reduce the power needed for the compression by "converting" the vapor into a liquid which will be pumped by a pump (liquid  $\rightarrow$  lower  $v \Rightarrow$  lower  $w$  for the same pressure difference).

To do so, several equipments are added to the conventional cycle. These equipments are: the absorber; the pump; the heat exchanger; the generator and a regulating valve.

The most widely used absorption cycle is the ammonia-water system (Fig.10.5). It was patented by Ferdinand Carre (France) in 1859.



**Figure.10.5.** Ammonia-water system.

On the left side of the figure, it is exactly the same processes as for a conventional refrigeration cycle: condensation, throttling and evaporation. But on the right side, the compressor is replaced by the following process:

The pure ammonia  $\text{NH}_3$  in the vapor state enters the absorber where it dissolves and reacts with water. The absorber contains therefore a mixture of  $\text{NH}_3 + \text{H}_2\text{O}$ .

As the amount of  $\text{NH}_3$  that can be dissolved in  $\text{H}_2\text{O}$  is inversely proportional to the temperature. The absorber is cooled to maintain its temperature as low as possible.

The liquid solution  $\text{NH}_3 + \text{H}_2\text{O}$ , which is rich in  $\text{NH}_3$ , is then pumped to the generator. Sometimes a heat exchanger is used between the pump and the generator to pre-vaporize the mixture  $\text{NH}_3 + \text{H}_2\text{O}$ . In the generator, an external source vaporize the mixture. The liquid is transferred to the absorber through an expansion valve to reduce its pressure. The pure  $\text{NH}_3$  vapor leaving the generator enters the condenser and follows the rest of the refrigeration cycle processes.

**Note:** to analyze the absorption cycle, we must know the amount of refrigerant contained in a mixture ( $\text{NH}_3 + \text{H}_2\text{O}$  here), both in liquid form and vapor form. This can be found with the aid of an equilibrium diagram.

### The gas refrigeration cycle

If the flow of gas is reverted in the Brayton cycle, the gas undergoes an isentropic expansion process as it flows through the turbine, resulting in a substantial reduction in temperature.

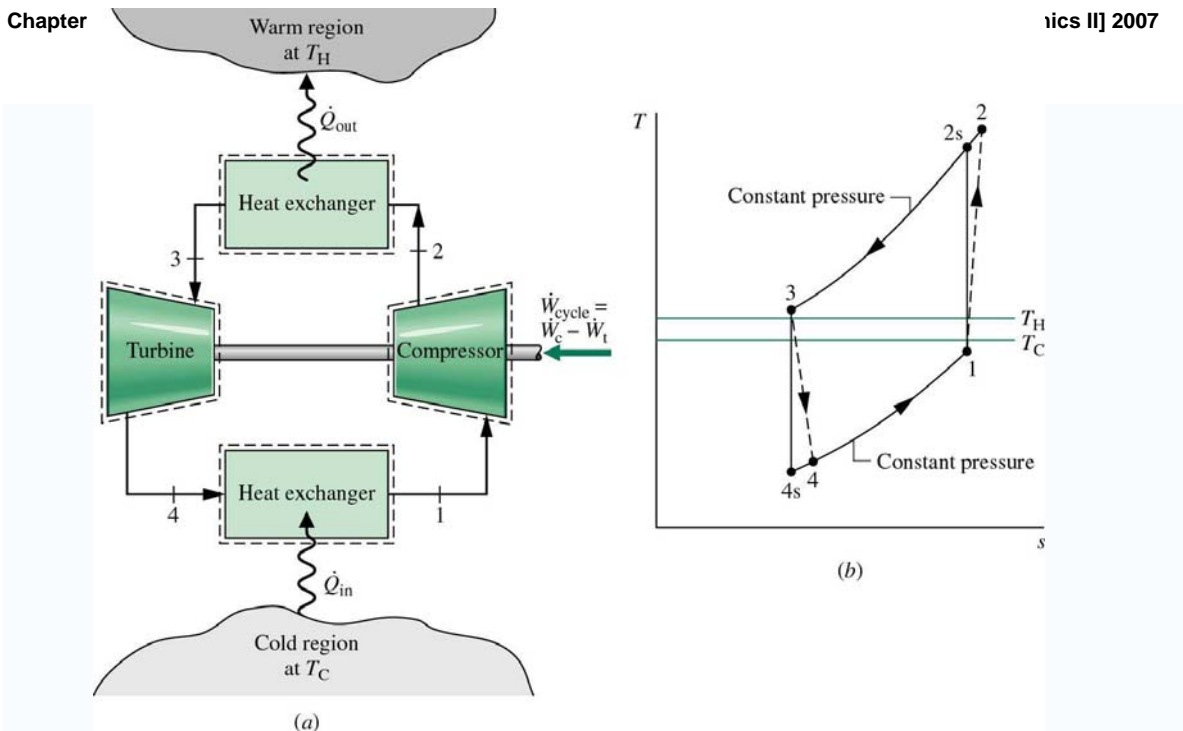


Figure.10.6. Reversed Brayton cycle.

An open cycle is used in aircraft ; air is extracted from the atmosphere at state 1 and inserted into the passenger compartment at state 4, this provides both fresh air and cooling.

Like for the regenerative Brayton cycle, the reversed Brayton cycle can be used with a regenerator **to lower** the temperature of the turbine inlet.

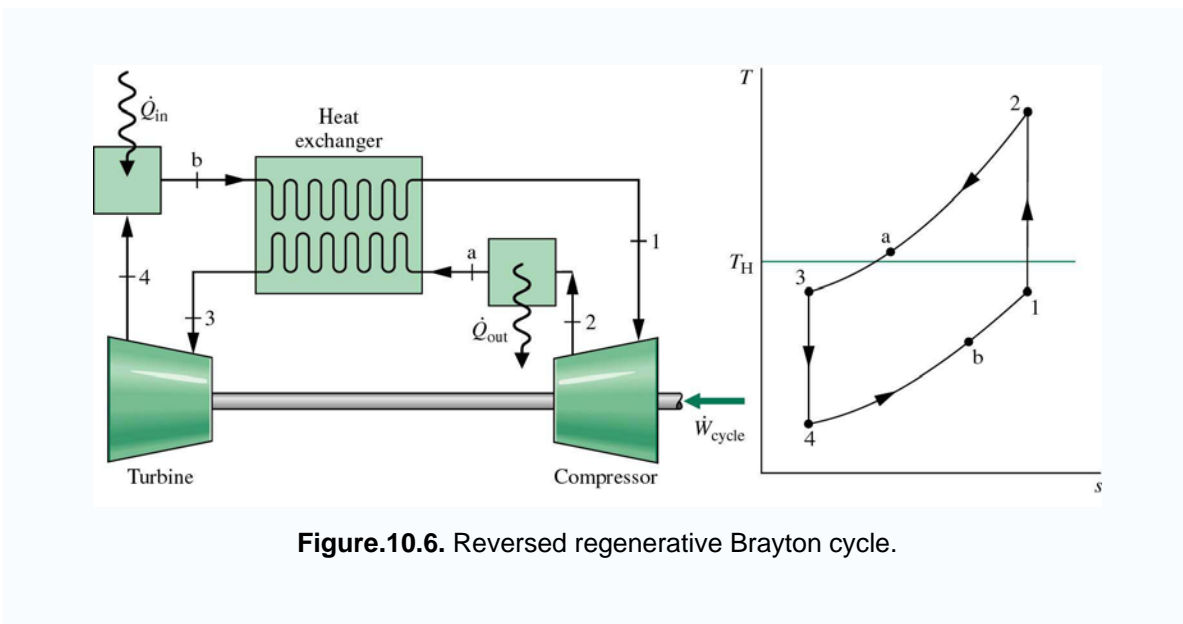


Figure.10.6. Reversed regenerative Brayton cycle.

## Heat pump

A heat pump utilizes the vapor refrigeration cycle, but to increase the temperature of the external medium, like a house (Figure).

Although using a heat pump for heating is more expensive than other conventional systems, it saves money in the long run.

The major problem with heat pumps occurs in humid regions where the temperature falls below 2 to 5°C. This may cause frosting. The accumulation of frost is highly undesirable, since it seriously disturbs heat transfer. This problem can be solved by running the system as an air conditioner.

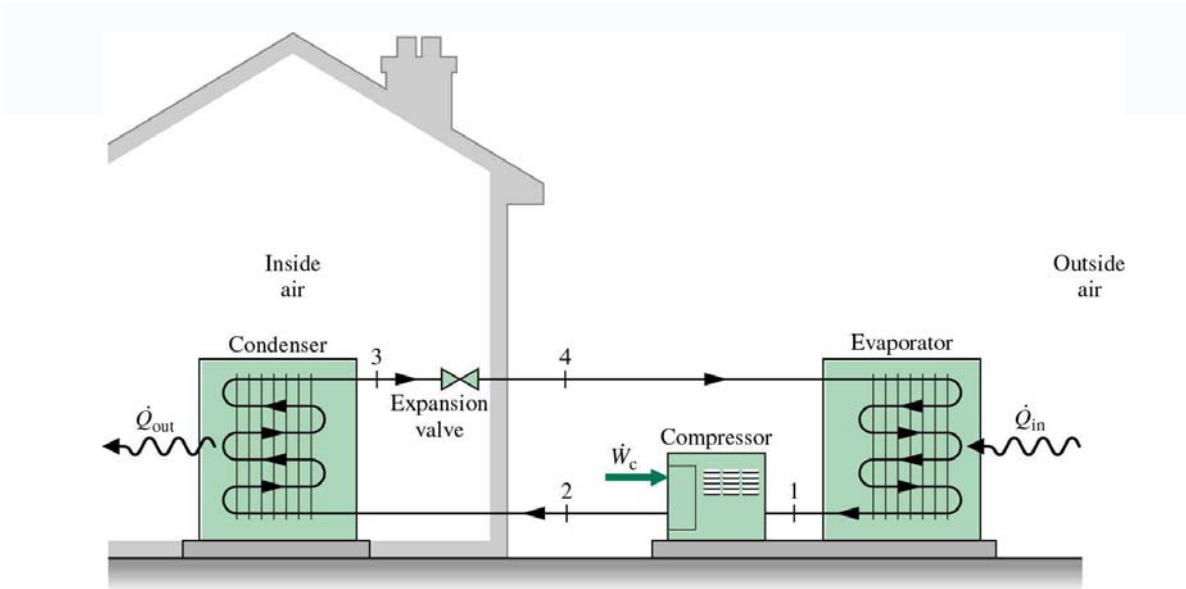


Figure.10.8. Heat pump.

### Additional information

**BTU:** the BTU is a common unit used in refrigeration industry. A BTU (British Thermal Unit ) is the amount of heat energy needed to rise the temperature of one pound of pure water by one degree F.

### Gaz liquefaction

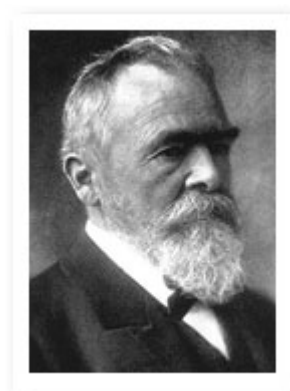
One of the “hottest” application of refrigeration cycles is gas liquefaction. In fact, several engineering processes require very low temperatures.

To liquefy a gas such as helium, hydrogen or nitrogen, the temperature must be lower than their critical temperature: -268°C, -240°C and -147°C respectively.



**Figure.10.9.** Transport of natural gas.

To reach so low temperatures several cycles may be used, usually using multistage compressors. The man who contributed the most significantly to gas liquefaction is Carl Von Linde [if you remember well, he was Diesel's professor at Munich Polytechnics].



Carl von Linde

Although discovering oxygen and investigating its role in chemical reactions proved to be of crucial importance in changing the science of chemistry, initially oxygen could be produced only in the laboratory and in limited quantities, by chemical or electrolytic means: it had little importance outside the laboratory. It was the achievement of Carl von Linde (1842–1934) in 1902 to take oxygen from the air itself—and he was soon extracting it in quantities approaching one thousand cubic feet per hour. Oxygen became a common commodity that was supplied to hospitals and industries and was later used in rocket fuel, but this was not the German engineer's first important contribution.

Linde, the son of a Lutheran minister, was educated in science and engineering at the Federal Polytechnic in Zurich, Switzerland. After working for locomotive manufacturers in Berlin and Munich, he became a faculty member at the Polytechnic in Munich. His research there on heat theory, from 1873 to 1877, led to his invention of the first reliable and efficient compressed-ammonia refrigerator. The company he established to promote this invention was an international success: refrigeration rapidly displaced ice in food handling and was introduced into many industrial processes.

After a decade Linde withdrew from managerial activities to refocus on research, and in 1895 he succeeded in liquefying air by first compressing it and then letting it expand rapidly, thereby cooling it. He then obtained oxygen and nitrogen from the liquid air by slow warming. In the early days of oxygen production the biggest use by far for the gas was the oxyacetylene torch, invented in France in 1904, which revolutionized metal cutting and welding in the construction of ships, skyscrapers, and other iron and steel structures.

One company formed to use Linde's later patents was the Linde Air Products Company, founded in Cleveland in 1907. In 1917 Linde Air Products joined with four other companies that produced acetylene, among other products, to form Union Carbide and Carbon Corporation. Recently, Linde Air again became an independent company—Praxair.

## Gas Mixtures

In this chapter we will develop methods for determining thermodynamic properties of a mixture in order to apply the first law to systems involving mixtures. This will be an essential step to understand chemical reactions and combustion.

The objective of this part is, therefore, to answer to this simple question:

**“If I give you the properties of a component A and the properties of a component B, what will be the properties of the mixture A+B”.**

The first solution to answer to this question will be to define a table of thermodynamic properties for each mixture. But obviously, this is not achievable since the number of combinations is endless. It will be much easier to determine the properties of the mixture using the properties of each component.

For that, we need to know the composition of the mixture, as well as, the properties of the individual components.

Let us start by some definitions:

**The total mass of the mixture:**

$$m_m = m_A + m_B + m_C + \dots = \sum_{i=1}^k m_i$$

**The mole number of a mixture:**

$$N_m = N_A + N_B + N_C + \dots = \sum_{i=1}^k N_i$$

**The mole fraction**

$$\frac{\text{mole number of a component}}{\text{mole number of the mixture}} = \frac{N_i}{N_m} \rightarrow \text{Mole fraction } y_i$$

$$\text{Note that, } \sum_{i=1}^k y_i = \sum_{i=1}^k \frac{N_i}{N_m} = \frac{1}{N_m} \sum_{i=1}^k N_i = \frac{N_m}{N_m} = 1 \quad \text{therefore: } \sum_{i=1}^k y_i = 1$$

**The mass fraction**

$$\frac{\text{The mass of a component}}{\text{The mass of the mixture}} = \frac{m_i}{m_m} \rightarrow \text{Mass fraction } m_{fi}$$

$$\text{Note that, } \sum_{i=1}^k m_{fi} = \sum_{i=1}^k \frac{m_i}{m_m} = \frac{1}{m_m} \sum_{i=1}^k m_i = \frac{m_m}{m_m} = 1 \quad \text{therefore } \sum_{i=1}^k m_{fi} = 1$$

The molecular weight of the mixture can be obtained as:

$$M_m = \frac{m_m}{N_m} = \frac{\sum_{i=1}^k M_i N_i}{N_m} = \sum_{i=1}^k y_i M_i$$

And the mixture gas constant will be:

$$R_m = \frac{R_U}{M_m} \quad \text{where } R_U \text{ is the universal gas constant (8.314 kJ/kmol K).}$$

When performing an analysis on a mixture it is important to state if the analysis is based on the mass [gravimetric analysis] or on the mole numbers or volume [volumetric analysis]

### Example

Molar analysis of air indicates that it is composed primarily of nitrogen (78%) and oxygen (22%). Determine:

- The mole fractions.
- The gravimetric analysis.
- Its molecular weight.
- Its gas constant.

### **P-v-T behavior of gas mixtures or ideal gas-law for mixtures:**

Two models are used to obtain the P-v-T relation for a mixture of ideal gases:

**The Amagat's model:** In this model each component is considered, as it exists separately at the same pressure and temperature of the mixture. The total volume is the sum of the volume of each component.

#### **Amagat's model same T and P**

$$\text{For the mixture (A+B)} \quad PV_m = N_m \bar{R}T$$

$$\text{For component A} \quad PV_A = N_A \bar{R}T$$

$$\text{For component B} \quad PV_B = N_B \bar{R}T$$

$$\text{But } N_m = N_A + N_B \Leftrightarrow \frac{PV_m}{\bar{R}T} = \frac{PV_A}{\bar{R}T} + \frac{PV_B}{\bar{R}T}$$

Therefore for the Amagat's model:  $V_m = V_A + V_B$

$$\text{The general form is: } V_m = \sum_{i=1}^k V_i(T_m, P_m)$$

$V_A$  and  $V_B$  are the partial volumes.

**The Dalton's model:** in this model each component occupies the same volume and has the same temperature of the mixture. The total pressure is the sum of the component pressures (partial pressures).

#### **Dalton's model same T and V**

$$\text{For the mixture (A+B)} \quad P_m V = N_m \bar{R}T$$

$$\text{For component A} \quad P_A V = N_A \bar{R}T$$

$$\text{For component B} \quad P_B V = N_B \bar{R}T$$

$$\text{But } N_m = N_A + N_B \Leftrightarrow \frac{P_m V}{RT} = \frac{P_A V}{RT} = \frac{P_B V}{RT}$$

Therefore for the Dalton's model:  $P_m = P_A + P_B$

$$\text{The general form is: } P_m = \sum_{i=1}^k P_i(T_m, V_m)$$

$P_A$  and  $P_B$  are the partial pressures.

We can show that,

$$\frac{P_A}{P_m} = \frac{N_A}{N_m} = y_A \quad \text{and} \quad \frac{P_B}{P_m} = \frac{N_B}{N_m} = y_B$$

### Example

A rigid tank contains 2 kg of  $N_2$  and 4 kg of  $CO_2$  at a temperature of  $25^\circ C$  and 2 MPa. Determine:

- The partial pressures of the two gases.
- The gas constant of the mixture.

### Properties of mixtures of ideal gases

The extensive properties of a mixture, such as H, U and S can be found by simply adding the contribution of each component, for example for enthalpy:

$$H_m = H_A + H_B + \dots = \sum_{i=1}^k H_i$$

In term of specific enthalpy h:

$$H_m = m_m h_m = \sum_{i=1}^k m_i h_i$$

$$\text{Therefore, } h_m = \sum_{i=1}^k m_{f_i} h_i$$

$$\text{This can be also expressed on a molar basis } H_m = N \bar{h}_m = \sum_{i=1}^k N_i \bar{h}_i \Leftrightarrow \bar{h}_m = \sum_{i=1}^k y_i \bar{h}_i$$

So in general form:



$$u_m = \sum_{i=1}^k m_{fi} u_i$$

$$h_m = \sum_{i=1}^k m_{fi} h_i$$

$$(C_p)_m = \sum_{i=1}^k m_{fi} C_{pi}$$

$$(C_v)_m = \sum_{i=1}^k m_{fi} C_{vi}$$

$$s_m = \sum_{i=1}^k m_{fi} s_i$$

### Example

A mixture is composed of 2 kmol CO<sub>2</sub> and 4 kmol N<sub>2</sub>. It is compressed isentropically in a cylinder from 100 kPa and 20°C to 2 MPa. Assuming constant specific heats. Calculate:

- The final temperature.
- The work required.
- The change in entropy.

### John Dalton



Figure.10.1. John Dalton.

English meteorologist who switched to chemistry when he saw the applications for chemistry of his ideas about the atmosphere. He proposed the *Atomic Theory* in 1803 which stated that (1) all matter was composed of small indivisible particles termed atoms, (2) atoms of a given element possess unique characteristics and weight, and (3) three types of atoms exist: simple (elements), compound (simple molecules), and complex (complex molecules). Dalton's theory was presented in *New System of Chemical Philosophy* (1808-1827). This work identified chemical elements as a specific type of atom, therefore rejecting Newton's theory of chemical affinities.

Instead, Dalton inferred proportions of elements in compounds by taking ratios of the weights of reactants, setting the atomic weight of hydrogen to be identically one. Following Richter, he proposed that chemical elements combine in integral ratios. Despite the importance of the work as the first view of atoms as physically real entities and introduction of a system of chemical symbols, *New System of Chemical Philosophy* devoted almost as much space to the caloric theory as to atomism.

## Mixture of real Gases

Dalton's law and Amagat's law can also be applied to real gases (non-ideal gases) with a reasonable accuracy. However, the deviation from the ideal gas law must be taken into account by:

- 1- Using more appropriate (and complex ☹) relations for a real gas.
- 2- Using the compressibility factor (Z)

$$PV = ZNR_uT$$

For a mixture,  $Z_m$  can be computed as:  $Z_m = \sum_{i=1}^k y_i Z_i$

Remember that:  $y_i = \frac{\text{mole number of a component}}{\text{mole number of the mixture}} = \frac{N_i}{N_m}$

The problem with using the compressibility factor is that this approach considers only the influence of like molecules on each other, neglecting the effect of the molecules of the component A on the molecules of the component B. In practice, the predicted values using the approach of the compressibility factor, maybe far from the experimentally determined values.

The solution?

### Kay's rule ☺

Another more accurate approach to predict the behavior of a real gas is to use the Kay's rule (Form W.B. Kay 1963).

For that, pseudo critical pressure and pseudo critical temperature have to be computed. Then, the compressibility factor will be determined using the Nelson-Obert generalized compressibility chart (chart page 868 [Cengel's book]).

$$\text{Pseudo pressure: } P'_{cr,m} = \sum_{i=1}^k y_i P_{cr,i}$$

$P_{cr,i}$  is the critical pressure for each component of the mixture.

$$\text{Pseudo temperature: } T'_{cr,m} = \sum_{i=1}^k y_i T_{cr,i}$$

$T_{cr,i}$  is the critical temperature for each component of the mixture.

From (table A.1, page 824 [Cengel's book])

The results obtained by using Kay's rule is accurate to within 10% over a wide range of temperatures and pressures. This accuracy is acceptable for most engineering purposes.

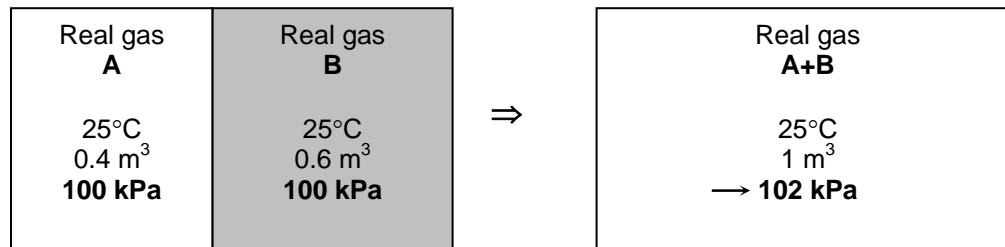
#### Example

An insulated rigid tank of volume  $0.2 \text{ m}^3$  contains  $0.25 \text{ kmol}$  of  $\text{O}_2$  and  $0.4 \text{ kmol}$  of  $\text{CO}_2$  at  $300 \text{ K}$ . Determine the pressure of the mixture using:

- a/ the ideal-gas equation of state.
- b/ compressibility factors based on Dalton's model.
- c/ compressibility factors based on Amagat's model
- d/ Kay's rule.

### Properties of real gas mixtures

The study of the properties of real gas mixtures maybe very complex and counterintuitive. To illustrate this, let us see the following example (Cengel book page 645).



**Figure.10.2.** Mixture of real gases.

While the pressure of both components is 100 kPa, the pressure of the mixture is 102 kPa.

This may be explained by the influence of the molecules of different gases on each other.

Even though, several approaches exist to determine the properties of real gas mixtures, the easiest way is to use the Kay's rule (... once again).

#### Example

Air is a mixture of  $N_2$ ,  $O_2$  and a small amounts of other gases, and it can be approximated as 79 percent  $N_2$  and 21  $O_2$  on a mole basis. During a steady flow process, air is cooled from 220 to 160 K at a constant pressure of 10 MPa. Determine the heat transfer during this process per kmol of air, using the Kay's rule.

## Gas-Vapor Mixtures

Air is a mixture of nitrogen and oxygen and argon plus traces of some other gases. When water-vapor is not included, we refer to it as **dry air**. If water-vapor is included, we must properly account for it.

Usually, we will consider air and water-vapor (even if water-vapor is at the saturation state) as ideal gases. The error using this assumption will be around 0.2%.

Therefore, from Dalton's law:

The total pressure is the sum of the partial pressure  $P_a$  of the dry air and the partial pressure  $P_v$  of water-vapor (called vapor pressure):


$$P = P_a + P_v$$

Since we assume the water-vapor as an ideal gas, its enthalpy is only dependent on the temperature. Therefore, we will consider the enthalpy of water-vapor as the enthalpy of saturated water-vapor at the same temperature.

$$h_v(T) = h_g(T)$$

This approach is acceptable for situations in which the pressure is relatively low (near atmospheric pressure) and the temperature is below about 60°C.


### 13.1. Some definitions:

**Montreal, Quebec**  (TextWeather: MTL)

Local Time: 10:11 am EST. Monday, 19 November, 2007

[RSS](#) °C | °E

**Current Weather**



[▶ view a webcam](#)

[▶ submit a webcam](#)

[▶ view traffic cams](#)

-1°C

A few clouds

WIND NE 9km/h

RELATIVE HUMIDITY 69%

DEWPOINT -6°C

PRESSURE 103.41 kPa ▼

VISIBILITY 48.0 km

CEILING unlimited

Updated: Monday Nov 19 2007, 10:00 EST -  
P.E. Trudeau Airport

#### 13.1.1. Relative humidity

It is the ratio of the mass of water-vapor  $m_v$  to the maximum amount of water-vapor  $m_g$  the air can hold at the same temperature.

$$\phi = \frac{m_v}{m_g}$$



**Example**

The air at 25°C and 100 kPa in a XXX m<sup>3</sup> room has a relative humidity of 60%. Calculate:

- c- The humidity ratio.
- d- The dew point.
- e- The mass of water-vapor in the air.

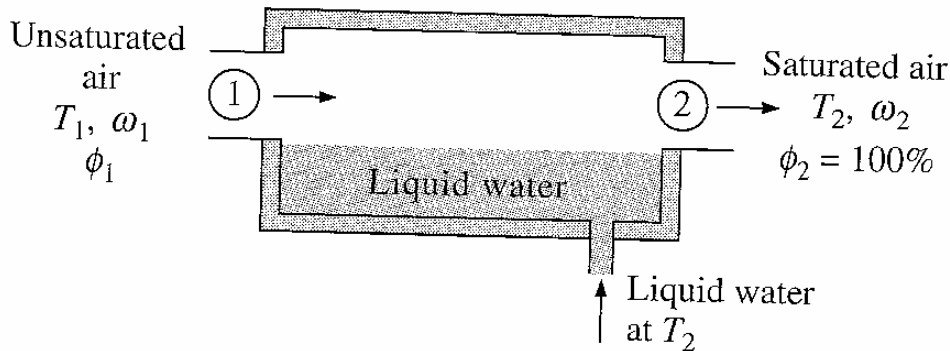
**13.1.5. Adiabatic saturation and wet-bulb temperature**

It is quit difficult to accurately determine directly the relative humidity and the humidity ratio. However, two indirect methods exists:

- Adiabatic saturation process.
- Wet bulb temperature.

**13.1.5.a. Adiabatic saturation process**

This method uses a relatively long insulated channel. Air with unknown relative humidity ( $\omega_1$ ) enters, moisture is added to the air by the pool of water, and saturated air exits. This process involves no heat transfer because the channel is insulated.



**Figure.13.2.** Adiabatic saturator.

An energy balance on this control volume, neglecting kinetic and potential energy changes, with  $Q=W=0$ , gives:

$$\dot{m}_{v1}h_{v1} + \dot{m}_{a1}h_{a1} + \dot{m}_f h_{f2} = \dot{m}_{a2}h_{a2} + \dot{m}_{v2}h_{v2}$$

but

$$\dot{m}_{a1} = \dot{m}_{a2} = \dot{m}_a$$

$$\dot{m}_{v1} + \dot{m}_f = \dot{m}_{v2}$$

using  $\omega$ :

$$\dot{m}_a \omega_1 + \dot{m}_f = \dot{m}_a \omega_2$$

substituting with,  $h_v \approx h_g$

$$\dot{m}_a \omega_1 h_{g1} + \dot{m}_a h_{a1} + (\omega_2 - \omega_1) \dot{m}_a h_{f2} = \dot{m}_a h_{a2} + \omega_2 \dot{m}_a h_{g2}$$

but at state 2,  $\phi_2=100\%$ .

$$\text{So: } \omega_2 = 0.622 \frac{P_{g2}}{P - P_{g2}}$$

$$\text{And, } \omega_1 = \frac{\omega_2 h_{fg2} + C_p (T_2 - T_1)}{h_{g1} - h_{f2}}$$

To know  $\omega_2$ , we have to measure  $T_1$  and  $T_2$  and the total pressure  $P$ .

The problem with adiabatic saturation process is that it requires a long channel to achieve saturation conditions at the exit.

**Note:** usually the amount of dry air in the air-water-vapor mixture remains constant, but the amount of water-vapor changes. Therefore, the enthalpy of atmospheric air is expressed per unit mass of dry air instead of per unit of air-water-air mixture.

### 13.1.5.b. Wet bulb temperature

A much simpler approach is to wrap the bulb of a thermometer with a cotton wick saturated with water. Then, we can blow air over the wick or swing the thermometer through the air until the temperature reaches a steady state: this is the wet-bulb temperature.

The adiabatic saturation temperature is essentially the same as the wet-bulb temperature if the pressure is approximately atmospheric.

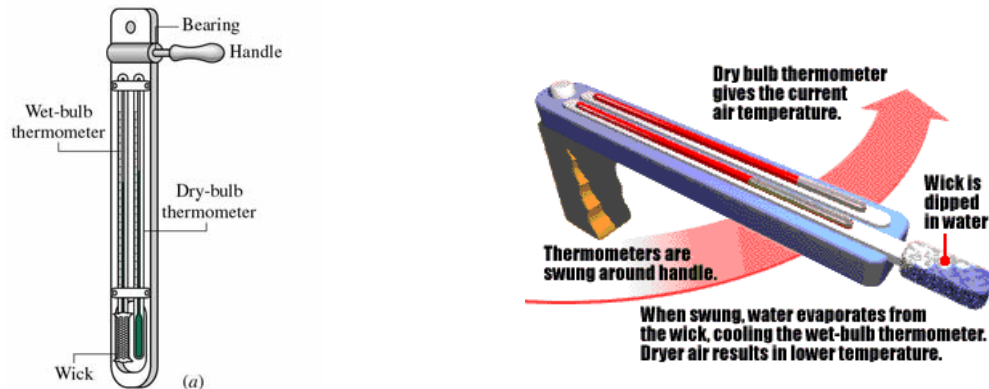


Figure.13.3. dry-bulb and wet bulb temperatures.

#### Example

The dry and the wet-bulb temperatures of atmospheric air at 1 atm (101.325 kPa) pressure, measured using an adiabatic saturation process are 15°C 25°C respectively. Determine:

- The specific humidity.
- The relative humidity.

## 13.2. Additional information:

### # Actual method to determine the relative humidity and the humidity ratio:

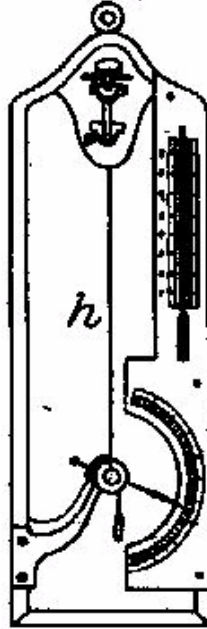
Actually new devices based on the capacitance change of a thin polymer film are used to determine  $\omega$  and  $\phi$ .

### # Did you know that hair length increases with humidity?

The range between dry and saturated air can account for a difference in hair length of about three per cent.

In moist air, people with naturally curly hair experience the frizzies as their hair increases in length. Under the same conditions, people with long, straight hair find it going limp.

Hair is such a reliable indicator of good or bad weather, in fact, that it is the primary element of the hair hygrometer, an instrument that was used for years to measure humidity. Invented in 1783, it was used until more sophisticated technology was developed in the 1960s. For its time, it was a very accurate humidity-measuring device, although not in widespread meteorological use today.



### # Humidex factor:

"The humidex is a Canadian innovation, first used in 1965. It was devised by Canadian meteorologists to describe how hot, humid weather feels to the average person."

The humidex is based on the observation that intense heat accompanied by a high vapour content, bring about a physical malaise. In extreme cases, when the combined effects of the temperature and moisture approach the normal temperature of the body (37°C), this malaise becomes dangerous for the human body.

$$H = T + (5 / 9)(P_v - 10)$$

H is humidex index, T is temperature in °C,  $P_v$  is the water vapor pressure in millibar (mbar)}



**Range of humidex**

Less than 29  
 30 to 39  
 40 to 45  
 Above 45  
 Above 54

**Degree of comfort**

No discomfort  
 Some discomfort  
 Great discomfort; avoid exertion  
 Dangerous  
 Heat stroke imminent

**# Wind chill index:**

"The original wind chill formula was derived from experiments conducted in 1939 by Antarctic explorers, Paul Siple and Charles Passel. These hardy scientists measured how long it took for water to freeze in a small plastic cylinder when it was placed outside in the wind. Over the years, the formula was modified somewhat, but remained based on the Antarctic experiments."

This formula was obsolete and in certain circumstances created confusion. Rather than be based on a water cylinder, "the new index is based on a model of how fast a human face loses heat. We chose the face because it is the part of the body most often exposed to severe winter weather, assuming the rest of the body is clothed appropriately for the weather".

The wind chill formula is:

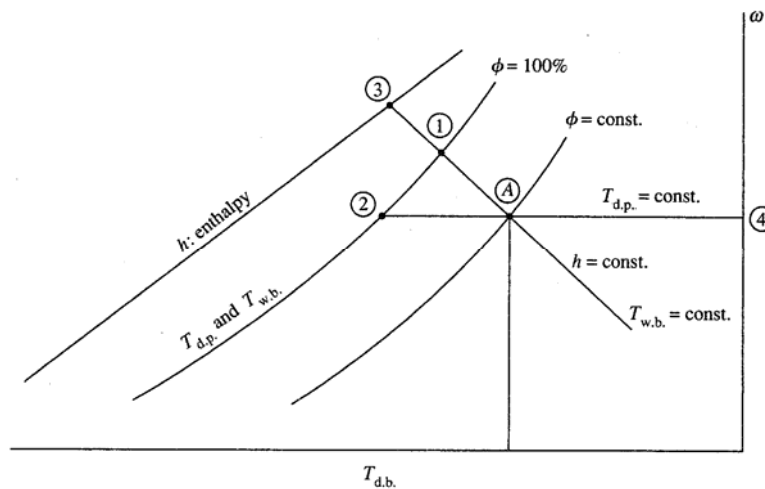
$$R = 13.12 + 0.6215 T - 11.37 (V^{0.16}) + 0.3965 T (V^{0.16})$$

where { R is the wind chill index; T is the air temperature in degrees Celsius (°C); V is the wind speed at 10 metres (standard anemometer height), in kilometres per hour (km/h) }

**13.3. The psychrometric chart and air-conditioning processes****13.3.1. The psychrometric chart**

All the equations introduced in the upper section are very useful when working at pressures higher than the atmospheric pressure.

For a standard atmospheric pressure, the most convenient way to determine the various properties associated with a water-vapor mixture is to use a psychrometric chart (Fig.13.4).



**Figure.13.4.** Psychrometric chart (principle).

**Example**

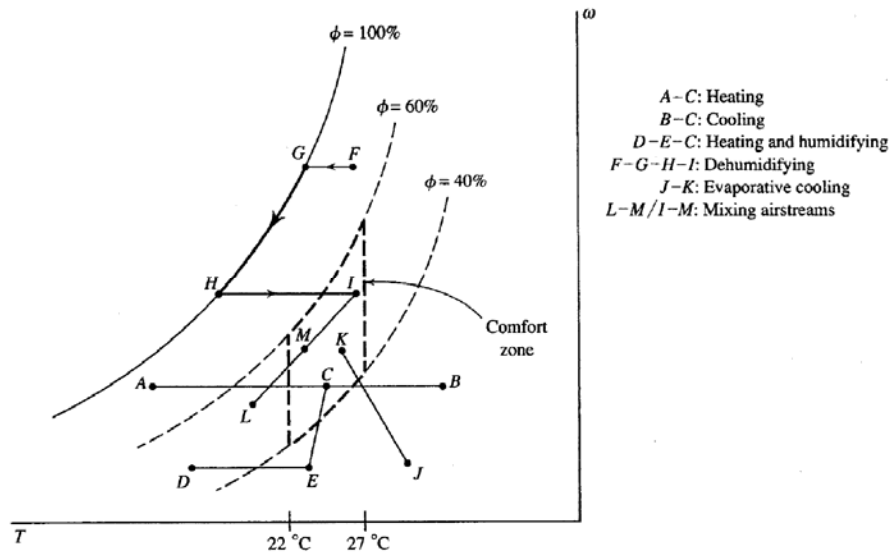
Find the dew-point temperature, the wet bulb temperature the enthalpy and the humidity ratio for the following conditions:

- a- dry bulb temperature ( $T=30^\circ$ ) and a relative humidity of 80%.
- b- dry bulb temperature ( $T=35^\circ$ ) and a relative humidity of 40%.

**13.3.2. Air conditioning processes:**

Generally, people feel most comfortable when the air is the “comfort zone”: the temperature is between  $22^\circ\text{C}$  and  $27^\circ\text{C}$  and the relative humidity is between 40% and 60% (Fig.13.5) (and usually a wind speed 15 m/min). The area enclosed by the heavy dotted lines represents the **comfort zone**. There are several situations in which air must be conditioned to put it the comfort zone:

Problem	Solution	Representation
The air is too cold or too hot	Heat is simply added or extracted	A-C and B-C
The air is too cold and the humidity is too low	The air can first be heated, and then moisture added	D-E-C
The temperature is acceptable but the humidity is too high	The air is first cooled, and then moisture is removed. Finally, the air is reheated	F-G; G-H and H-I
The air is too hot and the humidity is low	Moisture is added	J-K
An airstream from the outside is mixed with an airstream from the inside to provide natural cooling or fresh air		I (inside air) + L (outside air) = M (mixed air)



**Figure.13.5.** The conditioning of air.

### 13.3.2.1. Air-conditioning processes analysis

Most air-conditioning processes can be modeled as steady-flow processes.

$$\text{Mass balance for dry air: } \sum m_a|_{inlet} = \sum m_a|_{outlet}$$

$$\text{Mass balance for water: } \sum m_v|_{inlet} = \sum m_v|_{outlet}$$

Neglecting  $\Delta E_K$  and  $\Delta E_P$ , the first law can be written as:

$$\dot{Q}_{in} + \dot{W}_{in} + \sum \dot{m} h|_{inlet} = \sum \dot{m} h|_{outlet} + \dot{Q}_{out} + \dot{W}_{out}$$

### 13.3.2.2. Simple heating and cooling ( $\omega=C'$ )

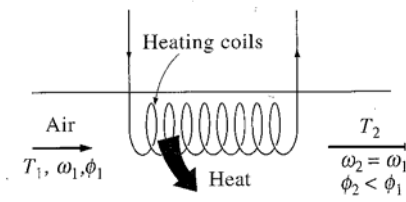


Figure.13.6. Simple heating.

Note: the relative humidity of air decreases during a heating process ( $\phi_2 < \phi_1$ ) even if the humidity ratio  $\omega$  remains constant. This is because the relative humidity is the ratio of moisture content to the moisture capacity of air at the same temperature, and the moisture capacity increases with temperature.

First law (neglecting  $\Delta E_K$  and  $\Delta E_P$  and usually the work of the fan is also neglected) can be written under the simple form:

$$\dot{Q} = \dot{m}_a (h_2 - h_1)$$

### 13.3.2.3. Heating with humidification:

To overcome the problem of decreasing  $\phi$  with simple heating, air is passed first through a heating section and then through a humidifying section

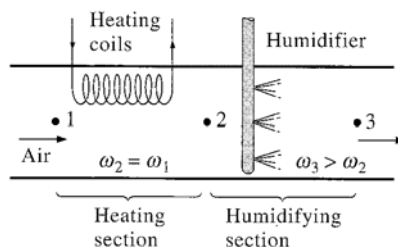


Figure.13.7. Heating and humidification.

If steam is used  $T_3 > T_2$

If liquid is used  $T_3 < T_2$

13.3.2.4. Cooling with dehumidification

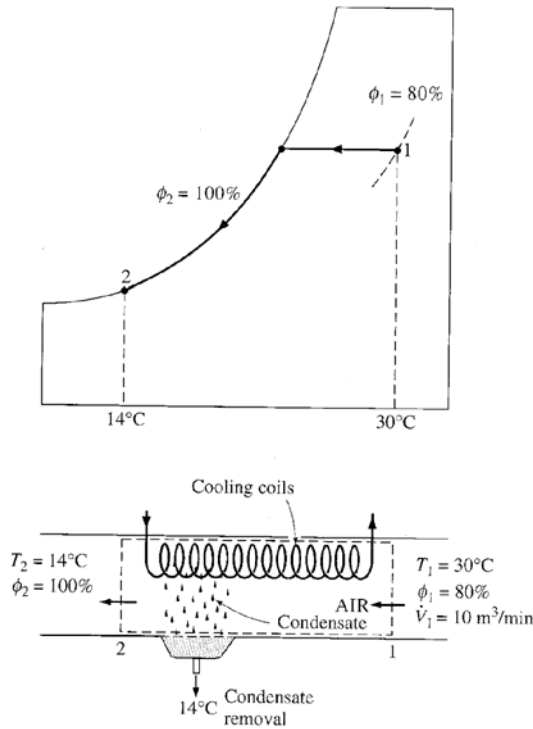


Figure.13.8. Cooling and dehumidification.

Note that if the  $T \downarrow$  then  $\phi \uparrow$

13.3.2.5. Evaporative cooling

Dry air enters the evaporative cooler where it is sprayed with liquid water. Part of the water evaporates during this process by absorbing heat from the stream. As a result the temperature decreases and humidity increases.

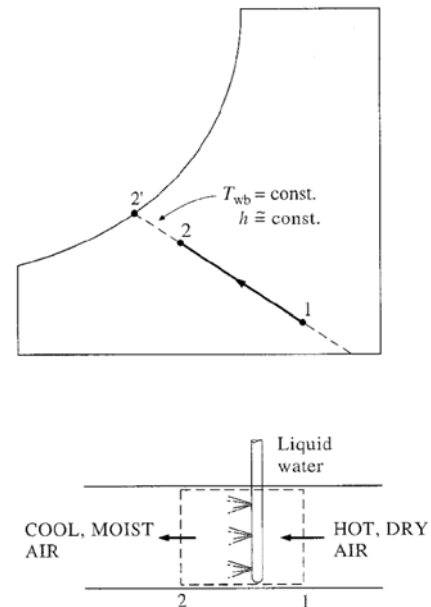


Figure.13.9. Evaporative cooling.

This process is at constant enthalpy and constant wet bulb temperature (constant enthalpy and constant wet bulb temperature lines on the psychrometric chart are almost the same).

### 13.3.2.6. Adiabatic mixing of airstreams

In large buildings (hospitals, process plants, ...), two streams are usually mixed (mixture of conditioned air and new fresh air). The heat transfer with the external medium is small and thus the mixing process can be assumed as adiabatic.

Mass balance for dry air:  $\dot{m}_{a,1} + \dot{m}_{a,2} = \dot{m}_{a,3}$

Mass balance for water:  $\omega_1 \dot{m}_{a,1} + \omega_2 \dot{m}_{a,2} = \omega_3 \dot{m}_{a,3}$

Neglecting  $\Delta E_K$  and  $\Delta E_P$ , the first law can be written as:

$$\dot{m}_{a,1} h_1 + \dot{m}_{a,2} h_2 = \dot{m}_{a,3} h_3$$

Eliminating  $\dot{m}_{a,3}$ , gives:  $\frac{\dot{m}_{a,1}}{\dot{m}_{a,2}} = \frac{\omega_2 - \omega_3}{\omega_3 - \omega_1} = \frac{h_2 - h_3}{h_3 - h_1}$

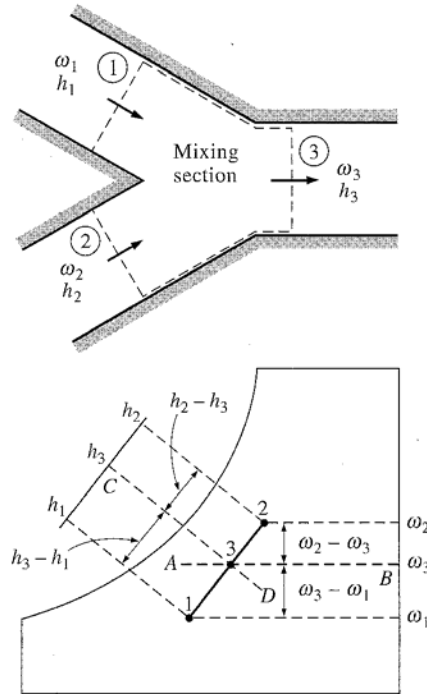


Figure.13.10. adiabatic mixing.

Therefore, when two airstreams at two different states (state 1 and 2) are mixed adiabatically, the state of the mixture (state 3) will lie on the straight line connecting states 1 and 2 on the psychrometric chart, and the ratio of the distances 2-3 and 3-1 is equal to the ratio of mass flow rates at 1 and 2.

Note: if 1 and 2 are close to the saturation line, point 3 may lie to the left of this line. As a consequence, some water will inevitably condense during the mixing process.

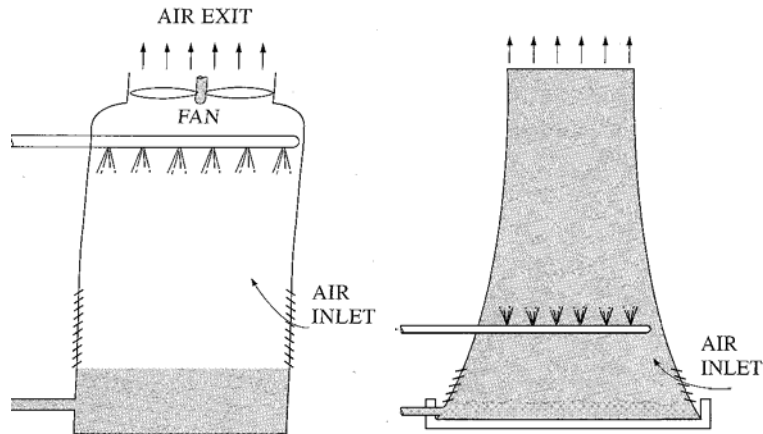
#### Example

Outside cool air at 15°C and 40% relative humidity (airstream 1) is mixed with inside air taken near the ceiling at 32°C and 70% relative humidity (airstream 2). Determine the relative humidity and temperature of the resultant airstream 3 if the outside flow rate is 40 m<sup>3</sup>/min and the inside flow rate is 20 m<sup>3</sup>/min.

### 13.3.2.7. Wet cooling towers

In power plants or refrigeration plants, the wasted heat is usually rejected to the sea, lake or river. However, when the water supply is limited, this heat must be rejected to the atmosphere. This is performed using a wet cooling tower.

Air is drawn into the tower from the bottom and leaves through the top. Warm water from the condenser is pumped to the top of the tower and is sprayed into the airstream. The purpose of spraying is to expose a large surface of water to air. As the water droplets fall under the influence of gravity, a small fraction of water (usually a few percent) evaporates and cools the remaining water. The temperature and the moisture content of the air increase during this process. The cooled water is collected at the bottom of the tower and is pumped back to the condenser to pick up additional waste heat (ref. Cengel).



**Figure.13.10.** Wet cooling towers. (left) An induced-draft counterflow cooling tower. (right) A natural-draft cooling tower.

### 13.3.3. Additional information

The human body operates like a heat engine, the energy input is food (many thanks to McDO ...) and some wasted energy is ejected to the environment. The rate of heat generation for a man depends on the level of activity:

Sleeping	87 W
Resting or doing office work	115 W
Bowling	230 W
Heavy physical effort	440 W

For a woman, the rate of generation is less by about 15% (due to a smaller body size area).

### Procedure For Calculating The Properties Of Moist Air

1. Determine what properties you need to calculate. This depends on the problem. Don't forget that the Principles of thermodynamics and the Process descriptions are independent of the method for calculating the Properties.
2. From the Process description, determine the pressure  $P$  of the moist air. This is the pressure that would be measured by a pressure gage.
3. From the Process description, determine the temperature  $T$  of the moist air. This is the temperature that would be measured by an ordinary thermometer or thermocouple. If the temperature is not known, you must solve the problem by trial and error, so guess a value.
4. Look up the value of the water vapor partial pressure at saturation,  $P_g$ , using the Saturated Steam Temperature Table for Water.
5. If the relative humidity,  $\phi$ , is known from the Process description, write it down and go on to calculating the actual partial pressure of the water vapor in the moist air,  $P_v$ , from the equation

$$\phi = P_v / P_g$$

Then calculate the humidity ratio, omega, from the equation

$$\omega = 0.622 * P_v / (P - P_v)$$

6. Once omega is known, you can calculate the moist air properties from the equations given above.
7. If the relative humidity (phi) is not known, but the humidity ratio (omega) is known and you want to know the relative humidity, you can calculate  $P_v$  from

$$P_v = \omega * P / (\omega + 0.622)$$

And then get phi from its definition,

$$\phi = P_v / P_g$$

8. If neither  $\omega$  nor  $\phi$  is known, but the wet bulb temperature  $T_{wb}$  is known, then  $T_{wb}$  can be used, along with  $T_{db}$  (the dry bulb temperature, where  $T_{db} = T$ ), to find omega from the equation given above,

$$\omega = (c_{pa} * (T_{wb} - T_{db}) + \omega_g * h_{fg}) / (h_v(T_{db}) - h_f)$$

Where  $\omega_{g}$  is the humidity ratio at saturation at the wet bulb temperature,  $T_{wb}$ ,

$$\omega_{g} = 0.622 * P_g / (P - P_g)$$

Note that  $P_g$ ,  $h_f$ , and  $h_{fg}$  are found from the Saturated Steam Temperature Table at the **wet bulb** temperature ( $T_{wb}$ ).

9. The relations between  $\omega$ ,  $\phi$ ,  $T_{db}$ ,  $T_{wb}$ , are shown graphically on the Psychrometric chart. The enthalpy and volume (per unit mass of dry air) can also be found, although not very accurately, from the chart, but the entropy is not shown at all.

# APPENDIX F

# Psychrometric Charts

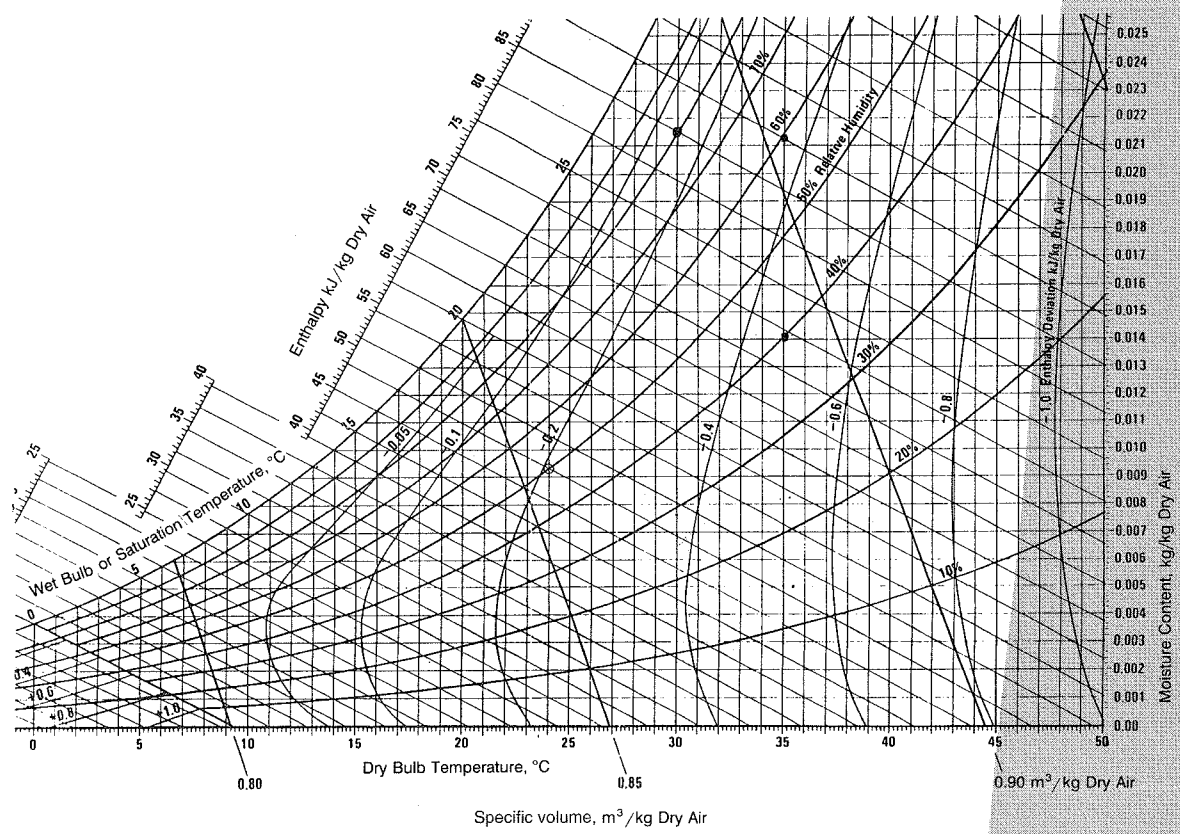


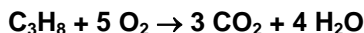
Fig. F-1 Psychrometric Chart, P = 1 atm. (Carrier Corporation.)



## Chemical reactions and Combustion

Until now, we limited our study to non-reacting systems: the chemical composition remains unchanged during the process. In a process involving combustion, new components are created and others are destroyed. It is important, therefore, to take into account the energy needed to create or destroy these components.

Let us take a simple example: Combustion of propane ( $C_3H_8$ ) in a pure oxygen environment:



To balance this reaction, the number of atoms of an element must remain the same before, after and during the chemical reaction. Note that during a chemical reaction there is a conservation of mass and number of atoms but not a conservation of the total number of moles (for the combustion of propane: 6 moles on the left side compared to 7 moles on the right side).

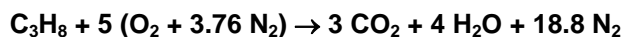
In this introduction to chemical reactions and combustion, we will consider a **complete combustion**, i.e, the products of the combustion of an hydrocarbon fuel will be  **$H_2O$  and  $CO_2$** . An **incomplete combustion** will result in products that contain  **$H_2$ ,  $CO$ ,  $C$  or  $OH$** . The causes of incomplete combustion are usually: insufficient oxygen or insufficient mixing.

For the above example, we hypothesized a combustion in a pure oxygen environment, which is obviously not the case in practice. In practice, air is used for combustion. Here, we will assume that air consists of 21%  $O_2$  and 79%  $N_2$  by volume. So for each mole of  $O_2$  involved in the reaction, we will have:

$$\frac{79}{21} = 3.76 \frac{mol N_2}{mol O_2}$$

And for air we will have: 1 kmol  $O_2$  + 3.76 kmol  $N_2$  = 4.76 kmol of air

But, as  $N_2$  will not undergo any chemical reaction, the combustion of propane with air can be written under the following form:



When analyzing a chemical reaction, the components that exist before the reaction are called reactants ( $C_3H_8$ ;  $O_2$  and  $N_2$ ) and the components that exist after the reaction are called products ( $CO_2$ ;  $H_2O$  and  $N_2$ ).

Complete combustion of an hydrocarbon does not occur with any amount of air, in fact, a minimum amount of air that supplies  $O_2$  is required. This amount of air is called: theoretical air. In practice however, the amount of air used is higher than the theoretical air. This is to increase the chances of complete combustion or to control the temperature of the combustion chamber. The amount of air in excess is called: ... excess air ... (what a surprise!!!). When we say **50%** excess air, you must understand that we used  $100\%+50\%=150\%$  of theoretical air.

As you may notice, the combustion of hydrocarbon fuels involves  $H_2O$ . The calculation of the dew point of the products is often of interest, because if the temperature drops below the dew point, the water vapor begins to condensate. This is not suitable, since this water droplets can combine with sulfure dioxide ( $SO_2$ ) that may be present in the combustion gases, forming sulfuric acid ( $H_2SO_4$ ), which is very corrosive.

**Air-Fuel ratio (AF)**

The parameter that relates the amount of air used in a combustion process is the air-fuel ratio (AF)

$$AF = \frac{\text{mass of air}}{\text{mass of fuel}} = \frac{m_a}{m_f}$$

As an example, for the above reaction, the AF for theoretical air is:

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{5(4.76)(29)}{1(44)} = 15.69 \frac{kg \text{ air}}{kg \text{ fuel}}$$

if we use an AF higher than 15.69, we are using a lean mixture. And if AF is less than 15.69, we are using a rich mixture.

**Example**

Butane is burned with dry air-fuel ratio of 20. Calculate:

- The percentage of excess air.
- The molar percentage of CO<sub>2</sub> in the products.
- The dew-point temperature of the products.

**Enthalpy of formation and enthalpy of combustion**

When a chemical reaction occurs, there may be considerable change in the chemical composition of a system. Thus, it will be problematic to define a control volume for the mixture: the input and the output are not the same components.

Furthermore, for the analysis of a single component, we do not have to worry about our reference for enthalpy, since for a process, we are interested in computing the variation in enthalpy and our reference enthalpy will be canceled.

$$\Delta h = (h_2 - h_{ref}) - (h_1 - h_{ref}) = h_2 - h_1$$

but, in combustion, the components are not the same at state 1 and 2. Therefore:

$$\Delta h = (h_2 - h_{ref 2}) - (h_1 - h_{ref 1}) \neq h_2 - h_1$$

the reference enthalpy for each component is taken as its enthalpy at 25°C and 1 atm and this state will be denoted h°.

And to compute enthalpy at a different temperature, follow this example for the enthalpy of N<sub>2</sub> at 500 K is:

$$\bar{h}_{500K} - \bar{h}^0 = 14581 - 8669 = 5912 \text{ kJ / kmol [from table A-18; page 851]}$$

Note 1: in chemical reactions, it is more convenient to work with quantities per mole (or kmol).

Note 2: some components exist at two phases at 25°C. The phase must be, therefore, specified: H<sub>2</sub>O (l) for liquid water and H<sub>2</sub>O (g) for vapor water.

### Enthalpy of formation

The enthalpy of formation is the enthalpy change when a component is formed, denoted ( $h_f^\circ$ ). The enthalpies of formation of numerous components are listed in tables. Note that some components have a positive enthalpy of formation, indicating that they require energy to form (an endothermic reaction); others have a negative enthalpy of formation, indicating that they give off energy when they are formed (a exothermic reaction).

### Enthalpy of combustion

It represents the amount of heat released during a steady state combustion process when 1 kmol of fuel is burned completely at a certain temperature and pressure.

Exp:

Enthalpy of formation for H<sub>2</sub> = 0 (H<sub>2</sub> is a stable component that exists under this form in nature)  
 Enthalpy of combustion for H<sub>2</sub> (to form H<sub>2</sub>O) = 285 830 kJ/kmol

Remark: If the products of combustion contains liquid water, the enthalpy of combustion is the higher heating value (HHV), and if the products contain water vapor, the enthalpy of combustion is the lower heating value (LHV). The difference between HHV and LHV is the heat of vaporization  $\bar{h}_{fg}$ .

### Applying the first law to combustion processes:

Before applying the first law to a combustion process, it is convenient to write the enthalpy of a component in a form suitable for use for reacting systems:

$$\text{Enthalpy} = \underbrace{\bar{h}_f^0}_{\text{formation}} + \left( \underbrace{\bar{h}}_{\text{actual}} - \underbrace{\bar{h}^0}_{\text{reference}} \right)$$

the first law can be written for an open system as:

$$Q_{in} + W_{in} + \underbrace{\sum N_r \left( \bar{h}_f^0 + (\bar{h} - \bar{h}^0) \right)}_{H_r} = Q_{out} + W_{out} + \underbrace{\sum N_p \left( \bar{h}_f^0 + (\bar{h} - \bar{h}^0) \right)}_{H_p}$$

$N_r$  and  $N_p$  are the number of moles of the reactant or the product per mole of fuel.

And, the first law can be written for a closed system as:

$$Q_{in} + W_{in} + \underbrace{\sum N_r \left( \bar{h}_f^0 + (\bar{h} - \bar{h}^0 - P\bar{v}) \right)}_{H_r} = Q_{out} + W_{out} + \underbrace{\sum N_p \left( \bar{h}_f^0 + (\bar{h} - \bar{h}^0 - P\bar{v}) \right)}_{H_p}$$

where the internal energy is expressed as a function of enthalpy ( $u=h-Pv$ ), pressure and specific volume. The choice of this form (with enthalpy rather than internal energy) is justified by the fact that enthalpy is tabulated.

For an ideal gas:  $P\bar{v}$  can be replaced by  $R_u T$ .

In the above relations, we employ one of the following methods to find  $(\bar{h} - \bar{h}^0)$ :

- For a solid or a liquid:

Use  $\bar{C}_p \Delta T$

- For gases: several methods can be applied, however the easiest one is:

Assume an ideal gas and use tabulated values for  $\bar{h}$ .

**Example** [Cengel page 717]

Liquid propane ( $C_3H_8$ ) enters a combustion chamber at  $25^\circ C$  at a rate of 0.05 kg/min where it is mixed and burned with 50% excess air that enters the combustion chamber at  $7^\circ C$ . An analysis of combustion gases reveals that all the hydrogen in the fuel burns to  $H_2O$  but only 90% of the carbon burns to  $CO_2$ , with the remaining 10% forming  $CO$ . If the exit temperature of the combustion gases is 1500 K, determine:

- The mass flow rate of air.
- The rate of heat transfer from the combustion chamber.

**Adiabatic flame temperature:**

If we consider a combustion process that takes place adiabatically, with no work or changes in kinetic and potential energies, the chemical energy released will be used only to raise the temperature of the combustion products, in this particular case, the temperature reached by the products is called: adiabatic flame temperature.

The adiabatic flame temperature is a function of excess air and it is maximal for 0% excess air, and thus for theoretical air.

Hence, the higher is excess air the lower will be the adiabatic flame temperature. As a practical consequence, excess air can be used to reach an adiabatic flame temperature lower than the maximum allowable blade turbine temperature (as an example).

The computation of the adiabatic flame temperature must be performed under the following assumptions:

- Complete combustion.
- No heat transfer from the combustion chamber.
- No dissociation of the products into other chemical species.

Applying the first law under these assumptions gives:

$$H_{\text{Prod}} = H_{\text{React}}$$

$$\sum N_P (\bar{h}_f^o + \bar{h} - \bar{h}^o)_P = \sum N_R (\bar{h}_f^o + \bar{h} - \bar{h}^o)_R$$

the calculation of the enthalpy of the products  $H_{\text{Prod}}$  is not straightforward, since the temperature of the products is not known prior to the calculation (it is exactly what we are looking for).

An iterative process has to be used, by considering as a first guess all the product gases are nitrogen ( $N_2$ ).

**Example**

Propane is burned with 250% theoretical air, both are at 25°C and 1 atm. Predict the adiabatic flame temperature in the steady flow combustion chamber.

**Entropy change of reacting systems**

The entropy balance for any system undergoing any process can be expressed as:

$$\underbrace{S_{in} - S_{out}} + \underbrace{S_{gen}} = \underbrace{\Delta S_{system}}$$

Net entropy transfer by heat and mass      Entropy generation      Change in entropy

or:

$$\sum \frac{Q_k}{T_k} + S_{gen} = S_{Prod} - S_{React}$$

Where  $T_k$  is the temperature at the boundary where  $Q_k$  crosses it.

For an adiabatic process ( $Q=0$ ):

$$S_{gen,adiabatic} = S_{Prod} - S_{React}$$

This expression includes the entropy of the components ( $CO_2$ ;  $O_2$ ; ...) not the variation in entropy and therefore it is essential to determine a common base for the entropy of all the substances (as we did with enthalpy).

**Third law of thermodynamics**

**“ The entropy of a pure crystalline substance at absolute zero temperature is zero”**

$$S|_{T=0K} = 0$$

the entropy values relative to this common base are called the **absolute entropy**  $\bar{S}^o$ .

To compute the entropy generation using the above expression, the absolute entropy of several components ( $CO_2$ ;  $O_2$ ;  $N_2$  ...) are listed in tables at 1 atm. However, entropy is more complex than enthalpy, since even under the assumption of an ideal gas, the entropy is a function of both T and P (the enthalpy depends only on T).

Therefore, the entropy of a component within a mixture **MUST BE COMPUTED USING ITS PARTIAL PRESSURE**

For a component (i) within a mixture:

$$\bar{S}_i(T, P_i) = \underbrace{\bar{S}_i^o\left(T, \overset{=1\text{atm}}{\bar{P}}_0\right)}_{\text{from table}} - R_U \ln\left(\frac{y_i P_m}{P_0}\right)$$

$P_m$  is the pressure of the mixture.

## Second law analysis of reacting systems

### Exergy destruction

$$\mathcal{X}_{destroyed} = T_0 S_{gen}$$

### Reversible work:

It defines the maximum (real or potential) work that can be done during a process.

$$W_{rev} = \sum N_P \left( \bar{h}_f^o + \bar{h} - \bar{h}^o - T_0 \bar{S} \right)_R - \sum N_R \left( \bar{h}_f^o + \bar{h} - \bar{h}^o - T_0 \bar{S} \right)_P$$

### Example [Cengel page 726]

Methane ( $\text{CH}_4$ ) gas enters a steady-flow adiabatic combustion chamber at  $25^\circ\text{C}$  and 1 atm. It is burned with 50% excess air that also enters at  $25^\circ\text{C}$  and 1 atm. Assuming complete combustion and an adiabatic flame temperature of 1789 K, determine the entropy generation.