

MECH 351: Thermodynamics II

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April 25, 2022

First Law equation for a closed system:

$$\begin{aligned}\Delta E_{1 \rightarrow 2} &= Q_{1 \rightarrow 2} - W_{1 \rightarrow 2} \\ &= \Delta E_{\text{kinetic}, 1 \rightarrow 2} + \Delta E_{\text{potential}, 1 \rightarrow 2} + \Delta U_{1 \rightarrow 2}\end{aligned}\quad (1)$$

First Law equation for an open system:

$$\begin{aligned}\dot{E}_{CV} &= \dot{Q}_{\text{in}} - \dot{W}_{\text{out}} + \sum_{\text{in}} \dot{m}_{\text{in}} \left(\frac{1}{2} v_{\text{in}}^2 + g z_{\text{in}} + h_{\text{in}} \right) \\ &\quad - \sum_{\text{out}} \dot{m}_{\text{out}} \left(\frac{1}{2} v_{\text{out}}^2 + g z_{\text{out}} + h_{\text{out}} \right)\end{aligned}\quad (2)$$

1 Rankine cycle

Assumptions:

- Steady flow, $\Delta \dot{m} = 0$
- Pumps and turbines are isentropic, $\Delta s_{\text{pumps}} = \Delta s_{\text{turbines}} = 0$
- Boilers and condensers are isobaric, $\Delta P_{\text{boilers}} = \Delta P_{\text{condensers}} = 0$
- No pressure losses in the cycle
- Temperature at the inlet and outlet of a closed regenerator are equal
- Kinetic and potential energy are negligible, $\Delta E_{\text{kinetic}} = \Delta E_{\text{potential}} = 0$
- Expansion valve is isenthalpic

1.1 Simple Rankine cycle

The Rankine cycle is a steam power cycle that operates with both liquid and gas states. Processes of a simple Rankine cycle:

- 1 \rightarrow 2 Compression in a pump from saturated liquid to compressed liquid
- 2 \rightarrow 3 Heating from compressed liquid to superheated gas
- 3 \rightarrow 4 Expansion in a turbine
- 4 \rightarrow 1 Cooling from gas to saturated liquid

For a compressed liquid at a temperature T and a pressure P , if $P \ll P_{\text{table}}$:

$$\begin{aligned}u_{\text{liq}} &\approx u_f(T) \\ \nu_{\text{liq}} &\approx \nu_f(T) \\ s_{\text{liq}} &\approx s_f(T) \\ h_{\text{liq}} &\approx u_f(T) + P \nu_f(T)\end{aligned}$$

For an incompressible liquid, the work of a pump can be approximated to $w_{1 \rightarrow 2} = \nu(P_1 - P_2)$

Efficiency of a simple Rankine cycle:

$$\begin{aligned}\eta_{\text{thermal}} &= \frac{\dot{W}_{\text{net}}}{\dot{Q}_{\text{in}}} = \frac{w_{1 \rightarrow 2} + w_{3 \rightarrow 4}}{q_{2 \rightarrow 3}} \\ &= \frac{h_1 - h_2 + h_3 - h_4}{h_3 - h_2}\end{aligned}$$

1.2 Improve the Rankine cycle

1.2.1 Simple Rankine cycle

To improve the efficiency of a simple Rankine cycle, there are several approaches, each with some operational constraints:

- $T_1 \searrow$
 - absolute limit of ground temperature
 - more leaks in
 - lower turbine flow quality
- $T_3 \nearrow$
 - temperature of the hot source based on application
 - T_3 too high could weaken the blade of the turbine
- $P_2 \nearrow$
 - increase in T_3
 - more stress on the boiler

1.2.2 Reheat Rankine cycle

A reheat Rankine cycle uses several turbines between which the fluid is reheated.

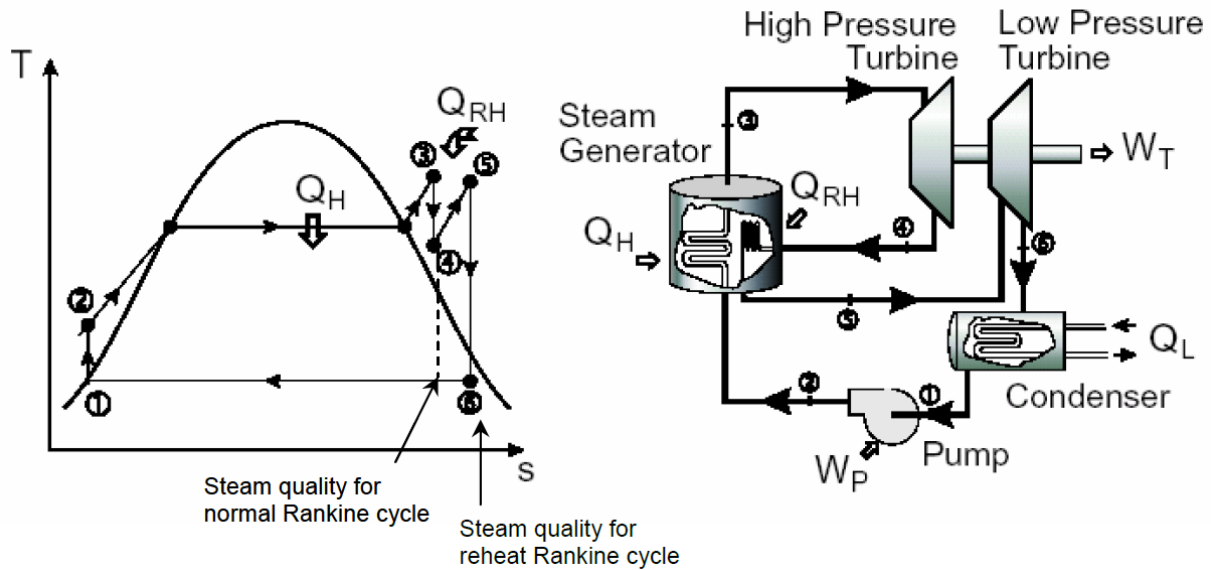
1.2.3 Regeneration Rankine cycle

A regeneration Rankine cycle uses a feed water heater: the hot fluid from the outlet of the turbine exchange heat with the cold fluid from the outlet for the pump. This can be done with two types of feed water heater:

Open feed water heater: the fluid from the pump and the turbine are mixed together, so there is a need of another pump before the boiler to raise the pressure.

Closed feed water heater: the fluid from the pump and the turbine are not mixed together, thus only one pump is needed for the cycle. Also, it is the most thermodynamically efficient as using a counter flow,

Figure 1: Ideal reheat Rankine cycle



the heating process is almost done at constant temperature, meaning it is almost a reversible process.

In order to have the most efficient cycle, we should have the inlet of the pumps as a saturated liquid with a pressure of $P_{\text{OFWH}} \approx \sqrt{P_{\text{boiler}} P_{\text{condenser}}}$

1.2.4 Cogeneration Rankine cycle

The cogeneration Rankine cycle uses the steam from the outlet of the turbine to heat something else called a process heater (e.g. heat a building, a house, etc). Since it can exceed Carnot efficiency μ_{Carnot} , the efficiency of the cogeneration cycle is called the utilization factor ε_u :

$$\varepsilon_u = \frac{\dot{W}_{\text{net}} + \dot{Q}_{\text{process heater}}}{\dot{Q}_{\text{in}}}$$

The cogeneration is very useful as at times of high demand for process heat, all the steam is redirected in the process heater, while at time of high demand for power, all the steam goes to the turbine.

1.3 Problem solving steps to find the efficiency

1. Draw cycle with all its components (pumps, boilers, turbines, condensers, feed water heaters, traps and process heaters)
2. Write the assumptions
3. Draw the T-s diagram
4. Build the table of states with the following thermodynamic variables:
 - Mass flow rate \dot{m} [kg s⁻¹] (do not forget split fractions y_i)
 - Temperature T [°C]
 - Pressure P [Pa]
 - Specific entropy s [J kg⁻¹ K⁻¹]

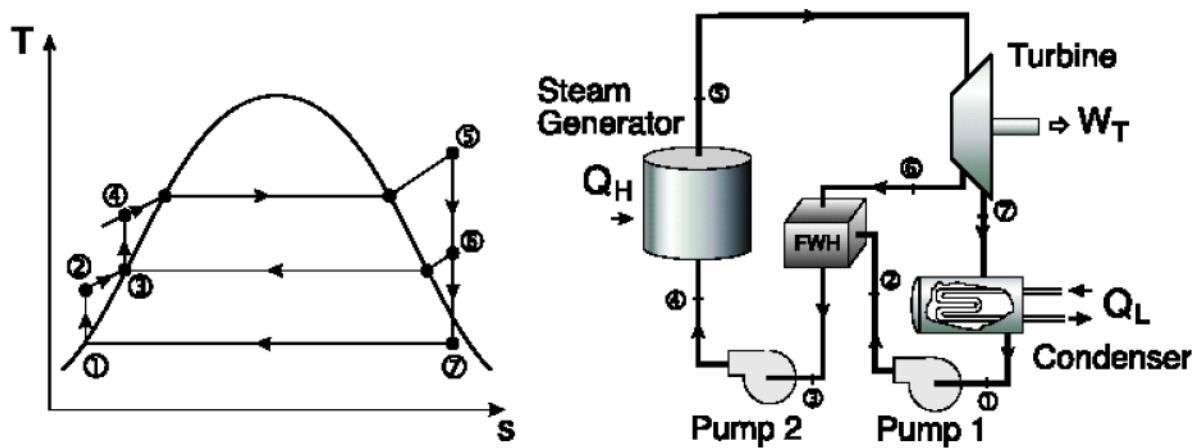
- Specific enthalpy h [J kg⁻¹]
 - Specific volume [m³ kg⁻¹]
5. Find the efficiency formula for this Rankine cycle (do not forget that at splitters, mass flow rate \dot{m} might be in term of split fractions y_i)
 6. Study each components (transition between states)
 - (a) Write the First Law equation for an open system (2)
 - (b) Simplify the First Law equation using the assumptions
 - (c) Find either the specific heat exchange q , specific work w , split fraction y_i , or specific enthalpy h
 7. Repeat previous step until finding every unknown of the efficiency formula found at step 5
 8. Compute the efficiency

2 Brayton cycle

Assumptions:

- Steady flow, $\Delta \dot{m} = 0$
- Air standard approximation (air everywhere, combustion replaced with equivalent external heat input)
- Ideal gas, $P\nu = RT$
- Compressors and turbines are isentropic, $\Delta s_{\text{compressors}} = \Delta s_{\text{turbines}} = 0$
- Boilers and condensers are isobaric, $\Delta P_{\text{boilers}} = \Delta P_{\text{condensers}} = 0$
- No pressure losses in the cycle
- Temperature at the inlet and outlet of a closed regenerator are equal
- Pressure ratio constant in the cycle, $r_P = \frac{P_2}{P_1} = \frac{P_3}{P_4}$
- Specific pressure heat is constant, $\Delta C_P = 0 \implies H_{1 \rightarrow 2} = m C_P (T_2 - T_1)$
- Kinetic and potential energy are negligible, $\Delta E_{\text{kinetic}} = \Delta E_{\text{potential}} = 0$
- Expansion valve is isenthalpic

Figure 2: Ideal regeneration Rankine cycle with an open feed water heater



2.1 Simple Brayton cycle

The Brayton cycle is a gas power cycle that operates only in gas states. Processes of a simple Brayton cycle:

- $1 \rightarrow 2$ Compression in a pump
 $2 \rightarrow 3$ Combustion using fuel
 $3 \rightarrow 4$ Expansion in a turbine

In a real Brayton cycle, the air is taken from the outside at state 1 and exhausted back outside at state 4 along with the combustion products.

Processes of a simple Brayton cycle with air standard approximation:

- 1 \rightarrow 2 Compression in a pump
2 \rightarrow 3 Heating
3 \rightarrow 4 Expansion in a turbine
4 \rightarrow 1 Cooling

Relations for an ideal gas in an isentropic process:

$$\begin{aligned} P_1 \nu_1^k &= P_2 \nu_2^k & (2.1) \\ \frac{T_2}{T_1} &= \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} = \left(\frac{V_1}{V_2} \right)^{k-1} \\ C_P &= \frac{kR}{k-1} \text{ and } C_V = \frac{R}{k-1} \end{aligned}$$

Efficiency of a simple Brayton cycle:

$$\eta_{\text{thermal}} = \frac{\dot{W}_{\text{net}}}{\dot{Q}_{\text{in}}} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{r_P^{\frac{k-1}{k}}}$$

where $r_P = \frac{P_2}{P_1} = \frac{P_3}{P_4}$ is the pressure ratio of the cycle and $k = \frac{C_P}{C_V}$ is the isentropic constant.

The work of the pump in a Brayton cycle is not negligible compared to a Rankine cycle, thus the back-work ratio quantify the percentage of the turbine power that is used by the compressor:

$$r_{BW} = \left| \frac{\dot{W}_{\text{compressor}}}{\dot{W}_{\text{turbine}}} \right|$$

2.2 Improve the Brayton cycle

2.2.1 Simple Brayton cycle

Since the efficiency depends directly on the pressure ratio r_P , the efficiency can be improved by increasing the pressure ratio. This can be done only to a certain extent as too much pressure leads to very high temperatures which could melt the turbine blades.

2.2.2 Regeneration Brayton cycle

A regeneration Brayton cycle uses a regenerator: the hot air from the outlet of the turbine exchange heat with the cold air from the outlet for the pump. This can be done with closed regenerator: the air from the pump and the turbine are not mixed together.

When using an ideal regenerator, the efficiency of a Brayton cycle is:

$$\eta_{\text{thermal}} = 1 - r_{BW}$$

2.2.3 Reheat Brayton cycle

A reheat Brayton cycle uses several turbines between which the air is reheated.

2.2.4 Intercooling Brayton cycle

An inter-cooling Brayton cycle uses several compressors between which the air is cooled.

2.3 Problem solving steps to find the efficiency

1. Draw cycle with all its components (compressors, combustion chambers, turbines, condensers, regenerators)
2. Write the assumptions

3. Draw the T-s diagram
4. Build the table of states with the following thermodynamic variables:
 - Pressure P [Pa]
 - Temperature T [°C]
 - Temperature T [K]
5. Find the efficiency formula for this Brayton cycle
6. Study each components (transition between states)
 - (a) Write the First Law equation for an open system (2)
 - (b) Simplify the First Law equation using the assumptions
 - (c) Write the isentropic relations (2.1)
 - (d) Find either the specific heat exchange q , specific work w , temperature T or pressure P
7. Repeat previous step until finding every unknown of the efficiency formula found at step 5
8. Compute the efficiency

2.4 Jet engines

Assumptions changed:

- Kinetic and potential energy are negligible, $\Delta E_{\text{kinetic}} = \Delta E_{\text{potential}} = 0$
- Presence of a diffuser and a nozzle
- Pressure ratio no longer constant in the cycle, $r_{P,\text{turbine}} \neq r_{P,\text{compressor}}$
- Back-work ratio is 100%, $|\dot{W}_{\text{compressor}}| = |\dot{W}_{\text{turbine}}|$

Thrust equation for generic propulsive device:

$$F_{\text{thrust}} = (\dot{m}_{\text{air}} + \dot{m}_{\text{fuel}})v_{\text{out}} + P_{\text{out}}A_{\text{out}} - \dot{m}_{\text{air}}v_{\text{in}} - P_{\text{in}}A_{\text{in}}$$

Thrust equation for generic propulsive device (air standard approximation, constant area):

$$F_{\text{thrust}} = \dot{m}_{\text{air}}(v_{\text{out}} - v_{\text{in}}) + A_{\text{engine}}(P_{\text{out}} - P_{\text{in}})$$

Maximum thrust is at $P_{\text{out}} = P_{\text{in}}$, meaning:

$$F_{\text{thrust}} = \dot{m}_{\text{air}}(v_{\text{out}} - v_{\text{in}})$$

Propulsive efficiency of a jet engine cycle:

$$\eta_{\text{propulsive}} = \frac{\dot{W}_{\text{propulsion}}}{\dot{Q}_{\text{in}}} = \frac{F_{\text{thrust}}v_{\text{in}}}{\dot{m}_{\text{fuel}}Q_{HV}}$$

where Q_{HV} is the heating value of the fuel.

2.4.1 Problem solving steps to find the efficiency

1. Draw cycle with all its components (diffusers, compressors, combustion chambers, turbines, condensers, regenerators, nozzles)
2. Write the assumptions
3. Draw the T-s diagram
4. Build the table of states with the following thermodynamic variables:
 - Pressure P [Pa]
 - Temperature T [°C]
 - Temperature T [K]

- Velocity v [m s⁻¹]
5. Write the efficiency and thrust formulas for this the jet engine cycle
 6. Study each components (transition between states)
 - (a) Write the First Law equation for an open system (2)
 - (b) Simplify the First Law equation using the assumptions
 - (c) Write the isentropic relations (2.1)
 - (d) Find either the specific heat exchange q , specific work w , temperature T , pressure P or velocity v
 7. Repeat previous step until finding every unknown of the efficiency formula found at step 5
 8. Compute the efficiency

3 Reciprocating devices (Otto, Diesel, Atkinson/Miller cycles)

These cycles are working with a piston-cylinder device. The processes are unsteady, meaning we have to use the First Law for a closed system (1).

Terms:

TDC: top dead center (piston at the top), minimum volume

BDC: bottom dead center (piston at the bottom), maximum volume

V_D : displacement volume, $V_D = \frac{\pi B^2}{4}L$ where B is the bore (cylinder radius) and L is the vertical displacement

V_C : clearance volume, $V_C = V_{\text{TDC}}$

V_{total} : total cylinder volume, $V_{\text{total}} = V_{\text{BDC}} = V_D + V_C$

r_C : compression ratio, $r_C = \frac{V_{\text{BDC}}}{V_{\text{TDC}}} = \frac{\nu_{\text{BDC}}}{\nu_{\text{TDC}}}$

Assumptions:

- Closed system
- Air standard approximation (air everywhere, combustion replaced with equivalent external heat input)
- Ideal gas, $P\nu = RT$
- No pressure losses in the cycle
- Specific volume heat is constant, $\Delta C_v = 0 \implies U_{1 \rightarrow 2} = mC_v(T_2 - T_1)$
- Kinetic and potential energy are negligible, $\Delta E_{\text{kinetic}} = \Delta E_{\text{potential}} = 0$

3.1 Otto cycle

The Otto cycle is the cycle found in gasoline engine cars. Processes of the Otto cycle:

- 1 \rightarrow 2 Isentropic compression from the BDC to the TDC
- 2 \rightarrow 3 Isochoric heating
- 3 \rightarrow 4 Isentropic expansion from the TDC to the BDC (the work is done here)
- 4 \rightarrow 1 Isochoric cooling

Efficiency of an ideal Otto cycle:

$$\eta_{\text{thermal}} = \frac{\dot{W}_{\text{net}}}{\dot{Q}_{\text{in}}} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{r_C^{k-1}}$$

where $k = \frac{C_P}{C_V}$ is the isentropic constant.

Mean effective pressure (way to quantify the efficiency of an engine):

$$MEP = \frac{W_{\text{net}}}{V_D} = \frac{w_{\text{net}}}{\nu_{\text{BDC}} - \nu_{\text{TDC}}} = \frac{w_{\text{net}}}{R \left(\frac{T_2}{P_2} - \frac{T_1}{P_1} \right)}$$

3.2 Otto vs Diesel vs Atkinson

The Otto cycle has an isochoric heating, the Diesel cycle has an isobaric heating, and the Atkinson cycle is an improvement of the Otto cycle which re-use the excess of pressure at the end of the cycle.

3.3 Diesel cycle

Since the Diesel cycle only compress air, the compression ratio is higher than the Otto cycle because there is no risk of auto-ignition. However, given the same compression ratio r_C , the Otto cycle is more efficient because the Diesel cycle stays at the same pressure during the fuel combustion phase.

Cutoff ratio:

$$\beta = \frac{\nu_{\text{intermediate}}}{\nu_{\text{minimum}}} = \frac{\nu_3}{\nu_2}$$

The cutoff ratio is used in determining the efficiency of the cycle and the pressure and temperature at the final state (usually state 4) since:

$$\frac{P_4}{P_3} = \left(\frac{\beta}{r_C} \right)^k$$

$$\frac{T_4}{T_3} = \left(\frac{\beta}{r_C} \right)^{k-1}$$

Efficiency of an ideal Diesel cycle:

$$\eta_{\text{thermal}} = \frac{\dot{W}_{\text{net}}}{\dot{Q}_{\text{in}}} = 1 - \frac{1}{r_C^{k-1}} \left[\frac{\beta^k - 1}{k(\beta - 1)} \right]$$

where $k = \frac{C_P}{C_V}$ is the isentropic constant.

3.4 Problem solving steps to find the efficiency

1. State that the control volume is the gas in the piston-cylinder device
2. Write the assumptions
3. Draw the P- ν and T-s diagrams according to the cycle
4. Build the table of state with the following thermodynamic variables:
 - Pressure P [Pa]
 - Temperature T [°C]
 - Temperature T [K]
 - Specific volume ν [m³ kg⁻¹]
5. Find the efficiency formula for this reciprocating device

6. Study each transition between states
 - (a) Write the First Law equation for a closed system (1)
 - (b) Simplify the First Law equation using the assumptions
 - (c) Write the isentropic relations (2.1)
 - (d) Find either the specific heat exchange q , specific work w , temperature T , pressure P or cutoff ration β
7. Repeat previous step until finding every unknown of the efficiency formula found at step 5
8. Compute the efficiency

4 Refrigeration

Assumptions:

- Steady flow, $\Delta \dot{m} = 0$
- Compressors are isentropic, $\Delta s_{\text{compressors}} = 0$
- Evaporators and condensers are isobaric, $\Delta P_{\text{evaporators}} = \Delta P_{\text{condensers}} = 0$
- No pressure losses in the cycle
- Kinetic and potential energy are negligible, $\Delta E_{\text{kinetic}} = \Delta E_{\text{potential}} = 0$
- Expansion valve is isenthalpic

4.1 Simple vapor-refrigeration cycle

The refrigeration cycle is very similar to a Rankine cycle:

- 1 \rightarrow 2 Compression in a compressor from saturated gas to superheated gas
- 2 \rightarrow 3 Cooling from superheated gas to saturated liquid
- 3 \rightarrow 4 Expansion in an expansion valve
- 4 \rightarrow 1 Heating from mixed phase to saturated gas

The refrigeration cycle has an other advantages: by looking at the heat rejection side, the refrigeration becomes a heat pump.

To quantify a refrigeration cycle and a heat pump, the coefficient of performance is used:

$$\text{COP}_{\text{ref}} = \beta_{\text{ref}} = \frac{\dot{Q}_{\text{in}}}{\dot{W}_{\text{in}}}$$

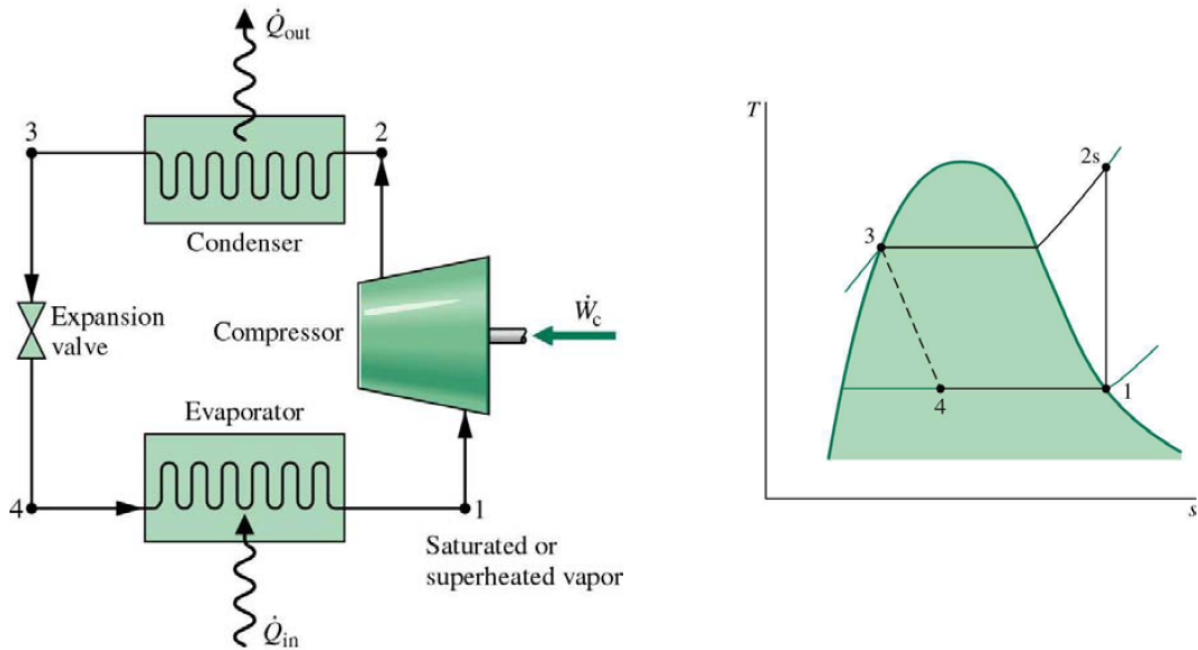
$$\text{COP}_{\text{HP}} = \beta_{\text{HP}} = \frac{\dot{Q}_{\text{out}}}{\dot{W}_{\text{in}}} = 1 + \frac{\dot{Q}_{\text{in}}}{\dot{W}_{\text{in}}} = 1 + \beta_{\text{ref}}$$

4.2 Improve the vapor-refrigeration cycle

4.2.1 Multi-stage refrigeration

The multi-stage refrigeration cycle has multiple refrigeration cycle in it:

Figure 3: Ideal vapor-refrigeration cycle



4.2.2 Ground power source heat pump

Since the coefficient of performance becomes low when the too much difference in temperature between the hot side and the cold side, one solution is to place the evaporator (or condenser if used as a heat pump) deep in the ground, where the temperature does not vary much during the year. This way the difference of temperature between the two side remains fairly constant throughout the year, letting us have a constant coefficient of performance.

4.3 Problem solving steps to find the efficiency

1. Draw cycle with all its components (compressors, evaporators, condensers, heat exchanger and expansion valve)
2. Write the assumptions
3. Draw the T-s diagram
4. Build the table of states with the following thermodynamic variables:
 - Mass flow rate \dot{m} [kg s^{-1}] (do not forget split fractions y_i)
 - Temperature T [$^{\circ}\text{C}$]
 - Pressure P [Pa]
 - Specific entropy s [$\text{J kg}^{-1} \text{K}^{-1}$]
 - Specific enthalpy h [J kg^{-1}]
 - Specific volume [$\text{m}^3 \text{kg}^{-1}$]
5. Find the coefficient of performance formula for this refrigeration cycle (do not forget that the mass flow rate \dot{m} might be different in each loop)
6. Study each components (transition between states)
 - (a) Write the First Law equation for an open system (2)

- (b) Simplify the First Law equation using the assumptions
 - (c) Find either the specific heat exchange q , specific work w , mass flow rate \dot{m} or specific enthalpy h
7. Repeat previous step until finding every unknown of the coefficient of performance formula found at step 5
 8. Compute the coefficient of performance

5 Mixtures

A mixture is a collection of different substances together. It is not the same a multiphase (liquid and gas phase commonly referred as a mixture) as a multiphase is only composed of one substance.

Example. Air is a mixture: 79% N_2 + 21% O_2 in mole.

In this class, we will only deal with ideal mixtures.

For ideal mixtures, every extensive variables add up:

$$m_{\text{mix}} = m_A + m_B + \dots = \sum m_i$$

$$n_{\text{mix}} = n_A + n_B + \dots = \sum n_i$$

$$\left| \begin{array}{l} m_i [\text{kg}]: \text{mass of component } i \\ n_i [\text{mol}]: \text{number of mole of component } i \end{array} \right.$$

We can define two properties using the mass and the number of mole:

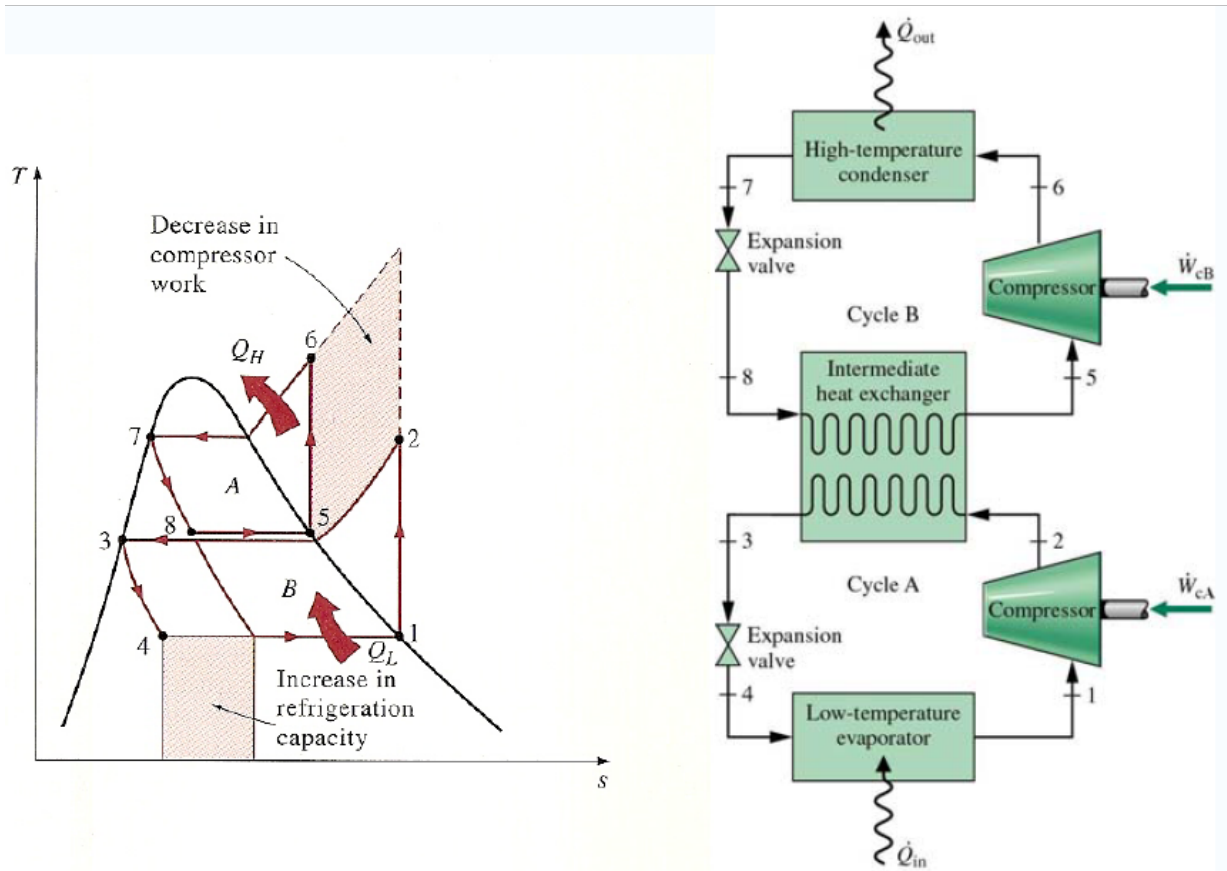
Mass fraction: $x_i = \frac{m_i}{m_{\text{mix}}} \implies \sum x_i = 1$

Mole fraction: $y_i = \frac{n_i}{n_{\text{mix}}} \implies \sum y_i = 1$

Molar mass of a mixture: $M_{\text{mix}} = \frac{m_{\text{mix}}}{n_{\text{mix}}} = \sum y_i M_i$

The composition of a mixture is completely defined by either the set of $\{x_i\}$ or the set of $\{y_i\}$.

Figure 4: Ideal two-stage refrigeration cycle



Example. Air defined by 79% N₂ + 21% O₂ in mole.

$$M_{\text{air}} = 0.79 \times 2 \times 14 + 0.21 \times 2 \times 16$$

$$= 28.84 \cdot 10^{-3} \text{ kg mol}^{-1}$$

$$\Rightarrow R_{\text{air}} = \frac{R}{M_{\text{air}}} \approx 288 \text{ J kg}^{-1} \text{ K}^{-1}$$

where $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$.

Example. Air defined by 79% N₂ + 20% O₂ + 1% CO₂ in mole.

$$M_{\text{air}} = 28.96 \cdot 10^{-3} \text{ kg mol}^{-1}$$

$$\Rightarrow R_{\text{air}} = \frac{R}{M_{\text{air}}} \approx 287 \text{ J kg}^{-1} \text{ K}^{-1}$$

where $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$.

Mass fraction in term of molar fraction and vice-versa:

$$x_i = \frac{y_i M_i}{\sum y_k M_k} \quad y_i = \frac{\frac{x_i}{M_i}}{\sum \frac{x_k}{M_k}}$$

Example. Air defined by 79% N₂ + 21% O₂ in mole.

	y_i	M_i	$m_i(1 \text{ mol})$	x_i
N ₂	0.79	28	6.72	0.233
O ₂	0.21	32	22.12	0.767
			28.84	1

Example. Car exhaust defined by 70% N₂ + 22% CO₂ + 8% H₂O in mass.

	x_i	M_i	$n_i(1 \text{ g})$	y_i
N ₂	0.70	28	0.025	0.735
CO ₂	0.22	44	0.005	0.147
H ₂ O	0.08	18	0.004	0.118
			0.034	1

Other extensive thermodynamic properties:

Internal energy: $U_{\text{mix}} = U_A + U_B + \dots = \sum U_i$ and $u_{\text{mix}} = \sum x_i u_i$

Enthalpy: $H_{\text{mix}} = H_A + H_B + \dots = \sum H_i$ and $h_{\text{mix}} = \sum x_i h_i$

Entropy: $S_{\text{mix}} = S_A + S_B + \dots + S_{\text{mixing}} = \sum S_i + S_{\text{mixing}}$

When dealing with mixtures, a state is defined using two independent intensive thermodynamic properties and $n - 1$ extra properties of the mixture per degree of freedom, where n is the number of components.

Moreover, in order to solve problems, two closure conditions are needed, the first one being thermal equilibrium ($T_{\text{mix}} = T_A = T_B = \dots = T_i$) and the second one, a choice between:

Dalton's law: $P_{\text{mix}} = P_A + P_B + \dots = \sum P_i$, which

implies that $V_{\text{mix}} = V_A = V_B = \dots = V_i$

Amagat's law: $V_{\text{mix}} = V_A + V_B + \dots = \sum V_i$, which implies that $P_{\text{mix}} = P_A = P_B = \dots = P_i$

5.1 Gas-vapor mixtures

If we have a mixture of air and water vapor, here is the enthalpy of the mixture using Dalton's law:

$$\begin{aligned} h_{\text{mix}} &= x_{\text{air}} h_{\text{air}}(T, P_{\text{air}}) + x_{\text{H}_2\text{O}} h_{\text{H}_2\text{O}}(T, P_{\text{H}_2\text{O}}) \\ \iff H_{\text{mix}} &= m_{\text{air}} h_{\text{air}}(T, P_{\text{air}}) + m_{\text{H}_2\text{O}} h_{\text{H}_2\text{O}}(T, P_{\text{H}_2\text{O}}) \\ \iff h &= h_{\text{air}} + \omega h_{\text{H}_2\text{O}} \end{aligned}$$

where $\omega = \frac{m_{\text{H}_2\text{O}}}{m_{\text{air}}}$ is the specific humidity ratio and h is in $\text{J kg}_{\text{air}}^{-1}$.

5.1.1 Specific humidity ratio

If we assume that both air and water vapor are ideal gases, the following relation for the specific humidity ratio ω is obtained:

$$\omega = \frac{m_{\text{H}_2\text{O}}}{m_{\text{air}}} = \frac{M_{\text{H}_2\text{O}}}{M_{\text{air}}} \frac{P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \approx 0.622 \frac{P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}}$$

The unit of the specific humidity ratio ω is $\text{kg}_{\text{H}_2\text{O}} \text{ kg}_{\text{air}}^{-1}$

Max ω : at $P_{\text{H}_2\text{O}} = P_{\text{sat}}(T)$ since the water vapor starts to condense and becomes liquid water, this state is called fully moist air

Min ω : at $P_{\text{H}_2\text{O}} = 0$, this state is called fully dry air

5.1.2 Relative humidity

The relative humidity ϕ has been defined since the specific humidity ratio ω depends on the pressure P and the temperature T , meaning the same value of ω does not represent the same felt-humidity.

$$\begin{aligned} \phi &= \frac{P_{\text{H}_2\text{O}}}{P_{\text{sat}}(T)} = \frac{\omega P}{\left(\omega + \frac{M_{\text{H}_2\text{O}}}{M_{\text{air}}}\right) P_{\text{sat}}(T)} \\ \iff \phi &\approx \frac{\omega P}{(\omega + 0.622) P_{\text{sat}}(T)} \\ \iff \omega &\approx 0.622 \frac{\phi P_{\text{sat}}(T)}{P - \phi P_{\text{sat}}(T)} \end{aligned}$$

5.1.3 Processes

Adiabatic saturation process The adiabatic saturation process takes an amount of air in, circulates it over a liquid water reservoir long enough so that the air is fully moist when it exit. This experiment is a way to measure the specific humidity ratio ω and the relative humidity ϕ . It leads to the equation:

$$\omega_1 = \frac{C_{P,\text{air}}(T_2 - T_1) + \omega_2 [h_g(T_2) - h_f(T_2)]}{h_g(T_1) - h_f(T_2)}$$

where $\omega_2 = \frac{P_{\text{sat}}(T_2)}{P - P_{\text{sat}}(T_2)}$, and T_1 , T_2 and P can be measured.

In order to simplify the way to find the specific humidity ratio ω and the relative humidity ϕ , the psychrometric chart is used (<http://www.flycarpet.net/en/PsyOnline>).

Heating Heating is a constant specific humidity ratio process ($\Delta\omega = 0$) and thus corresponds to a horizontal path to the right on the psychrometric chart.

This explains why houses feels dryer in the winter: heaters are heating the room, thus decreasing the relative humidity in the room.

Cooling Cooling is a constant specific humidity ratio process ($\Delta\omega = 0$), and thus corresponds to a horizontal path to the left on the psychrometric chart.

Cooling with dehumidification Cooling with dehumidification is a two step process:

1. Constant ω cooling until reaching a relative humidity $\phi = 100\%$
2. Constant ϕ cooling while water start to condensate

Evaporative cooling Evaporative cooling is cooling while humidifying the air and is a constant enthalpy process ($\Delta h = 0$).

Mixing Mixing corresponds to the mix of two or more state of air, with different properties, to get another state.

$$\frac{\dot{m}_{\text{air},2}}{\dot{m}_{\text{air},1}} = \frac{h_3 - h_1}{h_2 - h_3} = \frac{\omega_3 - \omega_1}{\omega_2 - \omega_3}$$

Those two equations can be used to solve mixing problems graphically as they represent straight lines on the psychrometric chart and ratio of lines between states.

6 Combustion

For combustion, we need to be aware that enthalpy at a temperature and pressure is with respect to a reference:

$$h(T) = h_f^0 + C_P(T - 298)$$

where h_f^0 is the enthalpy of formation, which is the amount of enthalpy needed for a substance to be in stable state at 25°C and 1 atm .

By definition:

H: stable in $\text{H}_2 \implies h_{f,\text{H}_2}^0 = 0$

O: stable in $\text{O}_2 \implies h_{f,\text{O}_2}^0 = 0$

N: stable in $\text{N}_2 \implies h_{f,\text{N}_2}^0 = 0$

C: stable in $\text{C(s)} \implies h_{f,\text{C(s)}}^0 = 0$

This is used in combustion problems because we are dealing with a reaction, meaning reactives react together by detaching their atoms and form products by attaching to other atoms. This change of molecular composition requires energy, which comes from the enthalpy of formation.

6.1 Combustion problems

Heat of reaction Heat produced by a combustion in a isobaric and isothermal process:

$$\dot{Q}_{\text{out}} = \dot{n}_k \left(\sum_{\text{reactives}} \nu_i \tilde{h}_{f,i}^0 - \sum_{\text{products}} \nu_i \tilde{h}_{f,i}^0 \right)$$

\dot{n}_k [mols⁻¹]: mole flow rate of a substance k of the reaction
 ν_i : substance i stoichiometric factor related to the substance k
 \tilde{h}_f^0 [J mol⁻¹]: enthalpy of formation

Adiabatic flame temperature Let us find the products temperature via an isobaric and adiabatic combustion:

$$0 = \sum_{\text{reactives}} \nu_i [\tilde{h}_{f,i}^0 + \tilde{C}_{P,i}(T_1 - 298)] - \sum_{\text{products}} \nu_i [\tilde{h}_{f,i}^0 + \tilde{C}_{P,i}(T_2 - 298)] \quad (6.1)$$

ν : stoichiometric factor
 \tilde{h}_f^0 [J mol⁻¹]: enthalpy of formation
 \tilde{C}_P [J mol⁻¹ K]: specific pressure heat
 T [K]: temperature

where T_2 is the adiabatic flame temperature.

Constant volume explosion Combustion at a constant volume:

$$\begin{aligned} \Delta E &= \Delta U \\ \iff U_1 &= U_2 \\ \iff H_1 - P_1 V &= H_2 - P_2 V \\ \iff H_2 - H_1 &= V(P_2 - P_1) \end{aligned}$$