Ideal Gas Equation

Ideal Gas Equation:
Ideal for: Low Pressures and High Temperature – relative to the critical point of the gas (which you can google).

$$PV = mRT$$

P= Kpa, V= m^3, T=K

$$PV = nR_0T$$

N = kmol, R_0 = 8.314 kJ/KmolK

$$R = \frac{R_0}{M}$$

Compressibility Factor:
Way to modify the ideal gas equation if P & T are out of range.

$$PV = zmRT$$

$$\frac{P}{P_{Critical}} = P_r\ (Reduced\ Pressure)$$

$$\frac{T}{T_{Critical}} = T_r\ (Reduced\ Pressure)$$

Once you have the Pr and Tr, just the chart to find the 'z' value. Then put into the gas equation

Gas Mixtures

- The behavior of mixtures of gases can be predicted based on available information of the individual gases that its made of.

m = Mass
mf = Mass Fraction
y = Molar Fraction
M = Molar Mass
$_m$ = Mixture
$_i$ = Individual Gas
$_{cr}$ = Critical

The Composition of Gas Mixtures

There are 2 main ways we can work out what a mixture is made of.

1. Mass Fraction (mf)

$$M_{mixture} = \sum M_{individual}$$

$$mf_i(mass\ fraction) = \frac{M_{individual}}{M_{mixture}}$$

- Mass of the mixture = sum of the individual gas masses: $m_m = \sum m_i$
- Mass fraction of each gas: $mf_i = \frac{m_i}{m_m}$
- Example: If a mixture has 3 kg O2, 5 kg N2, and 12 kg CH4:
  m_m = 3 + 5 + 12 = 20 and the mass fractions will be: mf_{O2} = 3/20 mf_{N2} = 5/20 mf_{CH4} = 12/20
- Check: **Sum of mass fractions must be 1.**

2. Molar Fractions (y)

$$N_i(mols\ ind.) = \frac{m_i(mass\ ind.)}{M_i(molecular\ mass\ ind.)}$$

$$Y_i(Molar\ Fraction\ ind.) = \frac{N_i}{N_m}$$

$$R_m = \sum mf_i * R_i$$

- Moles of a gas: $N_i = \frac{m_i}{M_i}$
- Molar fraction: $y_i = \frac{N_i}{N_m}$
- Example (using Molar Masses: $O_2 = 32$, $N_2 = 28$, $CH_4 = 16$):
  $N_{O2} = 3/32 = 0.0937$ $N_{N2} = 5/28 = 0.178$ $N_{CH4} = 12/16 = 0.75$
  The total no of moles of the mixture, $N_m = \Sigma N_i = 1.022$.

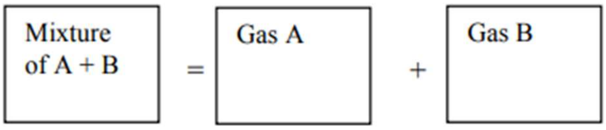
  Molar Fractions are:
  $y_{O2} = 0.0937/1.022 = 0.092$ $y_{N2} = 0.178/1.022 = 0.174$ $y_{CH4} = 0.75/1.022 = 0.734$
- Check that $\Sigma yi=1$

Usually mass and molar fractions are similar, the variation occurs due to different molar masses.

Mixtures of Ideal Gases

There are 2 models we can use: **Dalton's Law** (partial pressures) and **Amagat's Law** (partial volumes).

Dalton's Law (More commonly used).

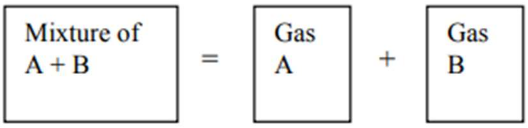


- Assumption: Each gas behaves as if others are not there.

$V_m = V_A = V_B$

- Total pressure = sum of partial pressures: $P_m = \sum P_i(T_m, V_m)$
- Key formula: $P_i = P_m y_i$

Amagat's Law:



- Assumption: Each gas behaves independently but at the same pressure.
- Total volume = sum of individual gas volumes: $V_m = \sum V_i(T_m, P_m)$
- Key formula: $V_i = V_m y_i$

Real Gases

2 main assumptions: that there is no interaction between molecules (or atoms), and that the molecules themselves occupy no space (i.e. they are point masses).
Ideal gas law assumes no molecular interactions, works well in **low pressures,** but is inaccurate at high pressures.

There are 2 ways to correct the equation for real gases:

1. Use a better equation of state: Van der Waals, Beattie-Bridgeman, Benedict-Webb-Rubin, etc.
2. The **Compressibility Factor (Z):** PV = Z mRT

- $Z = \frac{Pv}{RT}$ or $Z = \frac{v_{actual}}{v_{ideal}}$
- Find each component Pcrit, Tcrit and Z values.
  Combine the Z values to get the Z of a mixture.

$$Z_m = \sum y_i(molar\ fraction) * z_i$$

- **Kaye's Rule** (More Accurate)
  Finding each z is long and increases risk.
  We can combine the Pcrit and Tcrit first, then find the Zmixture.

$$P_{rm\ (red\ mix)} = \sum y_i(molar\ frac.) * P_{crit\ ind.}$$

$$T_{rm(red\ mix.)} = \sum y_i(molar\ frac.) * T_{crit\ ind.}$$

Then find the Pcm and Tcm:

$$\frac{P_{mixture}}{P_{crit\ mix.}} = P_{reduced\ mix}$$

$$\frac{T_{mixture}}{T_{crit\ mix.}} = T_{reduced\ mix}$$

Once you have the T&P reduced, you can find the Zmixture from the chart.

Humidity and Psychrometry

Mixture of an Ideal Gas and a Vapour

- Water vapour in air can be modelled as a mixture of an ideal gas and a vapour.
- According to Dalton's Law, each gas (air and water vapour) exerts a pressure equal to its partial pressure.
- If the partial pressure exceeds the saturation pressure, the vapour will condense.
- Such mixtures are referred to as gas-vapour mixtures.
- In psychrometry and air conditioning, cooling at constant pressure or volume impacts the behaviour of the vapour:
  I. Constant pressure cooling: Vapour condenses at the **dew point** temperature, which is the saturation temperature for the vapour's partial pressure.
  II. Partial pressures remain constant until condensation starts.

Air-Water Vapour Mixtures:

In -10 to 40*C (normal temp range) we have the following properties:

- Cp for dry air = 1.005kJ/kgK
- The enthalpy of water vapour depends only on temperature.
- Water vapour behaves as ideal gas.
- Enthalpy of water vapour in air-water mixtures is **approximately equal** to the enthalpy of unsaturated water vapour at the temperature (up to 40*C)

Relative Humidity (Φ)

The **degree of saturation** of a water-air vapour.

$$\phi = \frac{\text{mole fraction of vapour in mixture}}{\text{mole fraction of a saturated mixture at the same T \& P}}$$

$$= \frac{\text{partial pressure of vapour in a mixture}}{\text{saturation pressure of the vapour at the same T \& P}}$$

thus; $\varphi = \frac{P_v\ (Partical\ Pressure\ of\ Vapour)}{P_s\ (Saturation\ pressure\ of\ vapour)}$

Φ = 1.0 (100%) → Air is fully saturated.

Dew Point: when a mixture cools at constant pressure it will reach the dew point (any further will result in condensation.

$$Dew\ Point: \varphi = \frac{P_{sd}\ (saturated\ vapour\ pressure)}{P_s\ (Saturation\ pressure\ of\ vapour)}$$

Humidity Ratio (ω)

Is also called the moisture content/specific humidity/absolute humidity.

$$\omega = \frac{m_v (mass\ of\ water\ vapour)}{m_a (mass\ of\ dry\ air)}$$

It can be related to the specific volumes and densities of the water vapour and air, to derive:

$$\omega = \frac{v_a}{v_v} = \frac{\bar{R}T/P_a M_a}{\bar{R}T/P_v M_v} = \frac{P_v M_v}{P_a M_a}$$

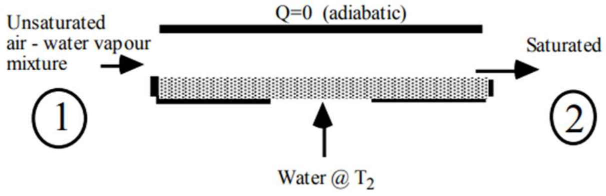
This gives an important equation

$$\phi = \frac{P_v}{P_s} \text{ then } \phi = \frac{\omega P_a}{0.622 P_s}.$$

Degree of Saturation (μ): the ratio of the actual humidity ratio to the humidity ration of a saturated mixture of the same temp and pressure.

Adiabatic Saturation Temperature and Wet & Dry Bulb Thermometer:

- Used to evaluate the **humidity ratio**



Process:

1. Unsaturated air enters a **long channel**, picking up moisture.
2. If the channel is long enough, the mixture reaches a **saturated state at T_2**.
3. T_2 is called the **adiabatic saturation temperature**.
4. From the energy balance equation we can derive that:

$$\omega_1 = \frac{C_{p_a}(T_2 - T_1) + \omega_2 h_{fg_2}}{h_{v_1} - h_{f_2}}$$

The above equation can be used with both wet and dry bulb thermometers to give reasonably accurate results.

Wet bulb temperature: related to dry bulb temp and humidity ratio
At 100% saturation, wet and dry bulb temperatures are equal.

Psychrometric Chart

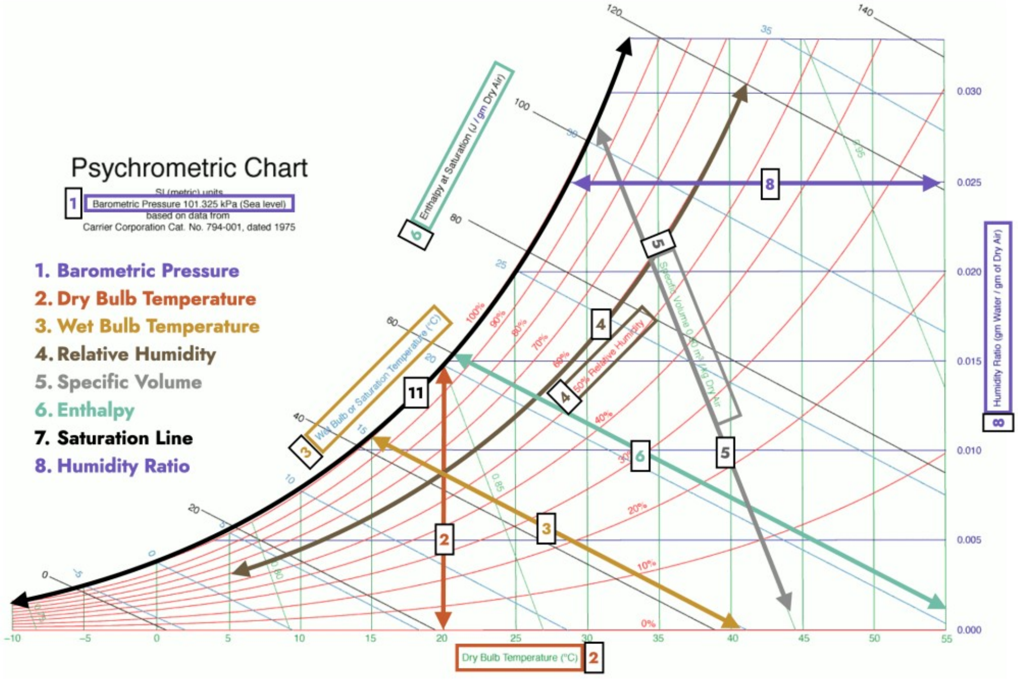
- Used for air-water vapour mixtures.
- Based on standard atmospheric pressure (101325Pa)

- Key components:

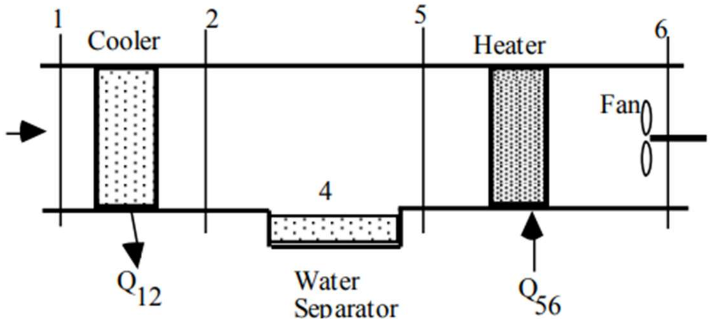
- Humidity ratio vs. dry bulb temperature (linear scales).
- Saturation curve, relative humidity, and enthalpy scales.
- Sensible heat vs. total heat ratio.

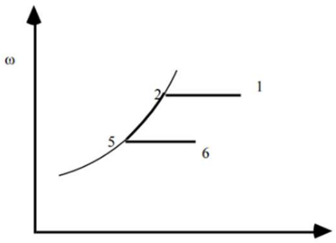
- Important notes:

- Lines of constant enthalpy ≈ constant wet bulb temperature (but slightly different).
- Enthalpy values based on zero for dry air and water vapour at 0°C.
- Constant specific volume lines also present.



Cooling and De-Humidification Systems:

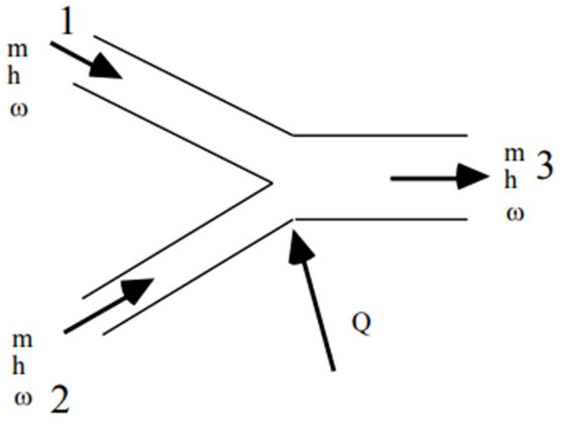




The main application of psychrometry is in cooling and de-humidification systems.

- Cooling to dew point (T_2) → condensation occurs → further cooling removes moisture.
- Final temperature may require reheating to match room conditions.

Adiabatic Mixing of 2 Moist Air Streams:



When 2 streams of moist air mix and you need to find the resulting conditions.

Energy and mass must be maintained.

On a psychrometric diagram, points 1, 2 and 3 all fall on a straight line

Energy Equation:

$$\dot{m}_{a_1} h_1 + \dot{m}_{a_2} h_2 = \left(\dot{m}_{a_1} + \dot{m}_{a_2}\right) h_3$$

or

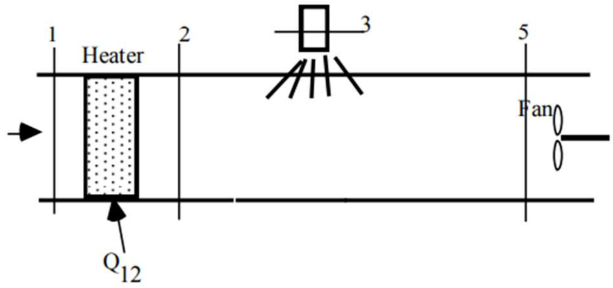
$$\frac{\dot{m}_{a_1}}{\dot{m}_{a_2}} = \frac{h_3 - h_2}{h_1 - h_3}$$

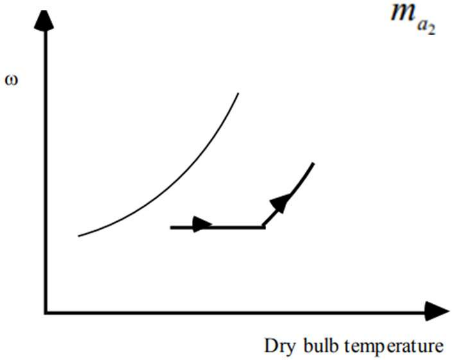
Vapour Mass Equation:

$$\omega_1 \dot{m}_{a_1} + \omega_2 \dot{m}_{a_2} = \omega_3 \left(\dot{m}_{a_1} + \dot{m}_{a_2}\right)$$

$$\frac{\dot{m}_{a_1}}{\dot{m}_{a_2}} = \frac{\omega_3 - \omega_2}{\omega_1 - \omega_3}$$

Heating and Moisture Addition:





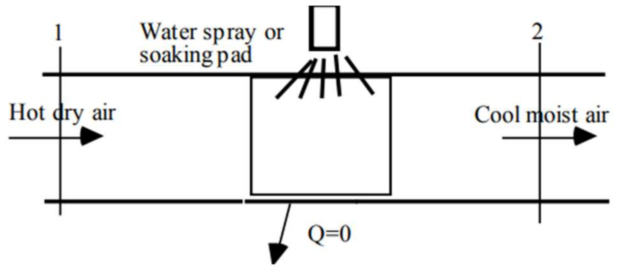
Air is at T1 as is heated to T2, but the air will be dry, so you add water at 3. The added water increases humidity but decreases temperature.

Energy Equation: $Q_{12} = m_a(h_{a2} - h_{a1}) + m_v(h_{v2} - h_{v1})$

Energy Equation for Moisture: $-W_{25} = m_a\left(h_{a5} - h_{a2}\right) + m_{v1}h_{v5} - m_{v2}h_{v2} + m_{f3}h_{f3}$

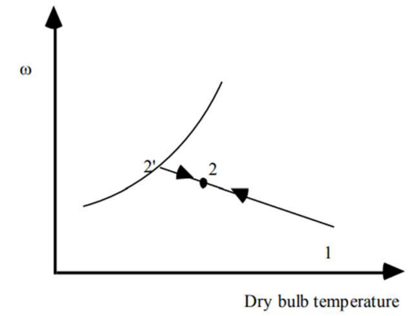
Mass Balance for Water: $m_f = m_v5 - m_v2$

Evaporative Cooling:



Hot air passes through a wet pad. This process is adiabatic (no heat transfer from environment) and the change in temperature is a result to the water evaporating.

$$m_a\left(h_{a1}+\omega_1 h_{v1}\right)+m_a\left(\omega_2-\omega_1\right)h_f=m_a\left(h_{a2}+\omega_2 h_{v2}\right)$$



The minimum temperature which can be obtained is thus at 2'.

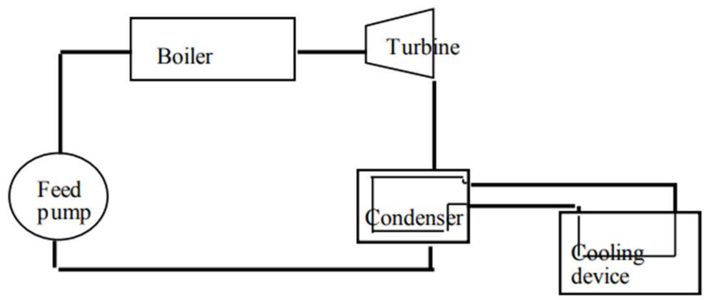
Follows the WBT and amount of water required is small so the temperature of the water doesn't have a big effect.

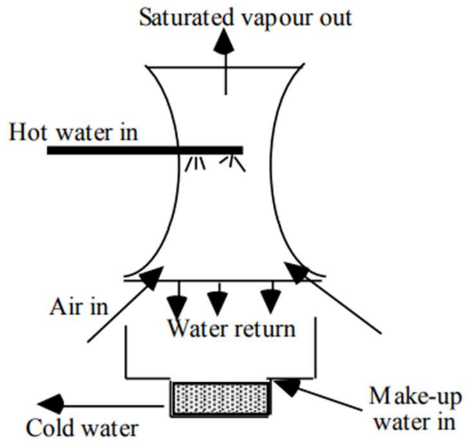
Minimum temperature achievable: Wet bulb temperature.

Cooling Tower: plants used for cooling water. Water flow is 15-20 times of steam flow and often requires circulation.
Process:

1. Hot water enters
2. Fine droplets evaporate
3. Latent heat cools the remaining water

- Efficiency depends on WBT





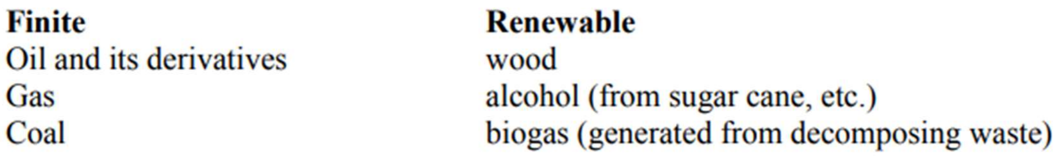
Energy Balance:

$$m_{f1}h_{f1}+m_{a3}h_{a2}+m_{v3}h_{v3}=m_{f2}h_{f2}+m_{a4}h_{a4}+m_{v4}h_{v4}$$

f =
a = air
v = vapour

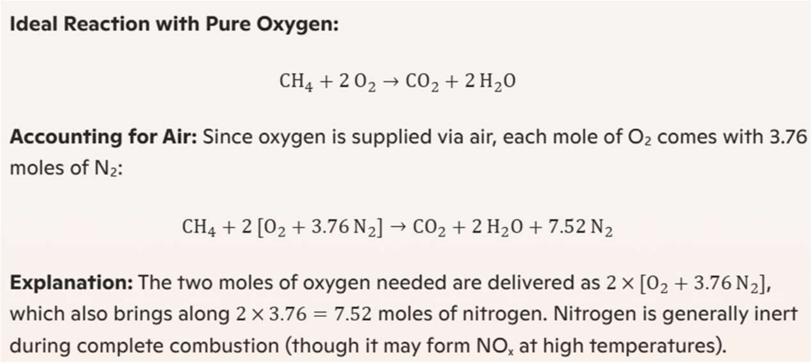
3. Combustion:

When a fuel (hydrocarbon) reacts with an oxidiser (O2) from the air to release energy.
Combustion involves chemical reactions (in the form of breaking bonds).



Finite	Renewable
Oil and its derivatives	wood
Gas	alcohol (from sugar cane, etc.)
Coal	biogas (generated from decomposing waste)

Air Combustion: For calcs, air is assumed to be a mixture of O2 and N2.
Molar Proportions: O2= 21% and N2= 79%.
For every 1kmol of Oxygen you have **3.79kmol** of N2. (21:79).



Ideal Reaction with Pure Oxygen:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

Accounting for Air: Since oxygen is supplied via air, each mole of O_2 comes with 3.76 moles of N_2:

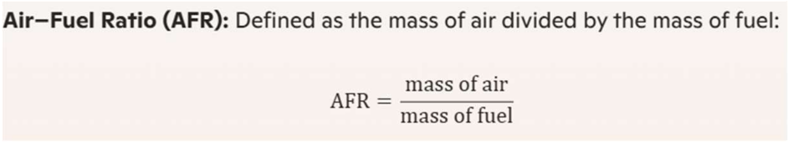
$$CH_4 + 2\,[O_2 + 3.76\,N_2] \rightarrow CO_2 + 2\,H_2O + 7.52\,N_2$$

Explanation: The two moles of oxygen needed are delivered as $2 \times [O_2 + 3.76\,N_2]$, which also brings along $2 \times 3.76 = 7.52$ moles of nitrogen. Nitrogen is generally inert during complete combustion (though it may form NO_x at high temperatures).

Note:

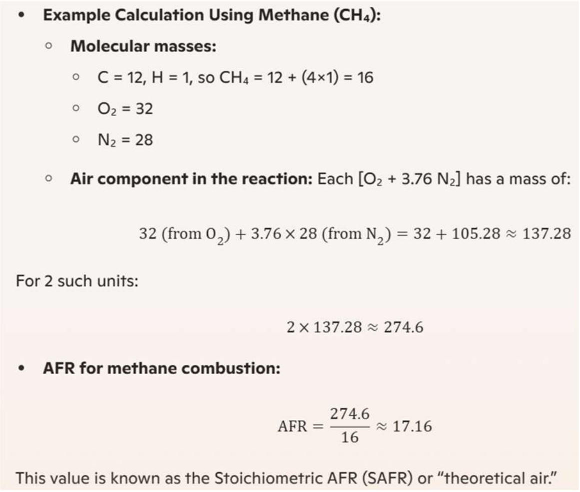
Mass is conserved throughout combustion.
Number atoms are conserved.
Number of moles is NOT conserved.

Air Fuel Ratios:
Stoichiometric Combustion (Theoretical Combustion): Occurs when the fuel is burned with exactly the right amount of oxygen such that there is no excess fuel or oxygen remaining.



Air–Fuel Ratio (AFR): Defined as the mass of air divided by the mass of fuel:

$$\text{AFR} = \frac{\text{mass of air}}{\text{mass of fuel}}$$



- **Example Calculation Using Methane (CH_4):**
  - **Molecular masses:**
    - C = 12, H = 1, so $CH_4 = 12 + (4\times1) = 16$
    - $O_2 = 32$
    - $N_2 = 28$
  - **Air component in the reaction:** Each $[O_2 + 3.76\,N_2]$ has a mass of:

$$32\ (\text{from } O_2) + 3.76 \times 28\ (\text{from } N_2) = 32 + 105.28 \approx 137.28$$

For 2 such units:

$$2 \times 137.28 \approx 274.6$$

- **AFR for methane combustion:**

$$\text{AFR} = \frac{274.6}{16} \approx 17.16$$

This value is known as the Stoichiometric AFR (SAFR) or “theoretical air.”

Lean Mixture: AFR>SAFR (excess air, more oxygen)
Rich Mixture: AFR<SAFR (excess fuel; not enough air)

Excess Air: The combustion process is usually ran with excess oxygen to ensure complete combustion since fuel is expensive and you don’t want to waste it.

% Excess Air = 100 x (AFR – SAFR)/SAFR

- If AFR=SAFr then there is 0% extra air
- 100% means the AFR is 2x the Stoichiometric value
- Negative indicates air deficiency.

Used for: to ensure complete combustion, allowing for incomplete mixing and to limit combustion temperature. (Expect for IC engine ignition).

Continuous Combustion Processes: Air addition over time is required in some reactions (gas burners).
Primary Air – added shortly after gas leaves valve.
Secondary Air – Introduced at the burner where combustion finally occurs.

Other Reactions During Combustion:

1. Dissociation of CO2: $CO_2 \leftrightarrow CO + O$
   At high temps, CO2 breaks down into CO and O.
   This reaction absorbs energy (endothermic) which can limit max temp of the combustion reaction.
   Meaning insufficient air.
   CO is toxic.
2. Dissociation of N2:
   It is usually very stable, but at high temps the triple bond can still be broken.
   Free N atoms can oxidise and form NO and NO2.
   These are pollutants and can react further for form ozone (O3).
3. Sulphur:
   Fuels contain a little bit of sulphur.
   Combustion forms sulphur oxides.
   This causes pollution and corrosion issues within engines when mixed with water vapour.
   We must exhaust combustion gases when above the dew point of water to prevent corrosion

Dew Point:

1. Determine the molar proportions of the exhaust mixture.
2. Calculate the molar and partial fractions of water vapour.
3. Use steam tables to find the temp that the partial pressure = the Psat.

IC Engines:
There are 2 main types:

1. Spark Ignitions (Petrol, gas, otto cycle): air/fuel is compressed and ignited with a spark.
2. Compression Ignition: Diesel: air is compressed and fuel injected into hot air where it auto ignites.

Petrol/Gas = C_8H_{18}
Diesel = $C_{12}H_{26}$

Spark Engines:
Ignition:

- Timing is crucial.
  Idle (800rpm): delay ~ 10* Crank Rotation
  3000rpm: Delay ~36* Crank Rotation

Igniting too Late:

- Pressure is reduced, so less power.
- Burning in the valve (because it did have time to fully burn in engine).
- Very late = popping back through the inlet tract.

Too early:

- Detonation of unburn mixture
- If very early, P max occurs before the TDC which means there's a big loss in power

Detonation: occurs when unburnt mixture ahead of the flame front experiences excess pressure and temperature, leading to an explosion.

- Causes shock load on engine (pinking).
- Limits size of engine cylinders
- Modern engines use electronic controls to time ignitions speed and load.

Fuels

Octane Rating: assesses petrol quality and its resistance to detonation. High means resists compression ignition. RON – Researched Octane Number (Aus standards). E.g. 98 RON = 98% Octane and 2% Heptane.

Lead in Petrol:

- Introduced in the 1920s to raise octane rating and efficiency
- Phased out in 2001 due to pollution

Replacements for Lead:
Aromatics: benzene, toluene, xylene.
Unsaturated Hydrocarbons: Olefins
Oxygenates: Hydrocarbons with oxygen molecules).

Australian standards permit up to:
- 1% benzene by volume.
- 42% aromatics.
- 18% olefins.

Environmental Concerns:

1. Fuel Evaporation: bad for storage and transfers.
2. Combustion by-products: unburnt hydrocarbons released due to incomplete combustion.
   Catalytic converters cant mitigate fuel evaporation.
3. Oxygenates in Fuel: Are responsible for the production of unwanted by products in catalytic converters

Reducing admissions:

1. Lean Burn Technology: burn petrol in lean mixture to lower Nox and unburnt HC
2. Plasma Ignition: encourages ignition of lean mixtures.
3. Stratified Charge Technology: reduces fuel content near walls for cleaner burns.

Diesel Engines:

Process: rapid compression heats air to ~600C before fuel injection.
Fuel enters as droplets, evaporates, and combusts in high temp

AFR: can operate a low AFR 100:1, highly efficient and low part load.

Ignition Lag:

- Combines evaporation/diffusion lag with injector large
- Longer than ignition lag meaning slower diesel engine operation

Fuel Quality:

- Diesel fuel: 10ppm sulphur max.
- Premium ULP: 50ppm sulphur max.

Centene Rating: indicates fuels tendency to burn spontaneously. High means detonates easily.

- Compared using Cetane (spontaneous combustion) and alpha-methyl naphthalene (slower burning).
- Cars ~50 Centene.
  Large engines down to ~30 Centene

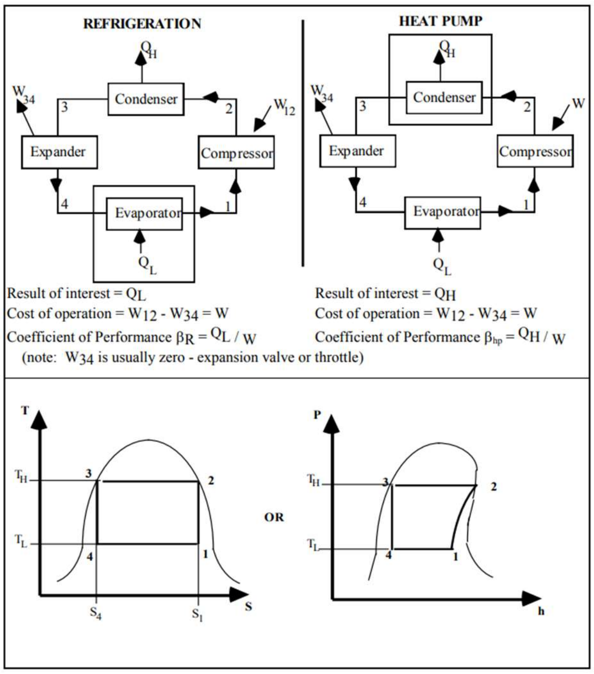
Envirnmental Impacts:

1. Ship Fuel: less emisions than regular fuels.
   But contribute to local harbor region.
   50 000 premature deaths in Europe due to ship pollution
2. Volkswagen scandal

Energy Content of Fuels:
Calorific Value:

- Measure content measured in KJ/kg (liquids) or MJ/m^3 (gases). Often higher and lower values are given.
- Higher Values = latent heat of vaporisation of water in exhaust if condensed.
- Lower Value = accounts for water vapor escaping, preferred by manufacturers for efficiency.

Refrigeration:



Types of Refrigeration:

- **Vapour Compression:** Most common and widely used.
- **Absorption Refrigeration:** Another popular method.

Other Methods: Steam jet, air cycle, and thermoelectric refrigeration.

Ideally modelled off the *reversed Carnot Cycle.*
Refrigerators: useful is the cooling QL relative to work in.
Heat Pumps: Heating QH to work in.

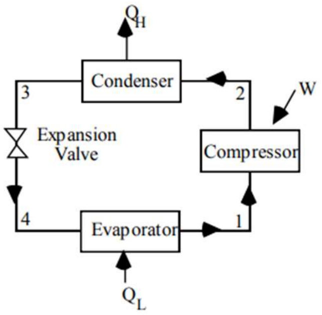
Coefficient of Performance (COP):

$$COP_R = \beta_R = \frac{Q_L}{W}$$

$$COP_{HP} = \beta_R = \frac{Q_H}{W}$$

$\beta_R = \frac{T_L}{T_H - T_L}$ and $\beta_{HP} = \frac{T_H}{T_H - T_L}$

Vapour Compression Cycle:

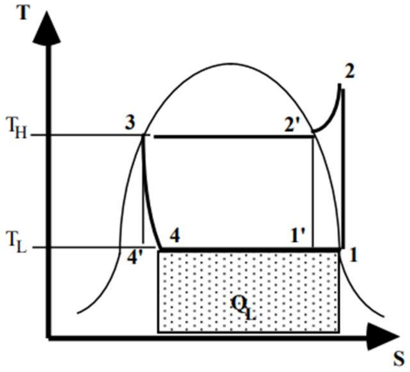


Stages 1-2: Compression refrigerant is compressed in superheated vapor state. Avoiding liquid entry to protect the compressor and maintain proper lubrication. Liquids in the compressor can cause damage, 2 problems:

1. Deprive compressor of lube
2. Surface films form on condenser parts

The work done in this cycle is: W = h2 – h1 = compressor work

Stages 2-3: Condensation.
Compressed vapor releases heat and becomes a saturated liquid by rejecting heat in the condenser.



The work done in this cycle is: W = h2 – h1 = compressor work

Stage 3-4: Expansion:
Refrigerant is *throttled* through an expansion valve

- Adiabatic and constant enthalpy.

Effects of a throttle:

1. Increases network (no work from expansion).
2. Cheaper (no engine)
3. Heat absorbed is reduced.
4. Heat rejection is NOT affected.
5. Reduces irreversibility and COP depends on working fluid.

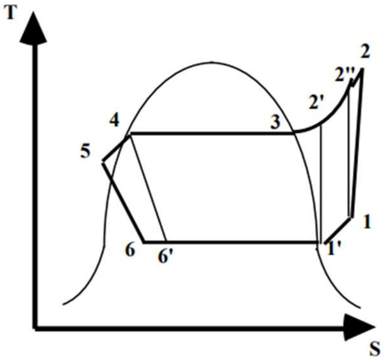
Stages 4-1: Evaporation: fluid evaporates at constant pressure.

QL = h1 – h4 = heat absorbed in evaporator.

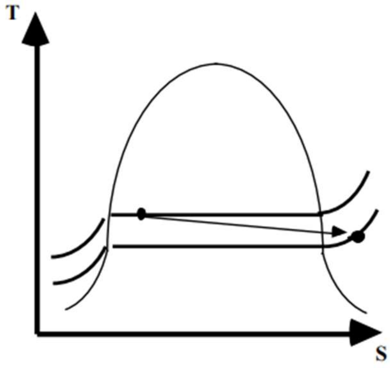
Real-World Deviations:

Practically there is lower COP and a decrease in the size of the evaporator for cooling effect.

1. Superheated Compression: no liquid enters the compressor introduces irreversibility (s2 - s1 > 0).
2. Sub-cooled liquid leaves condenser at point 5 = increases refrigeration.
3. Small pressure drops in condensers and evaporators.
4. Compressor work is greater than in the ideal cycle h2 - h1 > h2 ' - h1 '

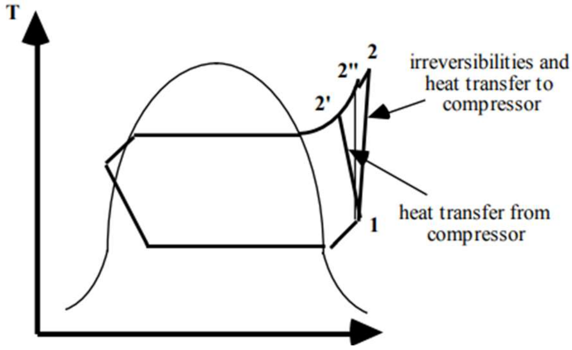


2.2.1 Pressure drops in evaporator and condenser

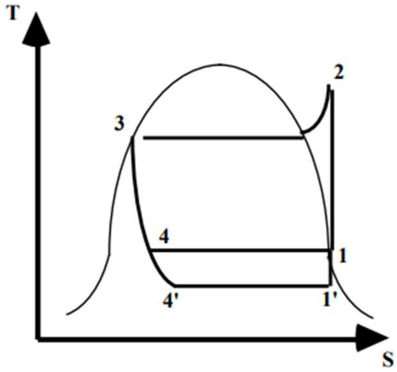


There are also pressure drops in the ductwork and the compressor inlet and outlet valves.

2.2.2 heat transfer to or from compressor



2.2.3 Effect of lowering evaporator temperature

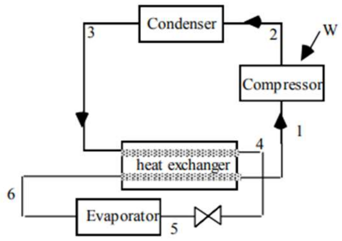


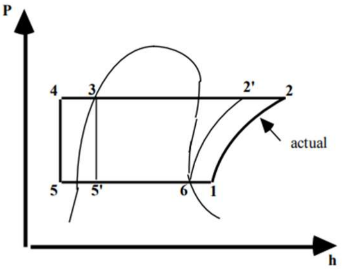
Lowering Evaporator Temp:

If the temp is lowered:

1. Volumetric efficiency decreases and mass flow rate decreases.
2. Work input increases per unit mass
3. Lowers overall refrigeration effect
4. Lowers COP.

Internal heat Exchanger: To avoid letting vapour into the compressor





- Increases refrigeration.
- Increases work input
- Small net effect on COP

Refrigerants

Desired Properties:

- High crit pressure (condensation at high pressure)
- High latent heat of vaporisation
- Low freezing point
- Good chemical stability, inert and low cost.
- Easy to spot leaking.

Examples of Refrigerants: (more found from ASHRAE)

- Traditional “Freons”: R12, R11, R13, R113, etc.
- Chlorine-Free Options: R134a, propane (R290), butane (R600), along with inorganic options like ammonia (NH_3) and carbon dioxide (CO_2).

Multistage Compression: utilizes multiple compression stages to improve efficiency and extend compressor life. Reduces pressure ratio at each stage.