- Recap: Lecture 23, 6th March 2014, 0930-1030 hrs.
 - -Properties of pure substances
 - Compressed liquid, saturated liquid, saturated vapour, superheated vapour
 - T-v, P-T diagrams
 - Critical point
 - Triple point
 - Property tables: saturated and superheated tables

Composition of a gas mixture

- Consider a gas mixture of k components.
- Let *mm* is the mass of the mixture and *Nm* is sum of the mole numbers.

$$m_m = \sum_{i=1}^k m_i \quad \text{and} \quad N_m = \sum_{i=1}^k N_i$$

- Mass fraction, *mf*, is the ratio of the mass of a component to the mass of the mixture
- Mole fraction, *Y*, is the ratio of the mole number of a component to the mole number of the mixture.

$$mf_i = m_i / m_m$$
 and $y_i = N_i / N_m$

Composition of a gas mixture

- The mass of a substance of mole number N and molar mass M is m = NM
- The average molar mass and gas constant:

$$M_{m} = \frac{m_{m}}{N_{m}} = \frac{\sum m_{i}}{N_{m}} = \frac{\sum N_{i}M_{i}}{N_{m}} = \sum_{i=1}^{k} y_{i}M_{i}$$

$$R_{m} = \frac{R_{u}}{M_{m}}$$

Mass and mole fractions of a mixture are related by

$$mf_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

P-v-T behaviour of gas mixtures

- Ideal gas equation of state with compressibility factor for real gases.
- The prediction of the P-v-T behaviour of gas mixtures based on two laws: Dalton's law of additive pressures and the Amagat's law of additive volumes.
- Dalton's law of additive pressures: The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume.

P-v-T behaviour of gas mixtures

- Amagat's law of additive volumes: The volume of a gas mixture is equal to the sum of the volumes each gas would occupy if it existed alone at the mixture temperature and pressure.
- Dalton's and Amagat's laws hold exactly for ideal-gas mixtures, but only approximately for real-gas mixtures.
- For ideal gases, these two laws are identical and give identical results.

P-v-T behaviour of gas mixtures

• Dalton's and Amagat's laws can be expressed as follows:

Dalton's law:
$$P_m = \sum_{i=1}^{\kappa} P_i(T_m, V_m)$$

Amagat's law:
$$V_m = \sum_{i=1}^k V_i(T_m, V_m)$$

- The above are exact for ideal gases, but approximate for real gases.
- *Pi* is called the component pressure and *Vi* is called the component volume.

Ideal gas mixtures

• For ideal gases, *Pi* and *Vi* can be related to the mole fraction *yi* by:

$$\frac{P_{i}(T_{m}, V_{m})}{P_{m}} = \frac{N_{i}R_{u}T_{m}/V_{m}}{N_{m}R_{u}T_{m}/V_{m}} = \frac{N_{i}}{N_{m}} = y_{i}$$

$$\frac{V_{i}(T_{m}, V_{m})}{V_{m}} = \frac{N_{i}R_{u}T_{m}/V_{m}}{N_{m}R_{u}T_{m}/V_{m}} = \frac{N_{i}}{N_{m}} = y_{i}$$
Therefore,
$$\frac{P_{i}}{P_{m}} = \frac{V_{i}}{V_{m}} = \frac{N_{i}}{N_{m}} = y_{i}$$

Ideal gas mixtures

- The quantity *yiPm* is called the partial pressure and the quantity *yiVm* is called the partial volume.
- For an ideal-gas mixture, the mole fraction, the pressure fraction, and the volume fraction of a component are identical.

Real gas mixtures

- Dalton's law of additive pressures and Amagat's law of additive volumes can also be used for real gases, with some approximations.
- We either use some of the advanced equations of state (like the Beattie–Bridgeman, Benedict–Webb–Rubin etc.)
- The other way is to use the compressibility factor: PV = ZNRuT

Real gas mixtures

• The compressibility factor of the mixture, Zm, can be expressed in terms of that of the constituents:

 $Z_m = \sum_{i=1}^m y_i Z_i$

• Here, Zi can be determined either at Tm and Vm (Dalton's law) or at Tm and Pm (Amagat's law) for each individual gas.

• It is however not necessary that both these methods give the same result

Properties of gas mixtures

- To evaluate the extensive properties of a non-reacting ideal or real gas mixture, we add the contributions of each component.
- The internal energy, enthalpy and entropy can be expressed as:

$$U_{m} = \sum_{i=1}^{k} U_{i} = \sum_{i=1}^{k} m_{i} u_{i}$$

$$H_{m} = \sum_{i=1}^{k} M_{i} = \sum_{i=1}^{k} m_{i} h_{i}$$

$$S_{m} = \sum_{i=1}^{k} S_{i} = \sum_{i=1}^{k} m_{i} S_{i}$$

Properties of gas mixtures

• The internal energy, enthalpy, and entropy of a mixture *per unit mass of the mixture can be determined by dividing the equations* above by the mass of the mixture:

$$u_m = \sum_{i=1}^k m f_i u_i \quad \text{and} \quad h_m = \sum_{i=1}^k m f_i h_i \quad \text{in (kJ/kg)}$$

$$s_m = \sum_{i=1}^k m f_i s_i \quad \text{(kJ/kg.K)} \quad \blacksquare$$

$$\text{Also, } c_{v,m} = \sum_{i=1}^k m f_i c_{v,i} \quad \text{(kJ/kg.K)} \quad \text{and } c_{p,m} = \sum_{i=1}^k m f_i c_{p,i}$$

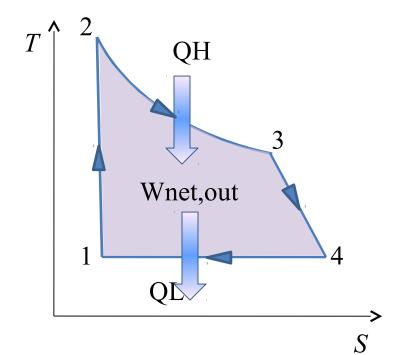
- Application of thermodynamics
 - Gas power cycles
 - Otto cycle, Diesel cycle, Stirling and Ericsson cycle,
 Brayton cycle, Rankine cycle
 - -Thermodynamic cycle of aero engines
 - -Brayton cycle analysis
 - -Ideal and real cycles

- Study of power cycles of immense importance in engineering.
- Actual cycles: irreversibilities (like friction etc.),not in thermodynamic equilibrium, non-quasi static processes etc.
- For thermodynamic analysis we assume none of the above effects present: ideal cycles
- Ideal cycle analysis starting point of in-depth analysis.

- The ideal cycles are internally reversible, but, unlike the Carnot cycle, they are not necessarily externally reversible.
- Hence, the thermal efficiency of an ideal cycle, in general, is less than that of a totally reversible cycle operating between the same temperature limits.
- But, the thermal efficiency is ideal cycles is higher than that of actual cycles.

- Gas power cycles are usually represented on *P-v* and *T-s* diagrams.
- On these diagrams the area enclosed by the process curves represent the net work done by the cycle.
- For a cyclic process this is also equal to the net heat transferred during the cycle.
- In an ideal power cycle, the only effect that can change the entropy of the working fluid during a process is heat transfer.

- On a T-s diagram, *Qin* proceeds in the direction of increasing entropy and *Qout* proceeds in the direction of decreasing entropy.
- The difference between areas under *Qin* and *Qout* is the net heat transfer, and hence the net work of the cycle.
- The ratio of the area enclosed by the cyclic curve to the area under the heat-addition process curve represents the thermal efficiency of the cycle.



Net heat input, QH = area under curve 2-3

Net work output,

Wnet = (area under curve 2-3)

– (area under curve 1-4)

Hence, thermal efficiency, $\eta th = Wnet/QH$

The Carnot cycle and its significance

- The Carnot cycle consists of four reversible processes: two reversible adiabatics and two reversible isotherms.
- Carnot efficiency is a function of the source and sink temperatures.

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

• The efficiency of a Carnot heat engine increases as *TH* is increased, or as *TL* is decreased.

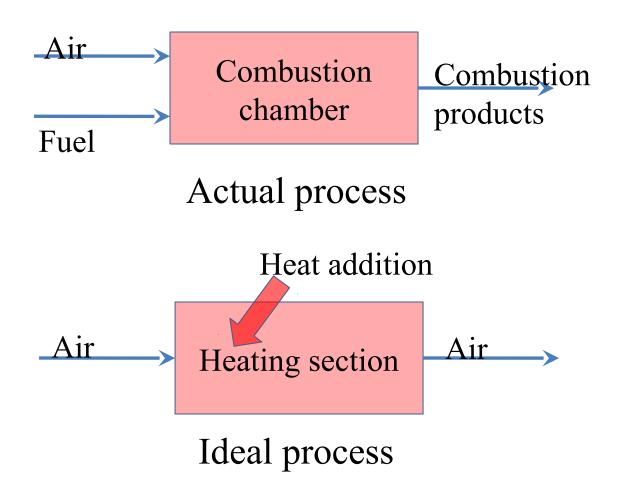
The Carnot cycle and its significance

- The Carnot cycle serves as a standard against which actual cycle performance can be compared.
- In practice the source and sink temperatures are also limited.
- Source temperature limited by the materials that are used in these devices.
- Sink temperature limited by the temperature of the medium to which heat is rejected like atmosphere, lake, oceans etc.

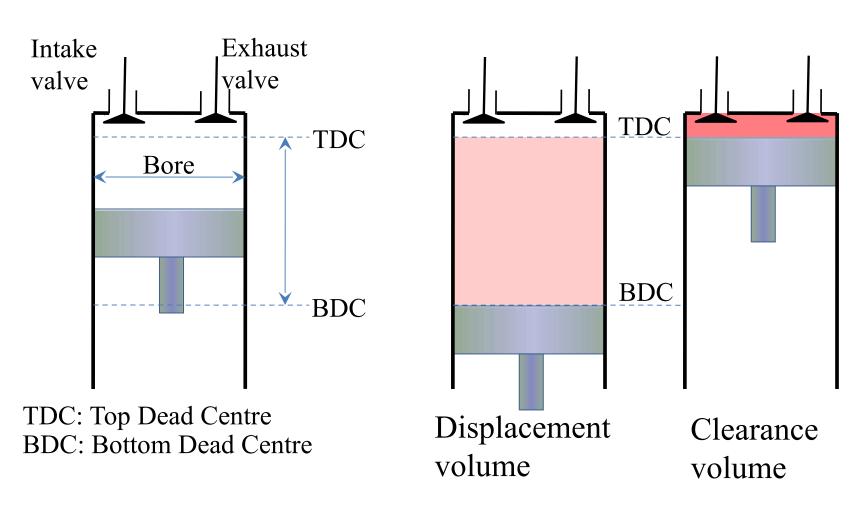
Air standard assumptions

- To simplify analysis, the following assumptions are made:
 - 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.

Air standard assumptions



- Reciprocating engines are one of the most commonly used power generating devices.
- These engines can operate on a variety of thermodynamic cycles.
- Piston and cylinder form the basic components of reciprocating engines, besides valves, connecting rods, flywheels and several other components.



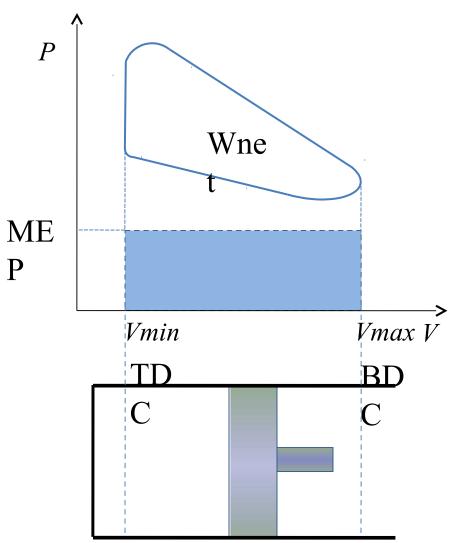
Nomenclature for reciprocating engines

- The minimum volume formed in the cylinder when the piston is at TDC is called the clearance volume.
- The volume displaced by the piston as it moves between TDC and BDC is called the displacement volume.
- The ratio of the maximum volume formed in the cylinder to the minimum (clearance) volume is called the compression ratio, r of the engine:

$$r = \frac{V_{\text{max}}}{V_{\text{min}}} = \frac{V_{BDC}}{V_{TDC}}$$

• Mean Effective Pressure (MEP): is a fictitious pressure that, if it acted on the piston during the entire power stroke, would produce the same amount of net work as that produced during the actual cycle.

$$MEP = \frac{W_{net}}{V_{\text{max}} - V_{\text{min}}} = \frac{w_{net}}{v_{\text{max}} - v_{\text{min}}}$$



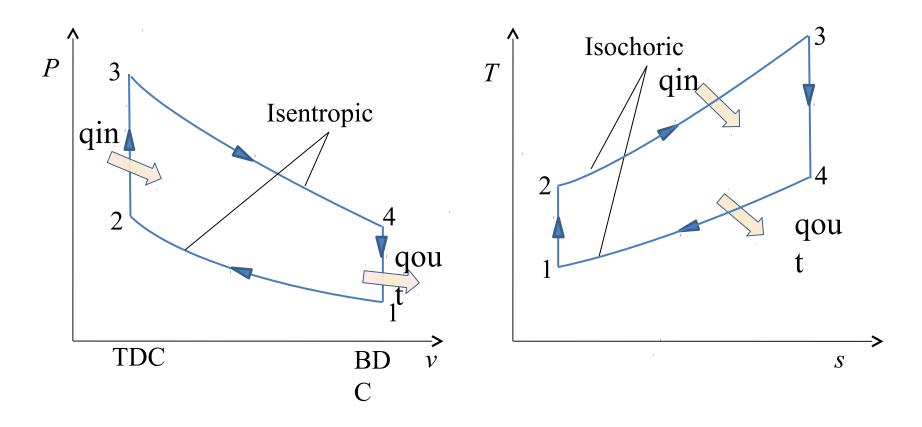
Wnet = MEP x (Vmax-Vmin)

The net work output of a cycle is equivalent to the product of the mean effective pressure and the displacement volume.

- Two types of reciprocating engines: Spark Ignition (SI) engines and Compression Ignition (CI) engines
- SI engines: the combustion of the air—fuel mixture is initiated by a spark plug.
- CI engines, the air—fuel mixture is self-ignited as a result of compressing the mixture above its self-ignition temperature.

- Otto cycle is the ideal cycle for spark-ignition reciprocating engines.
- Named after Nikolaus A. Otto, who built a successful four-stroke engine in 1876 in Germany.
- Can be executed in two or four strokes.
- Four stroke: Intake, compression, power and exhaust stroke
- Two stroke: Compression and power strokes.

- Otto cycle consists of four processes:
 - Isentropic compression (1-2)
 - Isochoric (constant volume) heat addition (2-3)
 - Isentropic expansion (3-4)
 - Isochoric (constant volume) heat rejection (4-1)
- All the processes are internally reversible.
- Currently we shall analyse the ideal Otto cycle.



Ideal Otto cycle on *P-v* and *T-s* diagrams

• Applying energy balance and assuming KE and PE to be zero:

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

The heat transfer to and from the working fluid can be written as:

$$q_{in} = u_3 - u_2 = c_v (T_3 - T_2)$$

$$q_{out} = u_4 - u_1 = c_v (T_4 - T_1)$$

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$
 and $s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$

For isentropic flows,

$$\ln \frac{T_2}{T_1} = -\frac{R}{c_v} \ln \frac{v_2}{v_1} \text{ or, } \ln \frac{T_2}{T_1} = \ln \left(\frac{v_2}{v_1}\right)^{R/c_v}$$

 $\sin ce$, $R = c_P - c_v$ and $\gamma = c_R c_v \rightarrow R/c_v = \gamma - 1$

$$\left| \therefore \left(\frac{T_2}{T_1} \right) = \left(\frac{v_1}{v_2} \right)^{\gamma - 1}$$

Similarly,
$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}$$
 and $\left(\frac{P_2}{P_1}\right) = \left(\frac{v_1}{v_2}\right)^{\gamma}$

In general, $Tv^{\gamma-1} = const.$, $TP^{(\gamma-1)/\gamma} = const.$, $Pv^{\gamma} = const.$

• The thermal efficiency of the ideal Otto cycle under the cold air standard assumptions becomes:

$$\eta_{th,Otto} = \frac{w_{net}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1(T_4 / T_1 - 1)}{T_2(T_3 / T_2 - 1)}$$

Processes 1 - 2 and 3 - 4 are isentropic and

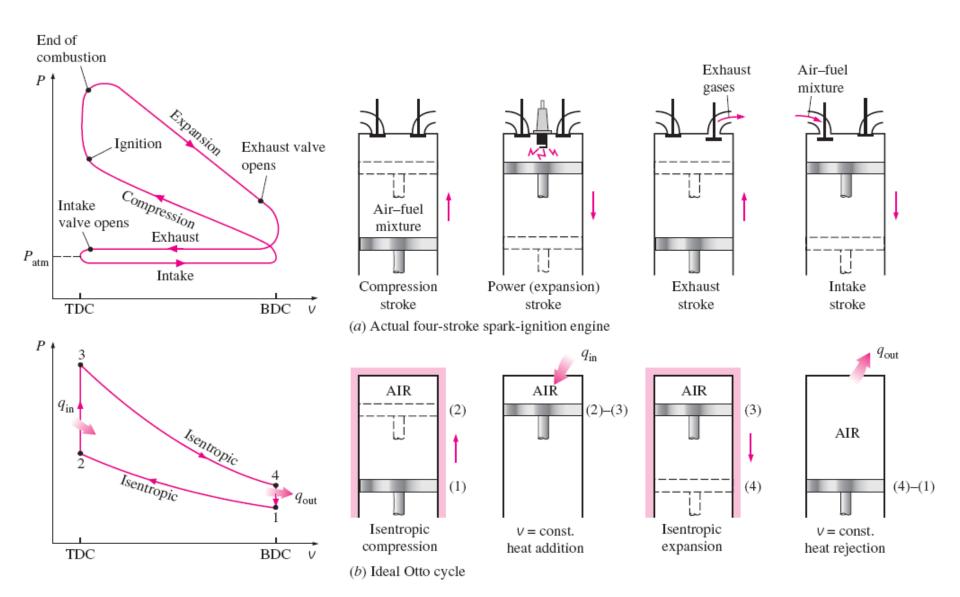
$$v_2 = v_3$$
 and $v_4 = v_1$.

Therefore,
$$\frac{T_1}{T_2} = \left(\frac{v_2}{v_1}\right)^{\gamma - 1} = \left(\frac{v_3}{v_4}\right)^{\gamma - 1} = \frac{T_4}{T_3}$$

• Substituting these equations into the thermal efficiency relation and simplifying:

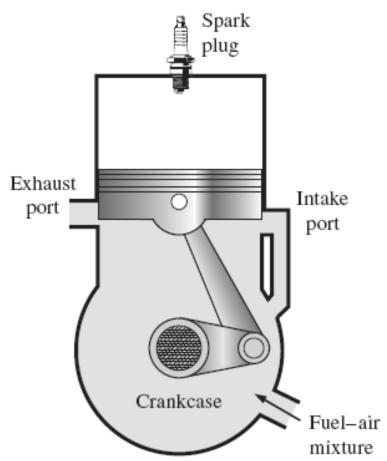
$$\eta_{th,Otto} = 1 - \frac{1}{r^{\gamma - 1}}$$
where, $r = \frac{V_{\text{max}}}{V_{\text{min}}} = \frac{V_1}{V_2} = \frac{v_1}{v_2}$ is the compression ratio.

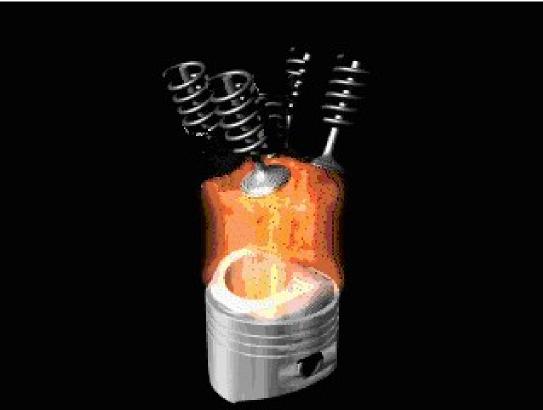
And γ is the ratio of specific heats c_n/c_v .



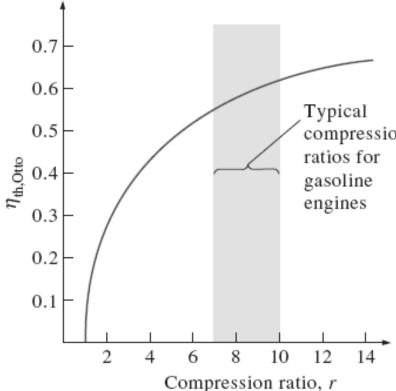
Ideal and actual Otto cycles

- In **two-stroke engines**, all four functions are executed in just two strokes: the power stroke and the compression stroke.
- The two-stroke engines are generally less efficient than their four-stroke counterparts
 - incomplete expulsion of the exhaust gases
 - partial expulsion of the fresh air—fuel mixture with the exhaust gases.
 - relatively simple and inexpensive
 - high power-to-weight and power-to-volume ratios
 - used in motorcycles, lawn movers, earlier generation ships etc.





Schematic of a two-stroke reciprocating engine.



Thermal efficiency of the ideal Otto cycle as a function of compression ratio (k = 1.4).

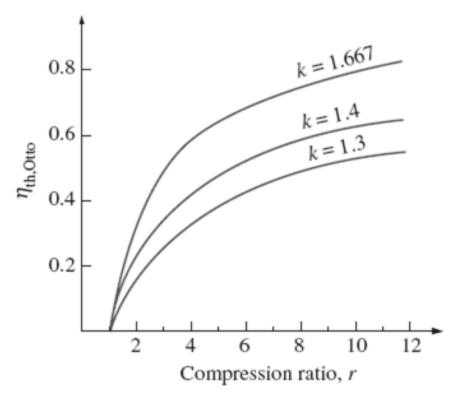
High compression: the temperature of the air—fuel mixture rises above the auto-ignition temperature of the fuel

Typical Causes an early and rapid burn of the fuel at compression some point or points ahead of the flame front

This premature ignition of the fuel, called **autoignition**, produces an audible noise, which is called **engine knock**.

Tetraethyl lead had been added to gasoline because it is an inexpensive method of raising the *octane rating*, *which is a measure of the* engine knock resistance of a fuel.

Leaded gasoline: releases toxic pollutants
Unleaded gasoline/petrol with high octane
rating



The thermal efficiency of the Otto cycle increases with the specific heat ratio *k* of the working fluid.

- Efficiency also depends upon the ratio of specific heats
- For air, $\gamma=1.4$
- At higher temperatures, it decreases