Lecture-17

The Second Law of thermodynamics

- The first law reflects the observation that energy is conserved, but it imposes no restriction on the process direction. Yet, all experience indicates the existence of such a restriction, the concise statement of which constitutes the second law.

- **Difference between work and heat:**

  → Work is readily transformed into other forms of energy: for example, into potential energy by elevation of a weight, into kinetic energy by acceleration of a mass. These processes can be made to approach a conversion efficiency of 100% by elimination of friction, a dissipative process that transforms work into heat. Indeed, work is readily transformed completely into heat, as demonstrated by Joule's experiments.

  → On the other hand, all efforts to devise a process for the continuous conversion of heat completely into work or into mechanical energy have failed. Evidently, heat is a form of energy intrinsically less useful and hence less valuable than an equal quantity of work.

- Joule's experiments amply demonstrate that energy, when supplied to a system in the form of work, Can be completely converted into heat. But the complete conversion of heat into work in a cycle is not possible. So, heat and work are not completely interchangeable forms of energy.

- Work is said to be a high grade energy and heat a low grade energy. The complete conversion of low grade energy into high grade energy in a cycle is impossible.

STATEMENTS OF THE SECOND LAW:

- The first law of thermodynamics states that a Certain energy balance will hold when a system undergoes a change of state or a thermodynamic process. But it does not give any information on whether that change of state or the process is at all feasible or not. The first law cannot indicate whether a metallic bar of uniform temperature can spontaneously become warmer at one end and cooler at the other. All that the law can state is that if this process did occur, the energy gained by one end would be exactly equal to that lost by the other.

It is the Second law of thermodynamics which provides the criterion as to the probability of various processes.

- Spontaneous processes in nature occur only in one direction. Heat always flows from a body at a higher temperature to a body at a lower temperature, water always flows downward. The reverse of these never happens spontaneously. The spontaneity of the process is due to a finite driving potential, sometimes called the 'force'. These processes can never spontaneously occur from a lower to a higher potential. This directional law puts a limitation on energy transformation other than that imposed by the first law.

Statements of the Second law

The Second law is equally well expressed in two statements that describe this restriction:

- **Statement 1:** No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert heat absorbed by a system completely into work done by the system.

(kelvin-planck statement of Second law)

- **Statement 2:** No process is possible which consists solely in the transfer of heat from one temperature level to a higher one.

(Clausius' statement of the second law)

Statement 1 does not say that heat cannot be converted into work; only that the process cannot leave both the system and its surroundings unchanged.

Statement 1 may be expressed in an alternative way:

Statement 1a It is impossible by a cyclic process to convert the heat absorbed by a system completely into work done by the system.

The word cyclic requires that the system be restored Periodically to its original state.

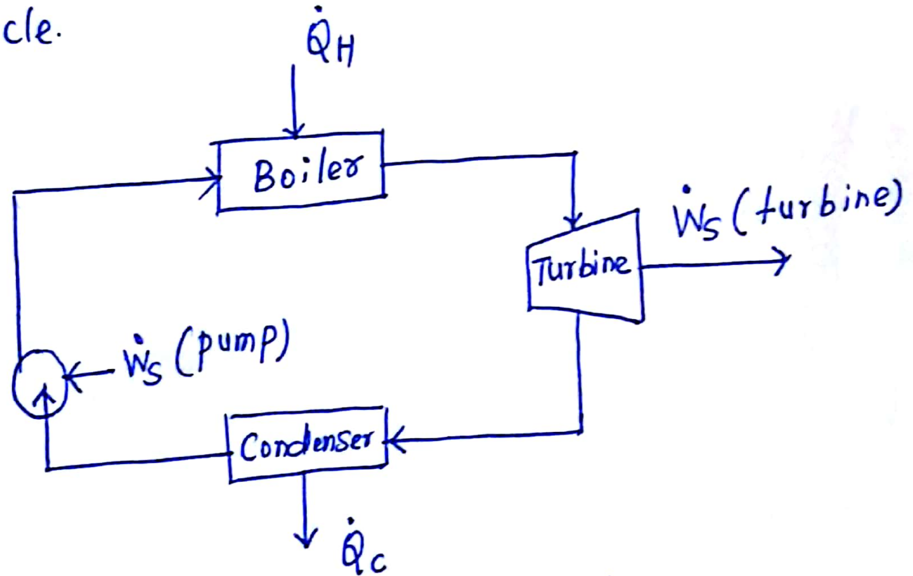
The Second law does not prohibit the production of work from heat, but it does place a limit on how much of the heat directed into a cyclic process can be converted into work done by the process.

Heat Engines :

The classical approach to the second law is based on a macroscopic viewpoint of properties, independent of any knowledge of the structure of matter or behaviour of molecules. It arose from the study of heat engines, devices or machines that produce work from heat in a cyclic process. An example is a steam power plant in which the working fluid (H_2O) periodically returns to its original state. This cycle (in its simplest form) consists of the following steps:

- Liquid water from a condenser is pumped into a boiler at elevated pressure.
- Heat from a fuel is transferred in the boiler to the water, converting it to high-temperature steam at the boiler pressure.

- Energy is transferred as shaft work from the steam to the surroundings by a device such as a turbine, in which the steam expands to reduced pressure and temperature.
- Exhaust steam from the turbine is condensed by transfer of heat to the surroundings, producing liquid water for return to the boiler, thus completing the cycle.



Simple steam power plant

Essential to all heat-engine cycles are absorption of heat into the system at a high temperature, rejection of heat to the surroundings at a lower temperature, and production of work.

In the theoretical treatment of heat engines, the two temperature levels which characterize their operation are maintained by heat reservoirs, bodies imagined capable of absorbing or rejecting unlimited quantities of heat without temperature change. In operation, the working fluid of a heat engine absorbs heat Q_H from a hot reservoir, produces a net amount of work W, discards heat Q_C to a cold reservoir, and returns to its initial state. The first law therefore reduces to:

$$W = Q_H - Q_C \longrightarrow (1)$$

The thermal efficiency of the engine is defined as:

$$\eta \equiv \frac{\text{net work output}}{\text{heat absorbed.}}$$

Thus,

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \longrightarrow (2)$$

For 'η' to be unity (100% thermal efficiency), Q_C must be zero. No engine has ever been built that approaches this result; heat is always rejected to the cold reservoir. This observation from engineering experience is the basis for statements 1 and 1a of the second law.

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If a thermal efficiency of 100% is not possible for heat engines, what then determines the upper limit? one would certainly expect the thermal efficiency of a heat engine to depend on the degree of reversibility of its operation. Indeed, a heat engine operating in a completely reversible manner is very special, and is called a carnot engine. The characteristics of such an ideal engine were first described by N.L.S. Carnot in 1824. The four steps that make up a carnot cycle are performed in the following order:

- **Step 1:** A system at an initial temperature of a cold reservoir at 'T_C' undergoes a reversible adiabatic process that causes its temperature to rise to that of a hot reservoir at 'T_H'.

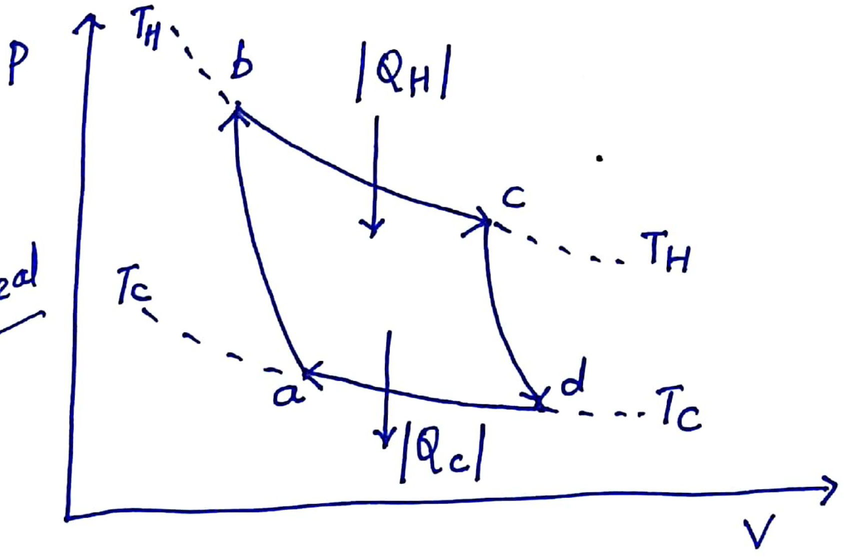
- **step 2:** The system maintains contact with the hot reservoir at 'T_H', and undergoes a reversible isothermal process during which heat '$|Q_H|$' is absorbed from the hot reservoir.

- **step 3:** The system undergoes a reversible adiabatic process in the opposite direction of step 1 that brings its temperature back to that of the cold reservoir at 'T_C'.

Step4: The system maintains contact with the reservoir at 'T_c', and undergoes a reversible isothermal process in the opposite direction of step 2 that returns it to its initial state with rejection of heat $|Q_c|$ to the cold reservoir.

* This set of processes can in principle be performed on any kind of system.

The cycle traversed by an ideal gas serving as the working fluid in a carnot engine is shown by a PV diagram



PV diagram showing carnot cycle for an ideal gas

It consists of four reversible processes corresponding to steps 1 through 4 of the general carnot cycle described in the preceding section:

- $a \rightarrow b$ Adiabatic compression until the temperature rises from T_C to T_H.
- $b \rightarrow c$ Isothermal expansion to arbitrary point 'c' with absorption of heat $|Q_H|$.
- $c \rightarrow d$ Adiabatic expansion until the temperature decreases to T_C.
- $d \rightarrow a$ Isothermal compression to the initial state with rejection of heat $|Q_C|$.

For the isothermal step $b \rightarrow c$:

$$Q_H + W = \underset{0}{\underset{\downarrow}{\Delta U}}$$

$$Q_H + W = 0 \Rightarrow Q_H = -W$$

$$W = -\int_{V_b}^{V_c} P\,dV = -RT_H \int_{V_b}^{V_c} \frac{dV}{V} = -RT_H \ln \frac{V_c}{V_b}$$

$$\therefore \boxed{Q_H = RT_H \ln \frac{V_c}{V_b}} \longrightarrow (1)$$

For the isothermal step $d \rightarrow a$:

$$W = -\int_{V_d}^{V_a} P\,dV = -RT_C \ln \frac{V_a}{V_d}$$

$$Q_C + W = \Delta U = 0 \Rightarrow Q_C = -W = RT_C \ln \frac{V_a}{V_d}$$

$$\boxed{Q_C = RT_C \ln \frac{V_a}{V_d}} \longrightarrow (2)$$

Now, $$\frac{Q_c}{Q_H} = \frac{T_c \ln(V_a/V_d)}{T_H \ln(V_c/V_b)} \longrightarrow (3)$$

For adiabatic process:

$$\underset{\substack{\downarrow \\ 0}}{dQ} + \underset{\substack{\downarrow \\ -PdV}}{dW} = dU \longrightarrow C_V dT$$

$$-PdV = C_V dT$$

$$\Rightarrow -RT\frac{dV}{V} = C_V dT$$

$$\Rightarrow \quad \frac{dV}{V} = -\frac{C_V}{R}\frac{dT}{T} \longrightarrow (4)$$

For step a→b:

$$\int_{V_a}^{V_b} \frac{dV}{V} = -\frac{C_V}{R}\int_{T_C}^{T_H} \frac{dT}{T}$$

$$\ln\frac{V_b}{V_a} = -\frac{C_V}{R}\ln\frac{T_H}{T_C} \longrightarrow (5)$$

For step c→d:

$$\int_{V_c}^{V_d} \frac{dV}{V} = -\frac{C_V}{R}\int_{T_H}^{T_C} \frac{dT}{T}$$

$$\ln\frac{V_d}{V_c} = -\frac{C_V}{R}\ln\frac{T_C}{T_H} = +\frac{C_V}{R}\ln\frac{T_H}{T_C} \longrightarrow (6)$$

Comparing (5) & (6), $\ln\left(\frac{V_d}{V_c}\right) = \ln\left(\frac{V_a}{V_b}\right)$

$$\ln V_d - \ln V_c = \ln V_a - \ln V_b$$

$$\Rightarrow \ln V_b - \ln V_c = \ln V_a - \ln V_d$$

$$\Rightarrow \ln \frac{V_b}{V_c} = \ln \frac{V_a}{V_d}$$

$$\Rightarrow \frac{\ln (V_a/V_d)}{\ln (V_c/V_b)} = -1 \longrightarrow (7)$$

From, (3) $$\frac{Q_C}{Q_H} = -\frac{T_c}{T_H}$$

$$\frac{|Q_C|}{|Q_H|} = \frac{T_c}{T_H} \longrightarrow (8)$$

Therefore,

Thermal efficiency, $\eta = \frac{|W|}{|Q_H|} = 1 - \left|\frac{Q_c}{Q_H}\right|$

$$\boxed{\eta = 1 - \frac{T_c}{T_H}} \longrightarrow (9)$$

Eq^n. (9) shows that the thermal efficieny of a Carnot engine can approach unity only when T_H approaches infinity or T_c approaches zero. Neither condition exists on earth. The cold reservoirs available on earth are the atmosphere, lakes and rivers, and the oceans, for which $T_c \simeq 300K$. Hot reservoirs are objects such as furnaces where the temperature is maintained by combustion of fossil fuels and nuclear reactors where the temperature is maintained by combustion of fossil fuels. For these, $T_H \simeq 600\,K$.

with these values, $\eta = 1 - \frac{300}{600} = 0.5$, an approximate limit for the thermal efficiency of a Carnot engine. Actual heat engines are irreversible, and 'η' rarely exceeds 0.35.

Example: A power plant, rated at 800,000 kW, generates steam at 585K and discards heat to a river 295K. If the thermal efficiency of the plant is 70% of the maximum possible value, how much heat is discarded to the river at rated power?

Solution: The maximum possible thermal efficiency is

$$\eta_{max.} = 1 - \frac{T_C}{T_H} = 1 - \frac{295}{585} = 0.4957$$

Actual efficiency $= 0.70\,\eta_{max} = (0.70)(0.4957) = 0.3470$

we also have, $\eta = \frac{|W_{net}|}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|}$

$$\Rightarrow \eta = 1 - \frac{|Q_C|}{|W_{net}| + |Q_C|}$$

$$\Rightarrow \frac{|Q_C|}{|W_{net}| + |Q_C|} = 1 - \eta = 0.653$$

$\Rightarrow \quad |Q_c| = 0.653|W_{net}| + 0.653|Q_c|$

$\Rightarrow \quad (1-0.653)|Q_c| = 0.653|W_{net}|$

$$\Rightarrow \quad |Q_c| = 0.653\frac{|W_{net}|}{0.347} = \frac{0.653 \times 800,000 \text{ KW}}{0.347}$$

$$\underline{\underline{|Q_c| = 1505476 \text{ KW}}}$$

Lecture-19

Entropy

Equation (8) for a Carnot engine may be written as.

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C}$$

The numerical value of Q_H is positive and that of Q_c is negative. The equivalent equation written without absolute-value signs is therefore

$$\frac{Q_H}{T_H} = -\frac{Q_C}{T_C}$$

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \longrightarrow (10)$$

Thus for a complete cycle of a Carnot engine, the two quantities Q/T associated with the absorption and rejection of heat by the working fluid of the engine sum to zero. The working fluid of a cyclic engine periodically returns to its initial state, and its properties, e.g., temperature, pressure and internal energy, return to their initial values. Indeed, a primary characteristic of a property is that the sum of its changes is zero for any complete cycle.

Thus, for a Carnot cycle eq^n. (10) suggests the existence of a property whose changes are given by the quantities Q/T.

Thus, (10) may be written as -

$$\oint \frac{dQ_{rev}}{T} = 0 \longrightarrow (11)$$

where the circle in the integral sign signifies integration over the cycle and the subscript "rev" indicates that the cycle is reversible.

Thus the quantities $\frac{dQ_{rev}}{T}$ sum to zero for the cycle, exhibiting the characteristic of a property. The property is called entropy and its differential changes are

$$ds^t = \frac{dQ_{rev}}{T} \longrightarrow (12)$$

where s^t is the total entropy of the system.

Alternatively, $dQ_{rev} = T ds^t \longrightarrow (13)$

* Δs^t is independent of path and is a property change.

* If the process is reversible and adiabatic, $dQ_{rev} = 0$; then $ds^t = 0$. Thus, the entropy of a system is constant during a reversible adiabatic process, and the process is said to be isentropic.

The discussion of entropy can be summarized as follows:

→ Entropy owes its existence to the second law, from which it arises in much the same way as internal energy does from the first law. Equation (12) is the ultimate source of all equations that relate the entropy to measurable quantities. It does not represent a definition of entropy; there is none in the context of classical thermodynamics. what it provides is the means for calculating changes in this property. Its essential nature is summarized by the following axiom:

There exists a property called entropy 'S', which is an intrinsic property of a system, functionally related to the measurable coordinates which characterize the system. For a reversible process, changes in this property are given by-

$$dS^t = \frac{dQ_{rev}}{T}$$

→ The change in entropy of any system undergoing a finite reversible process is-

$$\Delta S^t = \int \frac{dQ_{rev}}{T} \longrightarrow (14)$$

* the entropy change of a system caused by the transfer of heat can always be calculated by $\int dQ/T$, whether the heat transfer is accomplished reversibly or irreversibly.

→ when a system undergoes an irreversible process between two equilibrium states, the entropy change of the system is evaluated by application of Eq.(14) to an arbitrarily chosen reversible process that accomplishes the same change of state as the actual process. Integration is not carried out for the irreversible path. Because entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.

Mathematical statement of the second law:

Consider two heat reservoirs, one at temperature T_H and a second at the lower temperature T_c. Let a quantity of heat 'Q' be transferred from the hotter to the cooler reservoir. The entropy changes of the reservoirs at T_H and at T_C are:

$$\Delta S_H^t = \frac{-|Q|}{T_H} \quad \text{and} \quad \Delta S_C^t = \frac{|Q|}{T_c}$$

These two entropy changes are added to give-

$$\Delta S_{total} = \Delta S_H^t + \Delta S_C^t$$

$$= \frac{-|Q|}{T_H} + \frac{|Q|}{T_c} = |Q|\left(\frac{1}{T_C} - \frac{1}{T_H}\right)$$

$$= \frac{|Q|(T_H - T_c)}{T_H T_c}$$

Because $T_H > T_C$, the total entropy change as a resut of this irreversible process is positive. Also, ΔS_{total} becomes smaller as the difference $T_H - T_C$ gets smaller. when T_H is only infinitesimally higher than T_C, the heat transfer is reversible, and ΔS_{total} approaches zero. Thus for the process of irreversible heat transfer, ΔS_{total} is always positive, approaching zero as the process becomes reversible.

* Every process proceeds in such a direction that the total entropy change associated with it is positive, the limiting value of zero being attained only by a reversible process. No process is possible for which the total entropy decreases.

$$\boxed{\Delta S_{total} \geq 0}$$

$$\boxed{\Delta S_{system} + \Delta S_{surroundings} \geq 0}$$

Ex. A 40-kg steel casting ($C_p = 0.5\ \mathrm{kJ\,kg^{-1}\,K^{-1}}$) at a temperature of 450°c (723.15K) is quenched in 150 kg of oil ($C_p = 2.5\ \mathrm{kJ\,kg^{-1}\,K^{-1}}$) at 25°c. If there are no heat losses, what is the change of entropy of (a) the casting, (b) the oil, and (c) both considered together?

Solution: The final temperature 't' of the oil and the steel casting is found by an energy balance.

$$(40)(0.5)(450-t) = (150)(2.5)(t-25)$$

$$\Rightarrow \quad 20(450-t) = 375(t-25)$$

$$\Rightarrow \quad 9000 - 20t = 375t - 9375$$

$$\Rightarrow \quad 9000 + 9375 = 375t + 20t = \cancel{355t}\ 395t$$

$$t = 46.52°\mathrm{C}.$$

(a) change in entropy of the casting:

$$\Delta s^t = m\int_{T_1}^{T_2} \frac{C_p\,dT}{T} = mC_p \ln\frac{T_2}{T_1}$$

$$= (40)(0.5)\ln\frac{273.15+46.52}{273.15+450}$$

$$= -16.33\ \mathrm{kJ/K}.$$

(b) change in entropy of the oil:

$$\Delta s^t = (150)(2.5)\ln\frac{273.15+46.52}{273.15+25} = 26.13\ \mathrm{kJ/K}.$$

(c) Total entropy change:

$$\Delta S_{total} = -16.33 + 26.13$$
$$= \underline{\underline{9.8 \text{ kJ/K}}}.$$

Carnot's Theorem:

For two given heat reservoirs no engine can have a thermal efficiency higher than that of a Carnot engine.

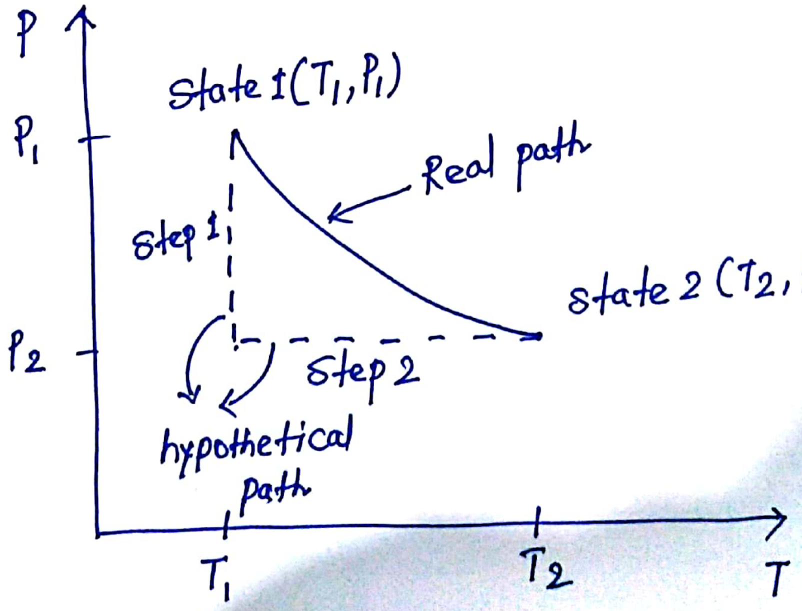
Corollary to Carnot's theorem:

The thermal efficiency of a Carnot engine depends only on the temperature levels and not upon the working substance of the engine.

Lecture-20

Calculation of ΔS for an ideal gas:

This Section illustrates how to calculate the change in entropy of an ideal gas between two states if 'P' and 'T' for each state are known. we will define the initial state as state 1, at P_1 and T_1, and the final state as state 2, at ~~st~~ P_2 and T_2. Since entropy is a state function, we can construct any path that is convenient between state 1 and state 2 to calculate ΔS. figure illustrates such a hypothetical path. we choose a reversible process for our hypothetical path so that we can apply the definition of entropy. The first step consists of isothermal expansion, while the second step is isobaric heating. To find ΔS, we will calculate the entropy change for each step and add them together. Details of the analysis for each step follow.



Step 1: Reversible, isothermal expansion.

The change in internal energy for an ideal gas is zero; thus, the differential energy balance is:

$$dU = dQ_{rev} + dW_{rev} = 0$$

$$\Rightarrow \quad dQ_{rev} = -dW_{rev} = PdV$$

Thus,

$$\Delta S_{step1} = \int \frac{dQ_{rev}}{T} = \int \frac{P}{T} dV$$

Using the ideal gas law,

$$\frac{P}{T} = \frac{R}{V}$$

$$= \int_{V_1}^{RT_1/P_2} \frac{R}{V} dV$$

$$= ~~R \ln \frac{RT_1}{P_2}~~$$

$$= R \ln\left(\frac{RT_1}{P_2 V_1}\right)$$

$$= R \ln\left(\frac{P_1 V_1}{P_2 V_1}\right)$$

$$= R \ln\left(\frac{P_1}{P_2}\right) = -R \ln\left(\frac{P_2}{P_1}\right)$$

[For step 1:

$P_1 V_1 = RT_1$

& $P_2 V = RT_1$ (at the end of state 1]

$P_1 V_1 = P_2 V$

$\Rightarrow V = \frac{P_1 V_1}{P_2} = \frac{RT_1}{P_2}$]

Step 2: Reversible, isobaric heating.

Applying the first law gives:

$$dU = dQ_{rev} + dW_{rev} = dQ_{rev} - PdV$$

$$\Rightarrow dQ_{rev} = dU + PdV$$
$$= dU + PdV + VdP$$
$$= dU + d(PV)$$
$$= d(U+PV) = dH$$

Thus,

$$\Delta S_{step2} = \int \frac{dQ_{rev}}{T} = \int \frac{dH}{T} = \int_{T_1}^{T_2} \frac{C_p\, dT}{T}$$

Therefore,

$$\Delta S = \Delta S_{step1} + \Delta S_{step2}$$

$$\boxed{\Delta S = \int_{T_1}^{T_2} \frac{C_p\, dT}{T} - R \ln\left(\frac{P_2}{P_1}\right)}$$

The above equation is true for the entropy change associated with an ideal gas between state 1 and state 2. In this expression, ΔS just depends on other properties, C_p, T, P - so it is independent of path. Therefore, the above equation can be applied to any process, be it reversible or irreversible.

Example : A piston-cylinder device initially contains 0.5 m^3 of an ideal gas at 150 kpa and 20°C. The gas is subjected to a constant external pressure of 400 kpa and compressed in an isothermal process. Assume the surroundings are at 20°C. Take $C_p = 2.5R$ and assume the ideal gas model holds.

(a) Determine the heat transfer (in KJ) during the process.

(b) what is the entropy change of the system, surroundings, and universe?

(c) Is the reversible, irreversible or impossible?

Soln: (a) Applying 1st Law of thermodynamics,

$$\Delta U = Q + W$$

Since the process is isothermal, $\Delta U = 0$

$$\Rightarrow Q = -W = +P_{ext}(V_2 - V_1)$$

For ideal gas at const. temp.

$$P_1 V_1 = P_2 V_2$$

$$\therefore V_2 = \frac{P_1 V_1}{P_2}$$

Thus, $Q = -W = +P_2\left[\frac{P_1V_1}{P_2} - V_1\right]$

$= \cancel{+P_1V_1 + P_2V_1} \quad P_1V_1 - P_2V_1$

$= \cancel{V_1(P_2 - P_1)} = V_1(P_1 - P_2)$

$= \cancel{(0.5m^3)(} \quad = (0.5m^3)(150-450)\,kpa$

$= \underline{\underline{-125\,kJ}}$

(b) Entropy change of the system is-

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{C_p dT}{T} - R\ln\left(\frac{P_2}{P_1}\right)$$

As Cp is constant & Temp. is constant, the first term is Zero.

$$\Delta S_{sys} = -R\ln\left(\frac{P_2}{P_1}\right) = -8.314 \times \ln\left(\frac{400}{150}\right) \ J/mol.K.$$

$$= -8.15 \ J/mol.K.$$

Thus, Total entropy change of the system,

$$= n\,\Delta S_{sys} = \left(\frac{PV}{RT}\right)_1 \Delta S_{sys}$$

$$= \frac{(150\times10^3\,pa)(0.5\,m^3)}{(8.314\,J/mol.k)(293\,K)} \times -8.15\,\frac{J}{K}$$

$$= -0.25\,\frac{KJ}{K}$$

The entropy change of the surroundings:

$$\Delta S_{surr} = \frac{Q_{surr}}{T} = -\frac{Q_{sys}}{T} = \frac{125\ kJ}{293\ K} = 0.43\ \frac{kJ}{K}$$

The entropy change of the universe is equal to that of the system and the surroundings:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

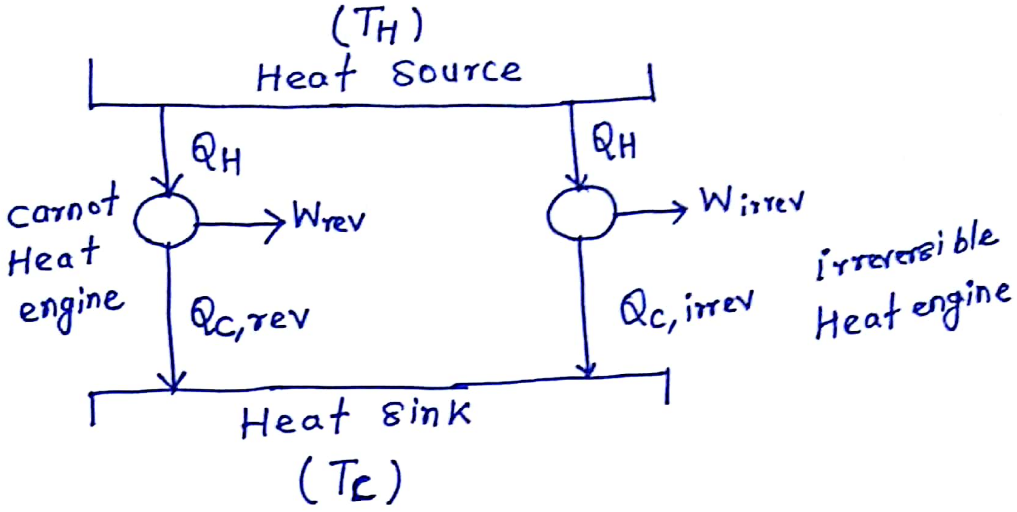
$$= -0.25 + 0.43$$

$$= 0.18\ \frac{kJ}{K}$$

(c) Since ~~th~~ entropy of the universe increases, this process is irreversible.

(Lecture-

Clausius Inequality:



Consider two heat engines, one a reversible (carnot) engine and the other an irreversible heat engine. Assume that both engines accept the same amount of heat 'Q_H' from the heat source. Since the irreversible engine must be less efficient than the carnot engine, it must reject more heat to the sink than that rejected by the carnot engine. i.e. $Q_{c,irrev} > Q_{c,rev}$.

Let $dQ = Q_{c,irrev} - Q_{c,rev}$

For carnot heat Engine:

$$\oint \frac{dQ}{T} = \frac{|Q_H|}{T_H} - \frac{|Q_c|}{T_C}$$

But for an ideal gas, as a working fluid, $\frac{|Q_H|}{T_H} = \frac{|Q_c|}{T_C}$

Thus $\oint \frac{dQ}{T} = 0.$ [For Reversible heat engine].

The cyclic integral for an irreversible heat engine:

$$\oint \frac{dQ}{T} = \frac{Q_H}{T_H} - \frac{Q_{c,irrev}}{T_c}$$

$$= \frac{Q_H}{T_H} - \left[\frac{Q + Q_{c,rev}}{T_c}\right]$$

$$= \frac{Q_H}{T_H} - \frac{Q}{T_c} - \frac{Q_{c,rev}}{T_c}$$

$$= \underbrace{\left[\frac{Q_H}{T_H} - \frac{Q_{c,rev}}{T_c}\right]}_{\oint \frac{dQ}{T} = 0 \text{ for reversible cycle}} - \frac{Q}{T_c}$$

$$= -\frac{Q}{T_c}$$

i.e $\boxed{\oint \frac{dQ}{T} < 0}$

Thus, for any reversible or irreversible heat Engine,

$$\boxed{\oint \frac{dQ}{T} \leq 0} \longrightarrow \text{clausius Inequality.}$$

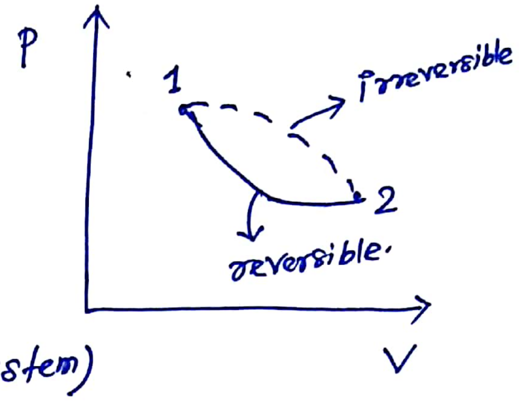
for reversible process: $\boxed{ds = \frac{dQ_{rev}}{T}}$

Assume reversible and irreversible paths between two states.

'dU' will be same for both the ~~parts.~~ paths.

Thus, $dU = dQ_{irrev.} + dW_{irrev.} = dQ_{rev} + dW_{rev}$

$\Rightarrow dQ_{rev} - dQ_{irrev.} = dW_{irrev.} - dW_{rev}$



Since, $dW_{irrev.} > dW_{rev.}$

('dW' is work done on the system)

$\Rightarrow dQ_{rev} - dQ_{irrev} \geq 0$

$$\Rightarrow \underbrace{\frac{dQ_{rev}}{T}}_{dS} \geq \frac{dQ_{irrev}}{T}$$

$$\Rightarrow \boxed{dS \geq \frac{dQ_{irrev}}{T}} \longrightarrow \text{clausius inequality.}$$

For an isolated system,

$dQ_{irrev} = 0$

Thus, $\boxed{dS \geq 0}$

i.e. entropy of an isolated system can never decrease. It always increases and remains constant only when the process is reversible. This is known as the principle of increase of entropy. It is the quantitative statement of the second law.

Helmholtz and Gibbs Energies

We had to consider the entropy change of both the system and its surroundings to determine the sign of $\Delta S_{universe}$ and establish whether a process is spontaneous or not. Although of great fundamental and theoretical importance, the criterion that $dS \geq 0$ for a spontaneous process is too restrictive for practical applications.

Let's consider a system with its volume and temperature held constant. The criterion that $dS \geq 0$ for a spontaneous process does not apply to a system at constant temperature and volume because the system is not isolated.; If the criterion $dS \geq 0$ does not apply, then what is the criterion for a spontaneous process that we can use for a system at constant temperature and volume?

Let's start with the expression of the First Law of thermodynamics,

$$dU = dQ + dW \longrightarrow (1)$$

$$dW = -PdV$$

since $V = const$; $dW = 0$

From clausius inequality,

$$dS \geq \frac{dQ}{T} \Rightarrow dQ \leq TdS$$

Thus, from (1),

$$dU \leq TdS \quad \text{(constant 'V')}$$

$\Rightarrow$ ~~$dU \leq T$~~ $dU - TdS \leq 0$

$$\Rightarrow dU - d(TS) \leq 0 \quad \text{(constant 'T')}$$

$$\Rightarrow d(\underbrace{U - TS}) \leq 0$$

$$\boxed{A = U - TS} \longrightarrow (2)$$

$\hookrightarrow$ Helmholtz energy (Thermodynamic state function)

$$\Rightarrow \boxed{dA \leq 0} \quad \text{(constant 'T' \& 'V')} \longrightarrow (3)$$

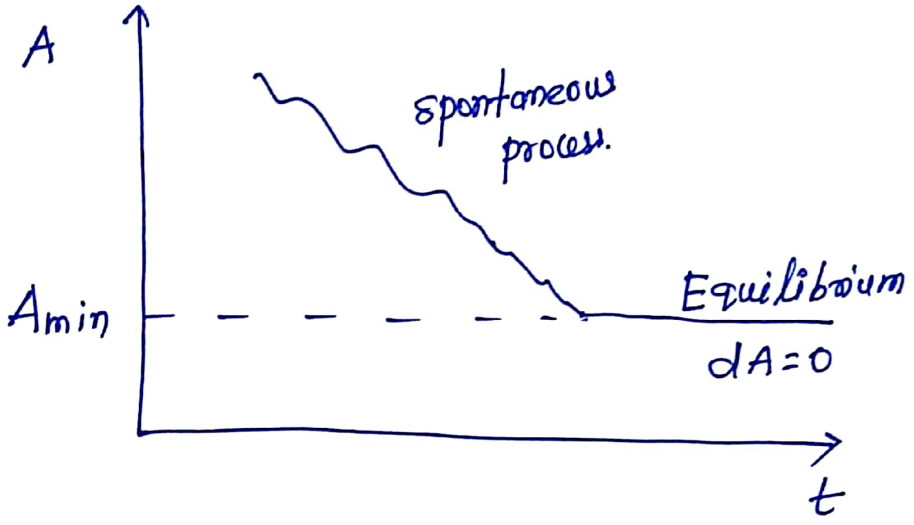
It is the analog of the criterion that $dS \geq 0$ for a spontaneous process to occur in an isolated system

In a system held at constant 'T' and 'V', the Helmholtz energy will decrease until all the possible spontaneous processes have occurred, at which time the system will be in equilibrium and 'A' will be a minimum. At equilibrium $dA = 0$.

For an isothermal change from one state to another,

$$\Delta A = \Delta U - T\Delta S \longrightarrow (4)$$

& $$\Delta A = \Delta U - T\Delta S \leq 0 \text{ (at constant 'T' \& 'V')} \longrightarrow (5)$$



For a reversible path, $\Delta S = \frac{q_{rev}}{T}$

Thus, from (4),

$$\Delta A = \Delta U - q_{rev}$$

But from first law, $q_{rev} + W_{rev} = \Delta U$

$$\Delta U - q_{rev} = W_{rev}$$

Thus, $$\boxed{\Delta A = W_{rev}} \text{ (isothermal, reversible)} \longrightarrow (6)$$

If $\Delta A < 0$, the process will occur spontaneously and W_{rev} represents the work that can be done by the system if this change is carried out reversibly. This quantity is the maximum work that could be obtained.

If $\Delta A > 0$, the process will not occur spontaneously and W_{rev} represents the work that must be done on the system to produce the change in a reversible manner.

Most reactions occur at constant pressure rather than at constant volume because they are open to the atmosphere. Let's see what the criterion of spontaneity is for a system at constant temperature and pressure.

From 1st law,

$$dQ + dW = dU$$

$$\Rightarrow dQ - PdV = dU$$

$$\Rightarrow dQ = dU + PdV$$

since, ~~dQ~~ $dS \geq \frac{dQ}{T}$

$$\Rightarrow dQ \leq TdS$$

$$\Rightarrow dU + PdV \leq TdS$$

$$\Rightarrow dU + PdV - TdS \leq 0$$

$$\Rightarrow dU + d(PV) - d(TS) \leq 0$$

$$\Rightarrow d\left[\underbrace{U + PV - TS}\right] \leq 0$$

Gibbs Energy $\longleftarrow$ $\boxed{G = U + PV - TS = H - TS}$ $\longrightarrow$ (7)

$\boxed{dG \lesssim 0}$ (constant T & P) $\longrightarrow$ (8)

In a system at constant 'T' and 'P', the Gibbs energy will decrease as the result of any spontaneous processes until the system reaches equilibrium, where $dG = 0$.

Also,

$$\Delta G = \Delta H - T\Delta S \lesssim 0 \quad (\text{constant 'T' \& 'P'})$$

The equality holds for a reversible process, whereas the inequality holds for an irreversible process.

Lecture-26

Two important areas of application for thermodynamics are power generation and refrigeration. Both are usually accomplished by systems that operate on a thermodynamic cycle. Thermodynamic cycles can be divided into two general categories: Power cycles and refrigeration cycles.

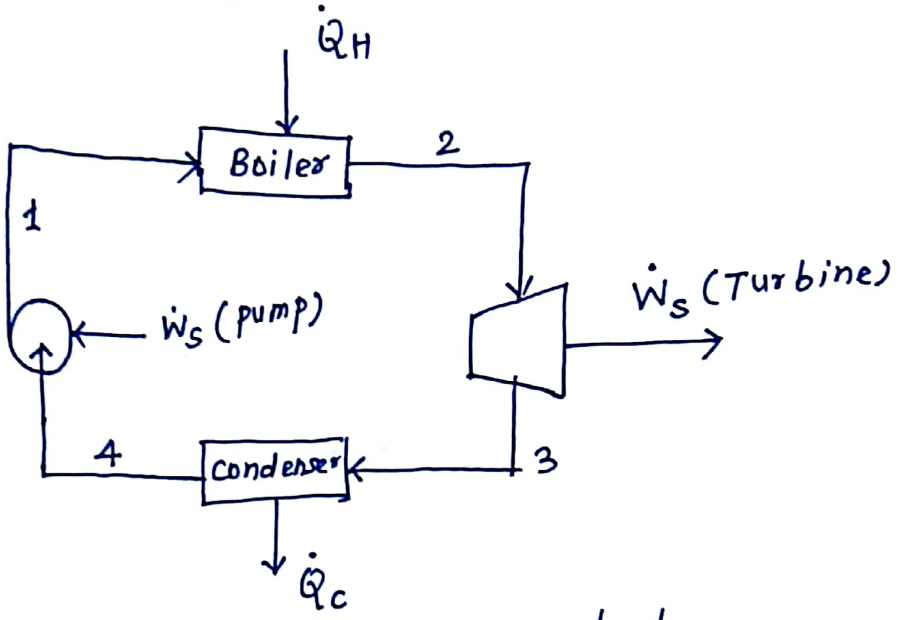
The devices or systems used to produce a net power output are often called engines, and the thermodynamic cycles they operate on are called power cycles. The devices or systems used to produce a refrigeration effect are called refrigerators, air conditioners or heat pumps, and the cycles they operate on are called refrigeration cycles.

Thermodynamic cycles can also be categorized as gas cycles and vapor cycles, depending on the phase of the working fluid. In gas cycles, the working fluid remains in the gaseous phase throughout the entire cycle, whereas in vapor cycles the working fluid exists in the vapor phase during one part of the cycle and in the liquid phase during another part.

Thermodynamic cycles can be categorized yet another way: closed and open cycles. In closed cycles, the working fluid is returned to the initial state at the end of the cycle and is recirculated. In open cycles, the working fluid is renewed at the end of each cycle instead of being recirculated. In automobile engines, the combustion gases are exhausted and replaced by fresh air-fuel mixture at the end of each cycle. The engine operates on a mechanical cycle, but the working fluid does not go through a complete thermodynamic cycle.

Heat engines are categorized as internal combustion and external combustion engines, depending on how the heat is supplied to the working fluid. In external combustion engines (such as steam power plants), heat is supplied to the working fluid from an external source such as a furnace. In internal combustion engines, this is done by burning the fuel within the system boundaries

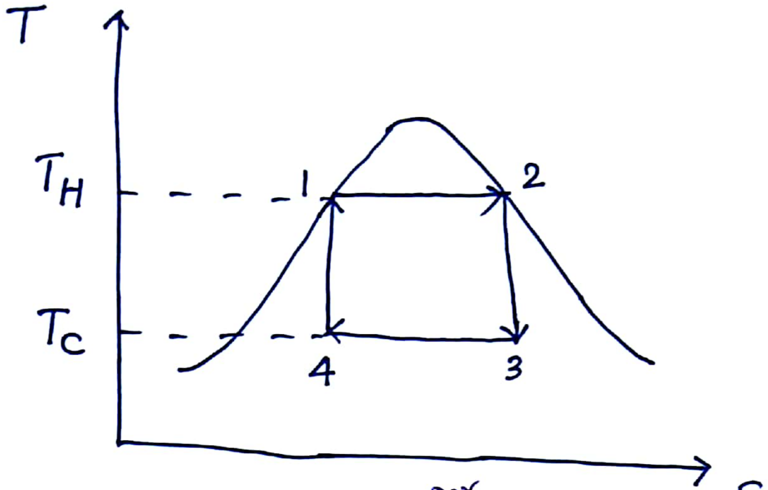
Vapor power cycles



Simple steam power plant

Figure shows a simple steady-state steady-flow process in which steam generated in a boiler is expanded in an adiabatic turbine to produce work. The discharge steam from the turbine passes to a condenser from which it is pump adiabatically back to the boiler. The power produced by the turbine is much greater than the pump requirement, and the net power output is equal to the difference between the rate of heat input in the boiler $|\dot{Q}_H|$ and the rate of heat rejection in the condenser $|\dot{Q}_C|$.

The processes that occur as the working fluid flows around the cycle can be represented on the TS diagram.



Carnot vapor cycle on a TS diagram.

Step 1→2 is the vaporization process taking place in the boiler, wherein saturated liquid water absorbs heat at the constant temperature T_H, and produces saturated vapor. Step 2→3 is a reversible, adiabatic expansion of saturated vapor into the two-phase region to produce a mixture of saturated liquid and vapor at T_C. This isentropic expansion is represented by a vertical line. Step 3→4 is a partial condensation process wherein heat is rejected at T_C. Step 4→1 takes the cycle back to its origin, producing saturated-liquid water at point 1. It is an isentropic compression process represented by a vertical line.

The Rankine cycle

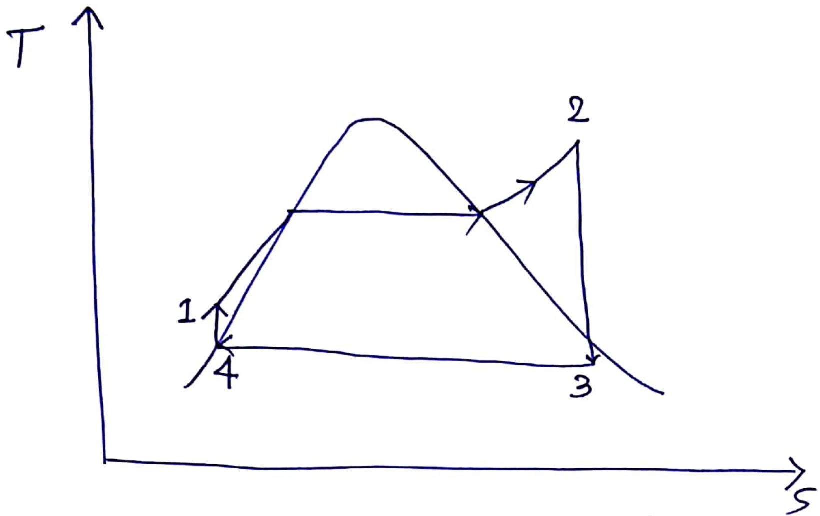
Carnot cycle could serve as a standard of comparison for actual steam power plants. However, several practical difficulties attend the operation of equipment intended to carry out steps 2→3 and 4→1.

Turbines that take in saturated steam produce an exhaust with high liquid content, which causes severe erosion problems. Even more difficult is the design of a pump that takes in a mixture of liquid and vapor (point 4) and discharges a saturated liquid (point 1).

For these reasons, an alternative model cycle is taken as the standard, at least for fossil-fuel-burning power plants. It is called the Rankine cycle, and differs from the carnot cycle in two major respects.

First, the heating step 1→2 is carried out well beyond vaporization, so as to produce a superheated vapor, and second, the cooling step 3→4 brings about complete condensation, yielding saturated liquid to be pumped to the boiler.

The Rankine cycle therefore consists of the four steps:

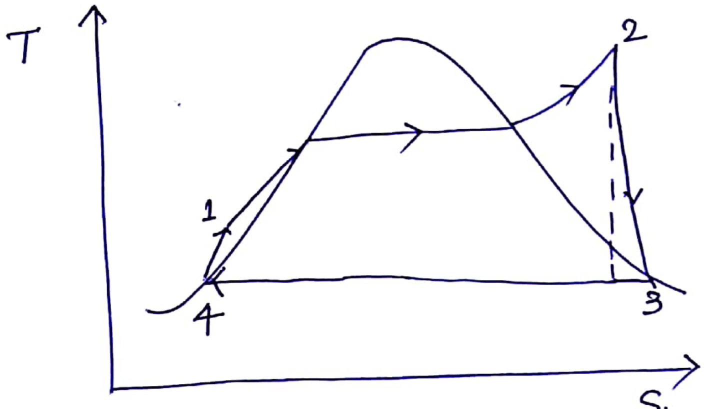


The Rankine cycle

- 1 → 2 A constant-pressure heating process in a boiler. The step lies along an isobar (the pressure of the boiler), and consists of three sections: heating of subcooled liquid water to its saturation ~~pre~~ temperature, vaporization at constant temperature and pressure, and superheating of the vapor to a temp. well above its saturation temperature.
- 2 → 3 Reversible, adiabatic (isentropic) expansion of vapor in a turbine to the pressure of the condenser. The step normally crosses the saturation curve, producing a wet exhaust. However, the superheating accomplished in step 1-2 shifts the vertical line far enough to the right so that the moisture content is not too large.

- 3 → 4 A constant-pressure, constant-temperature process in a condenser to produce saturated liquid at point 4.

- 4 → 1 Reversible, adiabatic (isentropic) pumping of the saturated liquid to the pressure of the boiler, producing compressed (sub cooled) liquid. The vertical line is very short, because the temp rise associated with compression of a liquid is small.



Simple practical power cycle.

Power plants can be built to operate on a cycle that departs from the Rankine cycle solely because of the irreversibilities of the work-producing and work-requiring steps. The above figure illustrates the effects of these irreversibilities on steps 2→3 and 4→1. The lines are no longer vertical, but tend in the direction of increasing entropy. The turbine exhaust is normally still wet, but as long as the moisture content is less than about 10%, erosion problems are not serious.

Lecture-27

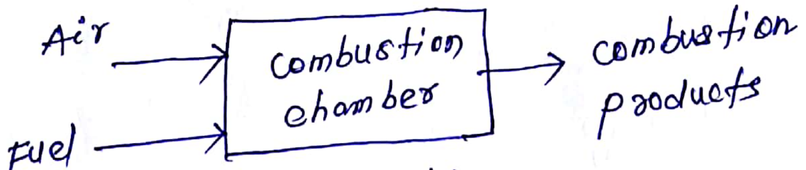
Air-standard Assumptions

In gas-power cycles, the working fluid remains a gas throughout the entire cycle. Spark-ignition engines, diesel engines, and conventional gas turbines are familiar examples of devices that operate on gas cycles. In all these engines, energy is provided by burning a fuel within the system boundaries. That is, they are internal combustion engines. Because of this combustion process, the composition of the working fluid changes from air and fuel to combustion products during the course of the cycle.

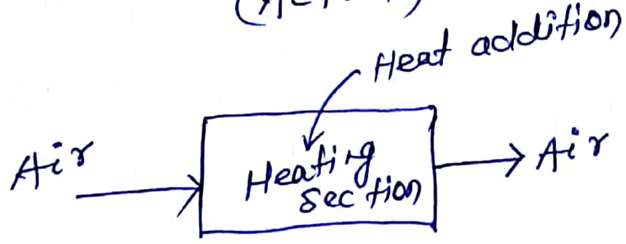
Even though internal combustion engines operate on a mechanical cycle (the piston returns to its starting position at the end of each revolution), the working fluid does not undergo a complete thermodynamic cycle. It is thrown out of the engine at some point in the cycle (as exhaust gases) instead of being returned to the initial state. Working on an open cycle is the characteristic of all internal combustion engines.

The actual gas power cycles are rather complex. To reduce the analysis to a manageable level, we utilize the following approximations, commonly known as the 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 replaled by a heat-addition process from an external source.
4. The exhaust process is replaled by a heat-rejection process that restores the working fluid to its initial state.



(Actual)



(Ideal)

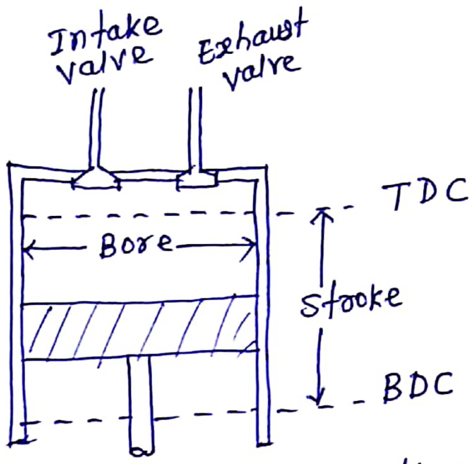
Another assumption that is often utilized to simplify the analysis is that air has constant specific heats whose values are determined at room temperature (25°C).

A cycle for which the air-standard assumptions are applicable is frequently referred to as an air-standard cycle.

The air-standard assumptions provide considerable simplification in the analysis without significantly deviating from the actual cycles. This simplified model enables us to study qualitatively the influence of major Parameters on the performance of the actual engines.

An overview of Reciprocating Engines

Despite its simplicity, the reciprocating engine (basically a piston-cylinder device) is one of the rare inventions that has proved to be very versatile and to have a wide range of applications. It is the powerhouse of the vast majority of automobiles, trucks, ships etc.



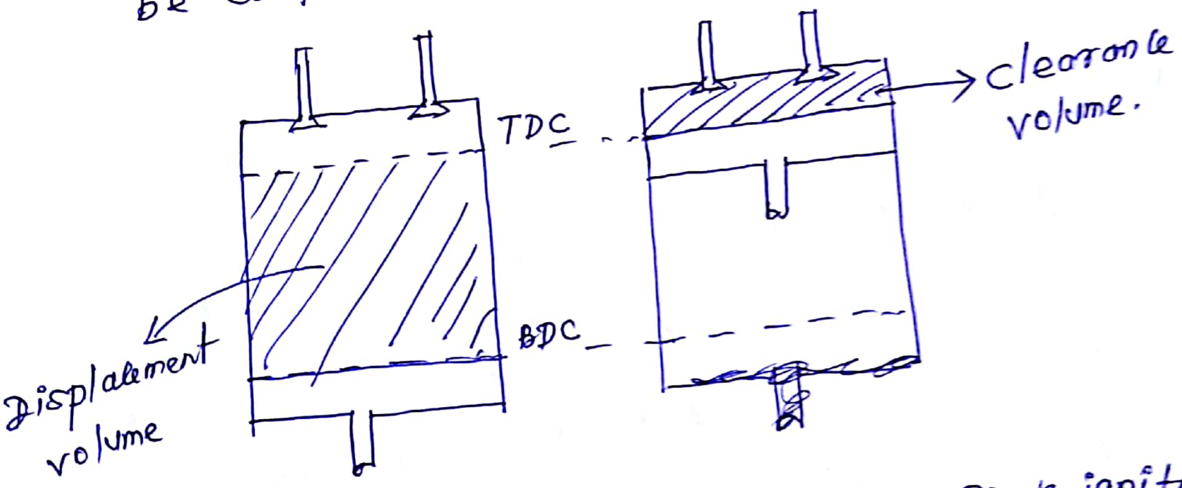
Nomenclature for reciprocating engines

The basic components of a reciprocating engines are shown. The piston reciprocates in the cylinder between two fixed positions called the top dead center (TDC) – the position of the piston when it forms the smallest volume in the cylinder – and the bottom dead center (BDC) – the position of the piston when it forms the largest volume in the cylinder. The distance between the TDC and the BDC is the largest distance that the piston can travel in one direction, and it is called the stroke of the engine. The diameter of the piston is called the bore. The air or air-fuel mixture is drawn into the cylinder through the intake valve, and the combustion products are expelled from the cylinder through the exhaust valve.

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 volume is called the compression ratio (r) of the engine:

$$r = \frac{V_{max}}{V_{mix}} = \frac{V_{BDC}}{V_{TDC}}$$

* Compression ratio is a volume ratio and should not be confused with the pressure ratio.

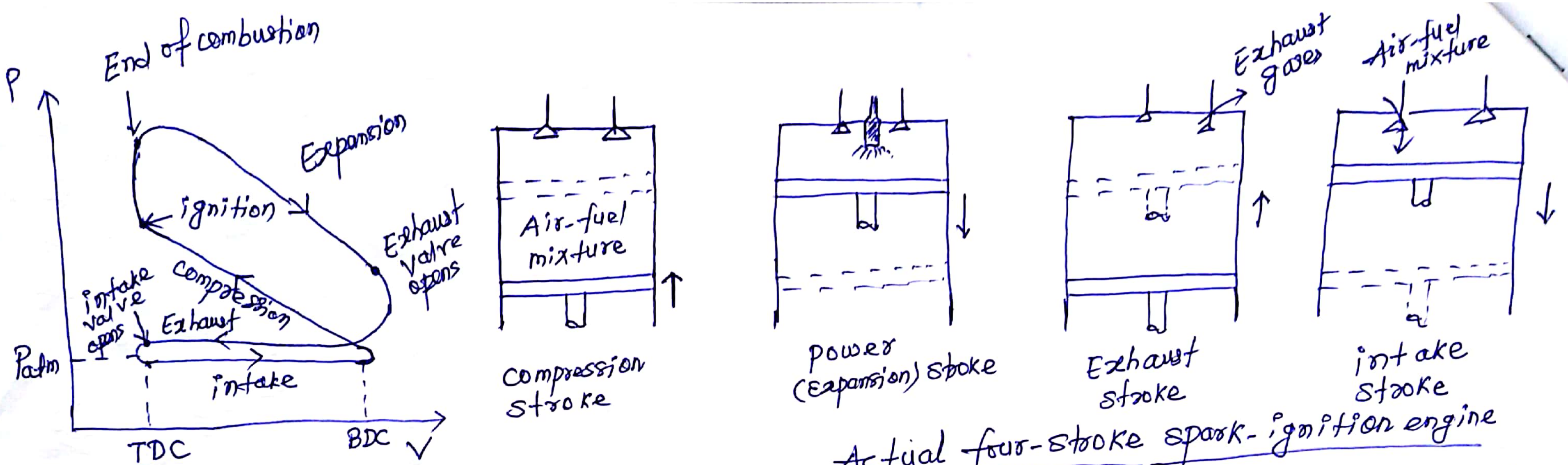


* Reciprocating engines are classified as spark-ignition (SI) engines or compression-ignition (CI) engines, depending on how the combustion process in the cylinder is initiated.

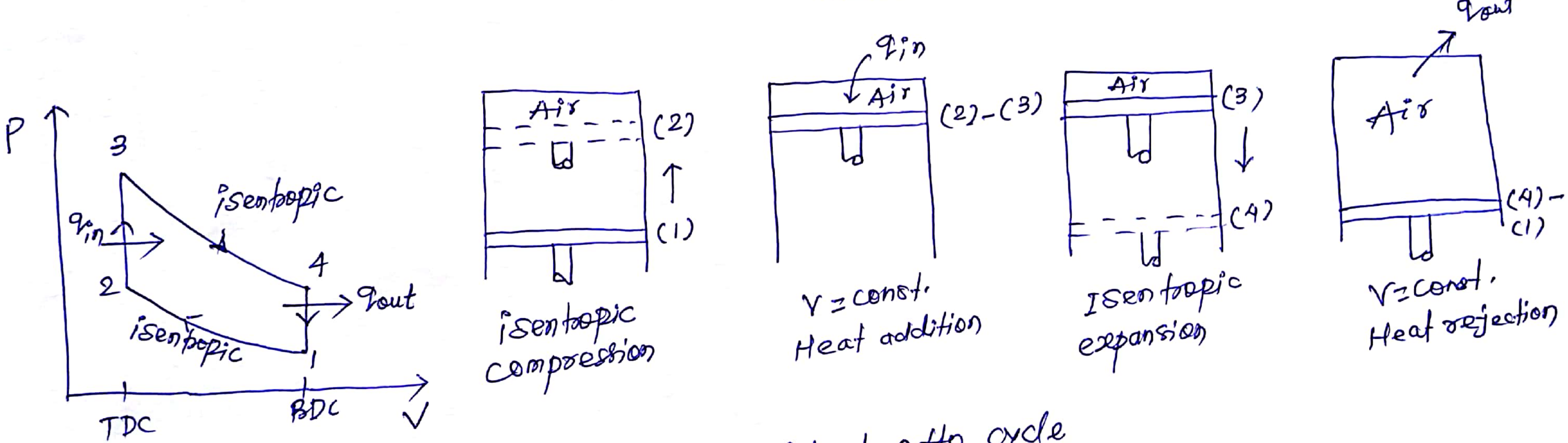
In SI engines, the combustion of the air-fuel mixture is initiated by a spark plug. In CI engines, the air-fuel mixture is self-ignited as a result of compressing the mixture above its self-ignition temperature.

OTTO cycle: The ideal cycle for spark-ignition Engines

The Otto cycle is the ideal cycle for spark-ignition reciprocating engines. It is named after Nikolaus A. Otto, who built a successful four-stoke engine in 1876 in Germany using the cycle proposed by Frenchman Beau de Rochas in 1862. In most spark-ignition engines, the piston executes four complete stokes (two mechanical cycles) within the cylinder, and the crankshaft completes two revolutions for each thermodynamic cycle. These engines are called four-stoke internal combustion engines. Initially, both the intake and exhaust valves are closed and the piston is at its lowest position (BDC). During compression stoke, the piston moves upward, compressing the air-fuel mixture. Shortly before the piston reaches its highest position (TDC), the spark-plug fires and the mixture ignites, increasing the pressure and temperature of the system.



Actual four-stroke spark-ignition engine



ideal otto cycle

The high-pressure gases force the piston down, which in turn forces the crankshaft to rotate, producing a useful work output during the expansion or power stroke. Towards the end of expansion stroke, the exhaust valve opens and the combustion gases that are above the atmospheric pressure rush out of the cylinder through the open exhaust valve. this process is called exhaust blowdown, and most combustion gases leave the cylinder by the time the piston reaches BDC. The cylinder is still filled by the exhaust gases at a lower pressure at BDC. Now the piston moves upward one more time, purging the exhaust gases through the exhaust valve (the exhaust stroke), and down a second time, drawing in fresh air-fuel mixture through the intake valve (the intake stroke). Notice that the pressure in the cylinder is slightly above the atmospheric value during the exhaust stroke and slightly below during the intake stroke.

The thermodynamic analysis of the actual four-stroke cycle is not a simple task. However, the analysis can be simplified significantly if the air-standard assumptions are utilized.

The resulting cycle, which closely resembles the actual operating conditions, is the ideal otto cycle. It consists of four internally reversible processes:

1-2 isentropic compression

2-3 constant-volume heat addition

3-4 Isentropic expansion

4-1 Constant-volume heat rejection.

The thermal efficiency of the air-standard Otto cycle is.

$$\eta = \frac{W_{net}}{q_{in}} = \frac{q_{in} - q_{out}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$$

For 1 mol of air;

$$q_{in} = C_V(T_3 - T_2) \quad \text{and} \quad q_{out} = C_V(T_4 - T_1)$$

Thus,

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} \longrightarrow (1)$$

Using ideal-gas equation at states 1, 2, 3, & 4, we get

$$T_1 = \frac{P_1 V_1}{R}; \quad T_2 = \frac{P_2 V_2}{R}; \quad T_3 = \frac{P_3 V_3}{R}; \quad T_4 = \frac{P_4 V_4}{R}$$

Thus, from eqn. (1),

$$\eta = 1 - \frac{\left(\frac{P_4 V_4}{R} - \frac{P_1 V_1}{R}\right)}{\left(\frac{P_3 V_3}{R} - \frac{P_2 V_2}{R}\right)} = 1 - \frac{(P_4 V_4 - P_1 V_1)}{(P_3 V_3 - P_2 V_2)}$$

$$\longrightarrow (2)$$

Since, $V_1 = V_4$ & $V_2 = V_3$

and compression ratio, $r = \frac{V_1}{V_2}$

Therefore, from eqn. (2),

$$\eta = 1 - \frac{V_1}{V_2}\frac{(P_4 - P_1)}{(P_3 - P_2)} = 1 - r\frac{(P_4 - P_1)}{(P_3 - P_2)} \rightarrow (3)$$

For the two adiabatic, reversible steps, $pV^\gamma =$ const.

Hence, $P_1 V_1^\gamma = P_2 V_2^\gamma$ and $P_3 V_3^\gamma = P_4 V_4^\gamma$

$$\downarrow$$

$$P_3 V_2^\gamma = P_4 V_1^\gamma$$

$$\frac{P_1 V_1^\gamma}{P_4 V_1^\gamma} = \frac{P_2 V_2^\gamma}{P_3 V_2^\gamma} \Rightarrow \frac{P_1}{P_4} = \frac{P_2}{P_3}$$

$$\Rightarrow \frac{P_1}{P_4} - 1 = \frac{P_2}{P_3} - 1$$

$$\Rightarrow \frac{P_1 - P_4}{P_4} = \frac{P_2 - P_3}{P_3}$$

$$\Rightarrow \frac{P_4 - P_1}{P_3 - P_2} = \frac{P_4}{P_3} = \left(\frac{V_2}{V_1}\right)^\gamma$$

From eqn. (3)

$$\eta = 1 - r\left(\frac{V_2}{V_1}\right)^\gamma = 1 - r \cdot \frac{1}{r^\gamma} = 1 - \frac{1}{r^{\gamma-1}}$$

$$\therefore \boxed{\eta = 1 - \frac{1}{r^{\gamma-1}}}$$

OTTO CYCLE -

THE IDEAL CYCLE FOR SPARK-IGNITION ENGINES

OTTO CYCLE

- ***Thermal efficiency*** of Otto cycle is given by:

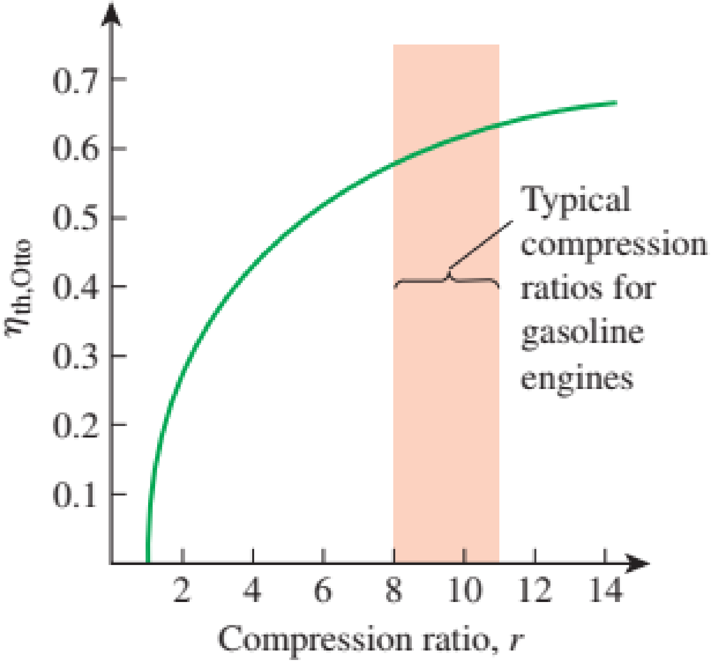
$$\eta_{th,Otto} = 1 - \frac{1}{r^{\gamma-1}}$$

Where ***r*** is compression ratio.

- Thermal efficiency of an ideal Otto cycle depends on the ***compression ratio (r)*** of the engine and the ***specific heat ratio (γ)*** of the working fluid.
- The ***thermal efficiency of the ideal Otto cycle increases with both the compression ratio and the specific heat ratio.*** *This is also true for actual spark-ignition internal combustion engines.*

EFFECT OF COMPRESSION RATIO

- ☐ Thermal efficiency curve is rather ***steep at low compression ratios*** but flattens out starting with a compression ratio value of about 8.
- ☐ The increase in thermal efficiency with the compression ratio is not as pronounced at high compression ratios.



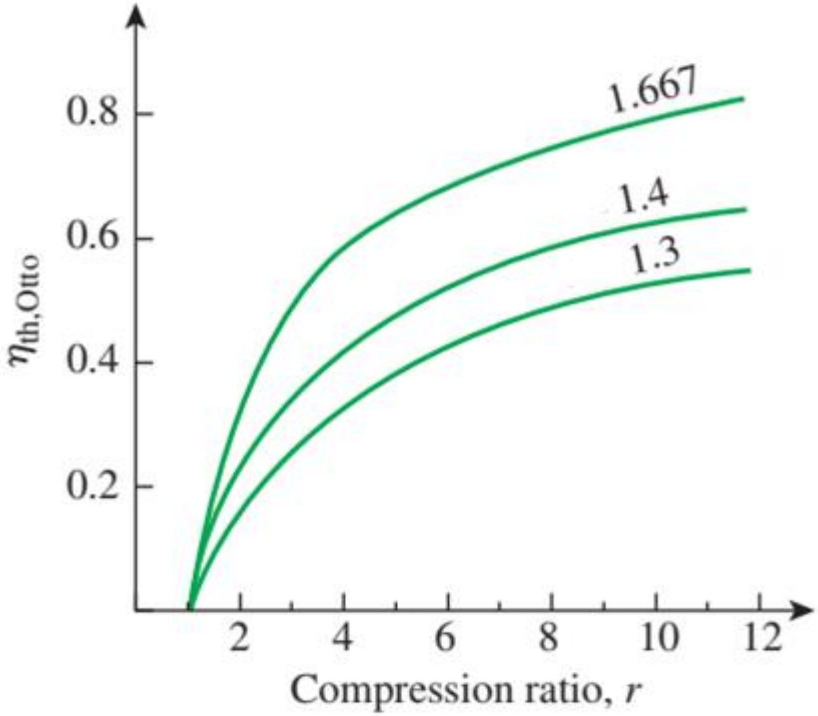
Thermal efficiency of the ideal Otto cycle as a function of compression ratio (γ=1.4; air at room temperature)

EFFECT OF COMPRESSION RATIO

- ❑ At high compression ratio, temperature of air-fuel mixture rises above the ***autoignition temperature*** of the fuel (***the temperature at which the fuel ignites without the help of a spark***), causing an early and rapid burn of the fuel at some point or points ahead of the flame front, followed by almost instantaneous inflammation of the end gas. This premature ignition of the fuel, called autoignition, produces an audible noise, which is called ***engine knock***.
- ❑ Autoignition in spark-ignition engines cannot be tolerated because it hurts performance and can cause engine damage.
- ❑ The requirement that autoignition not be allowed places an upper limit on the compression ratios that can be used in spark-ignition internal combustion engines.

EFFECT OF SPECIFIC HEAT RATIO (γ)

- ❑ For a given compression ratio, an ideal Otto cycle using a monatomic gas (such as argon or helium, γ = 1.667) as the working fluid will have the highest thermal efficiency.
- ❑ The specific heat ratio γ, and thus the ***thermal efficiency*** of the ideal Otto cycle, ***decreases as the molecules*** of the working fluid ***get larger***.



EFFECT OF SPECIFIC HEAT RATIO (γ)

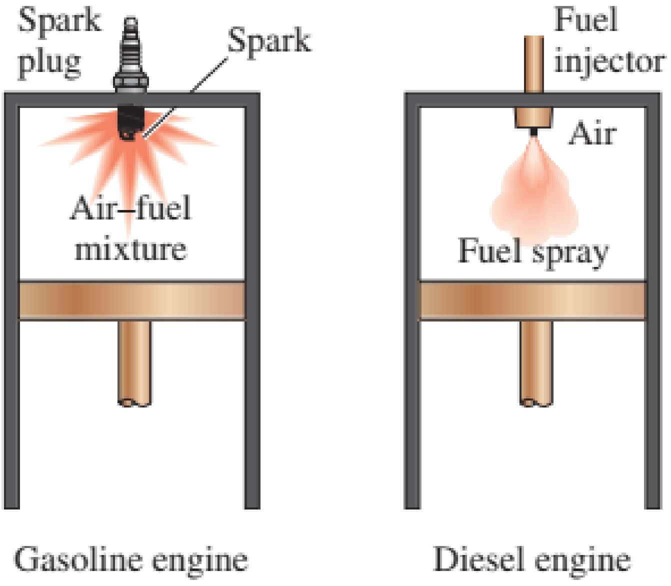
- ❑ The working fluid in actual engines contains larger molecules such as carbon dioxide, and the specific heat ratio decreases with temperature, which is one of the reasons that the actual cycles have lower thermal efficiencies than the ideal Otto cycle.
- ❑ The thermal efficiencies of actual spark-ignition engines range from about 25 to 30 percent.

DIESEL CYCLE -

THE IDEAL CYCLE FOR COMPRESSION-IGNITION ENGINES

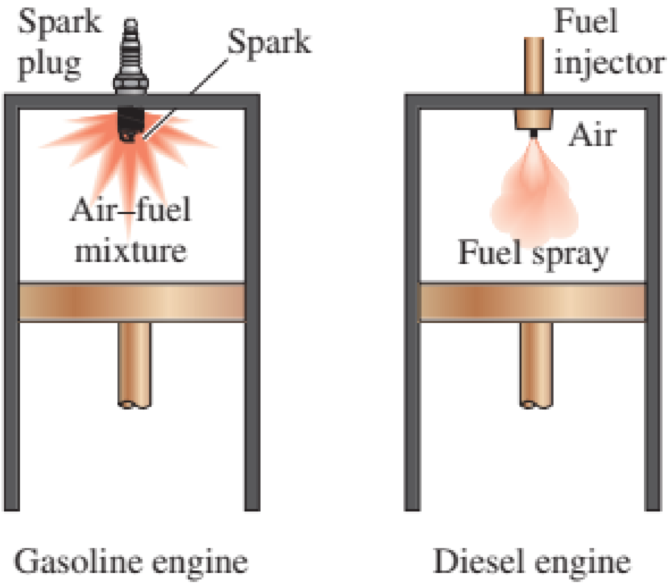
DIESEL CYCLE

- Ideal cycle for CI reciprocating engines.
- First proposed by Rudolph Diesel in the 1890s, is very similar to the SI engine ***differing mainly in the method of initiating combustion***.
- In diesel engines, the spark plug is replaced by a fuel injector, and only air is compressed during the compression process.



DIESEL CYCLE

- ☐ In SI engines, the ***air-fuel mixture is compressed*** to a temperature that is ***below the autoignition temperature of the fuel***, and the combustion process is initiated by firing a spark plug.



- ☐ In CI engines, the ***air is compressed*** to a temperature that is ***above the autoignition temperature of the fuel***, and combustion starts on contact as the fuel is injected into this hot air. Therefore, the spark plug is replaced by a fuel injector in diesel engines.

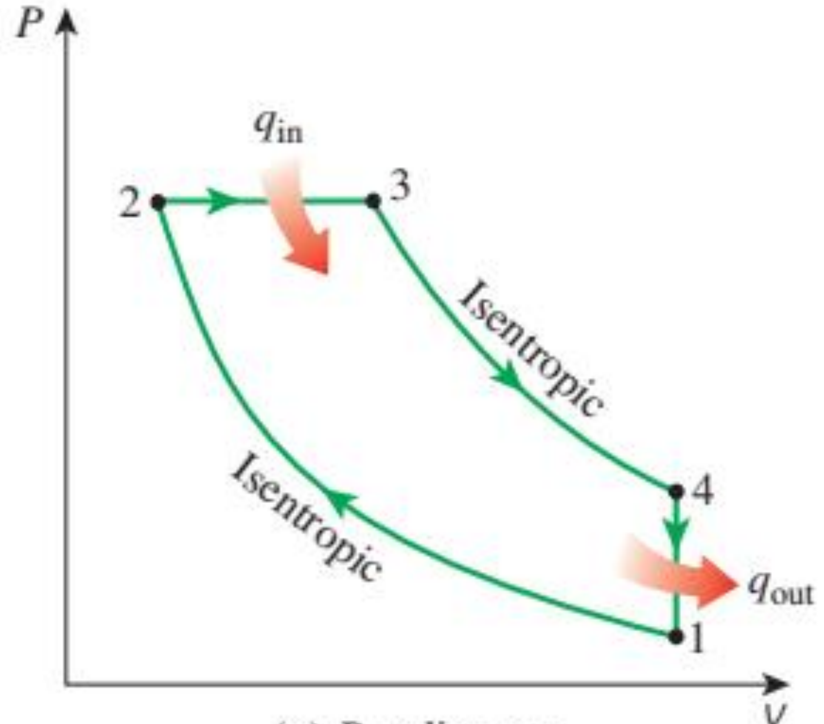
DIESEL CYCLE

- ☐ In gasoline engines, a mixture of air and fuel is compressed during the compression stroke, and the ***compression ratios*** are limited by the onset of autoignition or engine knock.
- ☐ In diesel engines, only air is compressed during the compression stroke, eliminating the possibility of autoignition. Therefore, diesel engines can be designed to operate at much ***higher compression ratios***, typically between *12 and 24.*

P-V DIAGRAM FOR DIESEL CYCLE

Diesel cycle, which is made up of four reversible processes:

- ✓ 1-2 Isentropic compression
- ✓ 2-3 Constant-pressure heat addition
- ✓ 3-4 Isentropic expansion
- ✓ 4-1 Constant-volume heat rejection

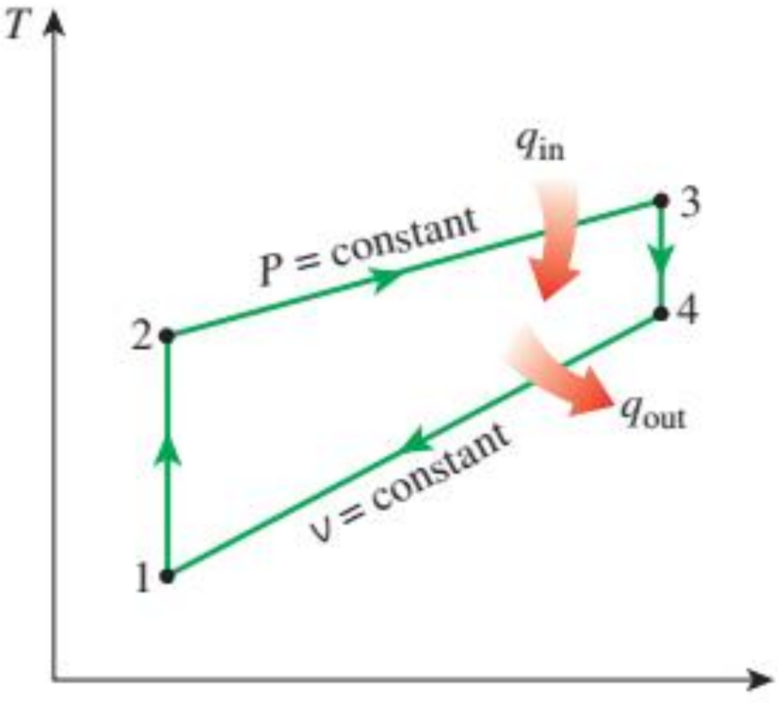


(*a*) *P*-v diagram

T-S DIAGRAM FOR DIESEL CYCLE

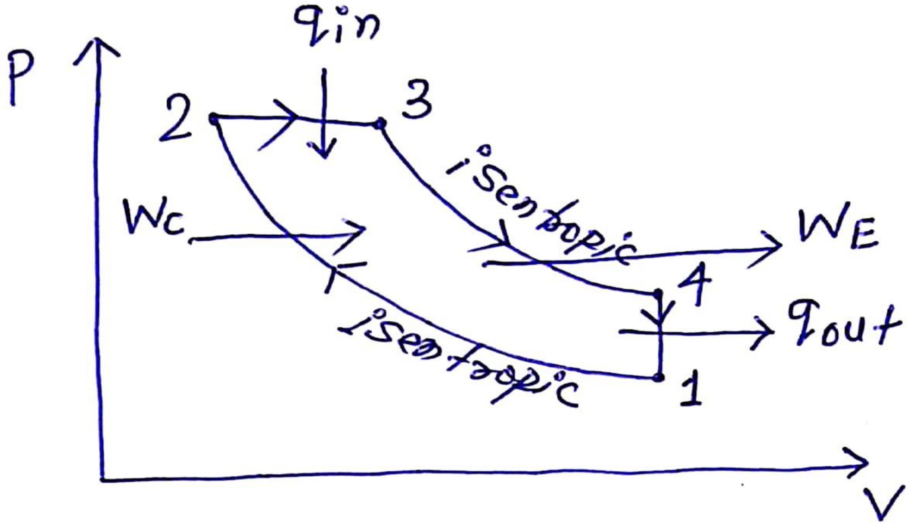
Diesel cycle, which is made up of four reversible processes:

- ✓ 1-2 Isentropic compression
- ✓ 2-3 Constant-pressure heat addition
- ✓ 3-4 Isentropic expansion
- ✓ 4-1 Constant-volume heat rejection



(*b*) *T-s* diagram

THERMAL EFFICIENCY OF DIESEL CYCLE



For 1 mol of air:

Heat supplied, $q_{in} = q_{2-3} = C_p(T_3 - T_2)$

Heat rejected, $q_{out} = q_{4-1} = C_v(T_4 - T_1)$

Thermal efficiency, $\eta = 1 - \frac{q_{out}}{q_{in}} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)}$

$$= 1 - \frac{(T_4 - T_1)}{\gamma(T_3 - T_2)} \longrightarrow (1)$$

THERMAL EFFICIENCY OF DIESEL CYCLE

The efficiency may be expressed in terms of any two of the following three ratios.

Compression ratio, $r_K = \frac{V_1}{V_2}$

Expansion ratio, $r_e = \frac{V_4}{V_3}$

cut-off ratio, $r_c = \frac{V_3}{V_2} = \frac{\text{cylinder volume after combustion}}{\text{cylinder volume before combustion}}$

It can be seen that,

$$r_K = r_e \cdot r_c = \frac{V_4}{V_3} \times \frac{V_3}{V_2} = \frac{V_4}{V_2} = \frac{V_1}{V_2}$$

$(\text{as } V_4 = V_1)$

THERMAL EFFICIENCY OF DIESEL CYCLE

Process 2-3 :

$$\frac{P_2 V_2}{T_2} = \frac{P_3 V_3}{T_3}$$

since, $P_2 = P_3$

$$\Rightarrow \quad \frac{V_2}{T_2} = \frac{V_3}{T_3}$$

$$\Rightarrow \quad T_2 = T_3 \frac{V_2}{V_3} = T_3 \cdot \frac{1}{r_c}$$

$$T_2 = T_3 \cdot \frac{1}{r_c} \quad \longrightarrow (2)$$

THERMAL EFFICIENCY OF DIESEL CYCLE

Process 3-4:

$$T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}$$

$$\Rightarrow T_4 = T_3 \left(\frac{V_3}{V_4}\right)^{\gamma-1} = T_3 \cdot \frac{1}{r_e^{\gamma-1}}$$

$$\Rightarrow T_4 = T_3 \frac{r_c^{\gamma-1}}{r_k^{\gamma-1}} \quad [\text{using } r_k = r_e r_c] \longrightarrow (3)$$

Process 1-2:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\Rightarrow T_1 = T_2 \left(\frac{V_2}{V_1}\right)^{\gamma-1} = T_2 \left(\frac{1}{r_k}\right)^{\gamma-1}$$

$$T_1 = \frac{T_3}{r_c} \cdot \frac{1}{(r_k)^{\gamma-1}} \quad [\text{using eq}^{n}.(2)] \longrightarrow (4)$$

THERMAL EFFICIENCY OF DIESEL CYCLE

Substituting the values of T_1, T_2 and T_4 in eq^n. (1),

$$\eta = 1 - \frac{\left(T_3 \cdot \frac{r_c^{\gamma-1}}{r_k^{\gamma-1}} - \frac{T_3}{r_c} \cdot \frac{1}{r_k^{\gamma-1}}\right)}{\gamma\left(T_3 - T_3 \cdot \frac{1}{r_c}\right)}$$

$$= 1 - \frac{\left(\frac{r_c^{\gamma-1}}{r_k^{\gamma-1}} - \frac{1}{r_c} \cdot \frac{1}{r_k^{\gamma-1}}\right)}{\gamma\left(1 - \frac{1}{r_c}\right)}$$

$$= 1 - \frac{\frac{1}{r_k^{\gamma-1}}\left(r_c^{\gamma-1} - \frac{1}{r_c}\right)}{\gamma\left(\frac{r_c - 1}{r_c}\right)}$$

THERMAL EFFICIENCY OF DIESEL CYCLE

$$= 1 - \frac{\frac{1}{r_k^{\gamma-1}}\left(\frac{r_c^{\gamma}-1}{r_c}\right)}{\gamma\left(\frac{r_c-1}{r_c}\right)}$$

$$= 1 - \frac{1}{\gamma}\cdot\frac{1}{r_k^{\gamma-1}}\cdot\frac{r_c^{\gamma}-1}{r_c-1}$$

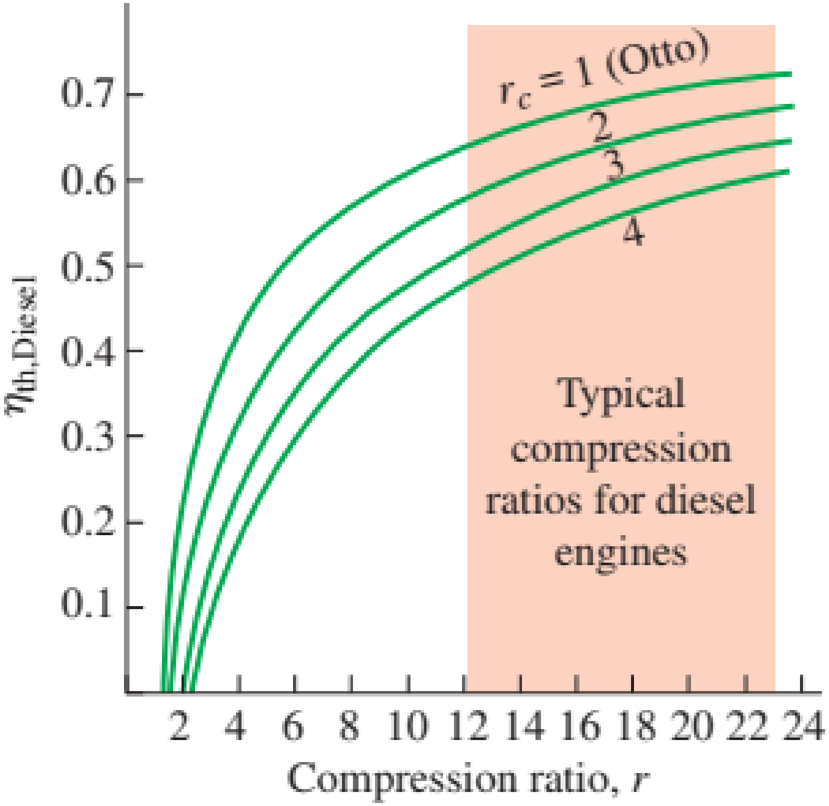
Thus,

$$\boxed{\eta_{diesel} = 1 - \frac{1}{\gamma}\cdot\frac{1}{r_k^{\gamma-1}}\cdot\frac{r_c^{\gamma}-1}{r_c-1}} \longrightarrow (5)$$

COMPARISON BETWEEN OTTO CYCLE AND DIESEL CYCLE

$$\eta_{th,Otto} = 1 - \frac{1}{r^{\gamma-1}}$$

$$\eta_{th,Diesel} = 1 - \frac{1}{r^{\gamma-1}}\left[\frac{1}{\gamma}\cdot\frac{r_c^{\gamma}-1}{r_c-1}\right]$$



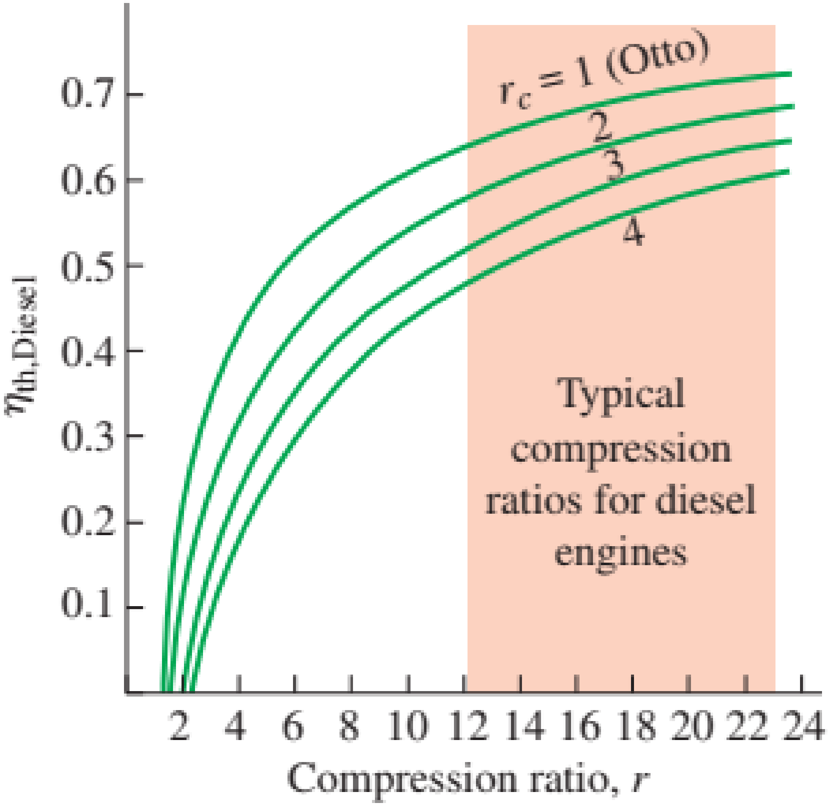
Efficiency of a Diesel cycle differs from the efficiency of an Otto cycle by the quantity in the brackets. This quantity is always greater than 1.

When both cycles operate on the same compression ratio

$$\eta_{th,Otto} > \eta_{th,Diesel}$$

COMPARISON BETWEEN OTTO CYCLE AND DIESEL CYCLE

- ☐ As the cut-off ratio decreases, the efficiency of the Diesel cycle increases.
- ☐ For the limiting case of (r_c=1), the quantity in the brackets becomes unity and the efficiencies of the Otto and Diesel cycles become identical.



COMPARISON BETWEEN OTTO CYCLE AND DIESEL CYCLE

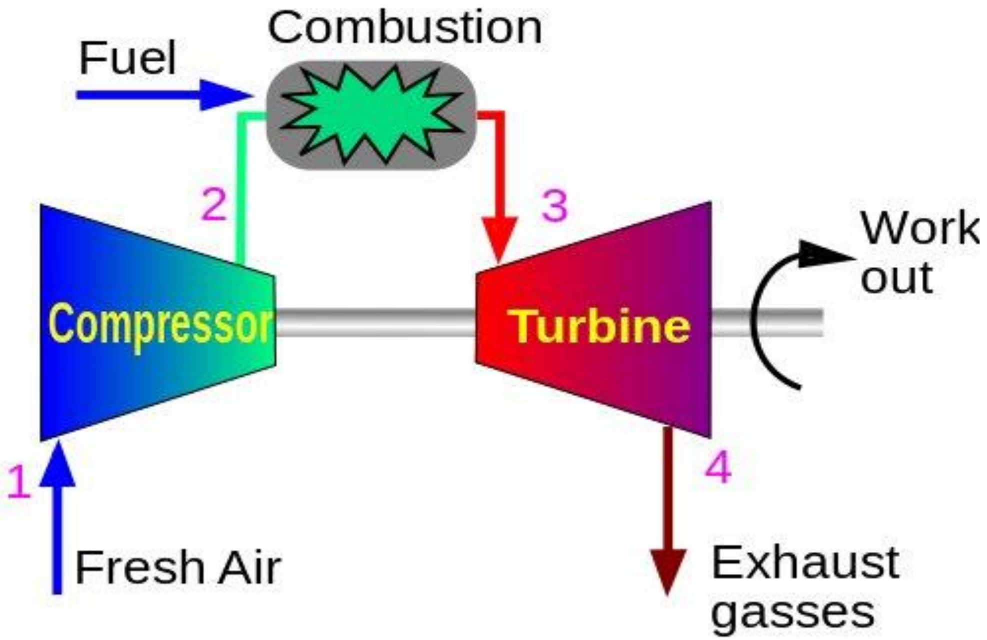
- ❑ Remember, though, that ***diesel engines*** operate at much higher compression ratios and thus are usually ***more efficient*** than the spark-ignition engines.
- ❑ Thermal efficiencies of large diesel engines range from about 35 to 40 %.

BRAYTON CYCLE

(THE IDEAL CYCLE FOR GAS-TURBINE ENGINES)

OPEN-CYCLE GAS-TURBINE ENGINE

- First proposed by **George Brayton**.
- Currently used for **Gas turbines.**
- **Gas turbine**:
  - ✓ Internal combustion engine.
  - ✓ Uses liquid fuel or gas.



- Gas turbines operate on an ***open cycle.***

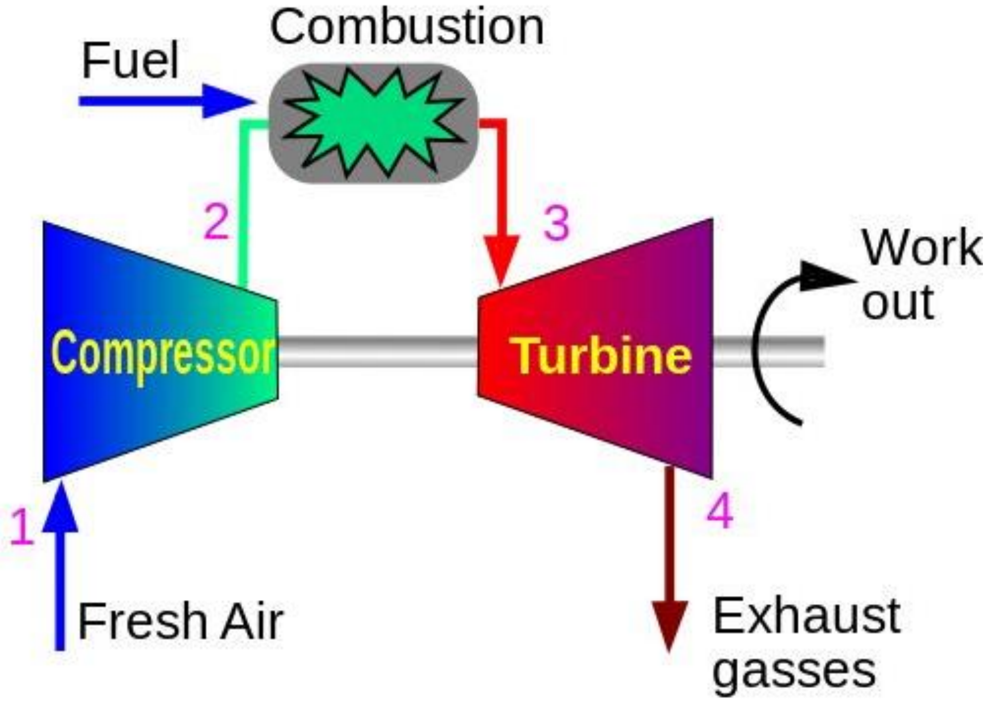
OPEN-CYCLE GAS-TURBINE ENGINE

1-2 : Fresh air is compressed to high temperature and pressure.

2-3: High-pressure air proceeds into the combustion chamber, where the fuel is burned at constant pressure.

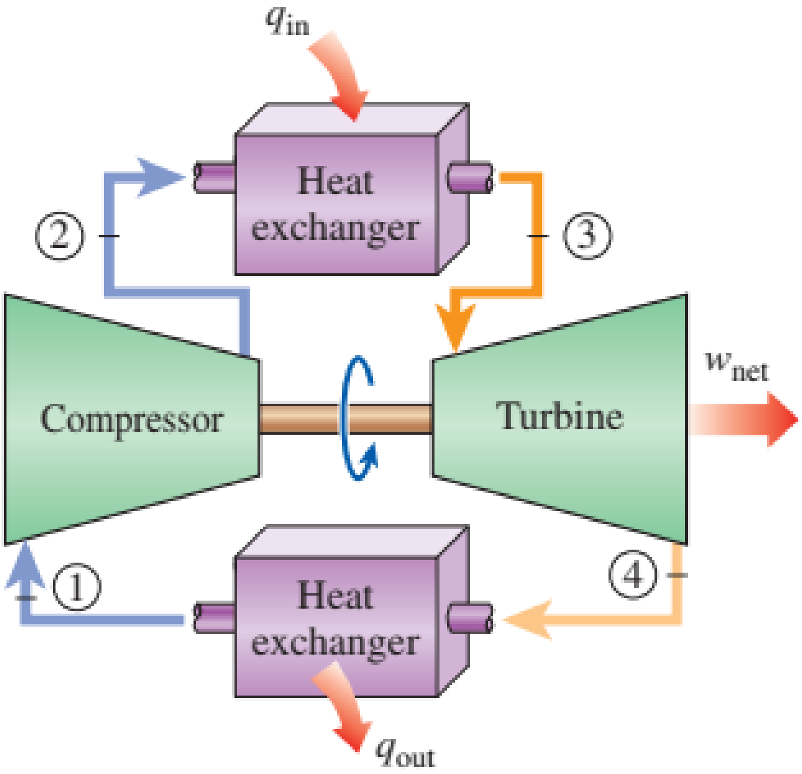
3-4: Combustion products enter the turbine for producing power.

The exhaust gases leaving the turbine are thrown out



BRAYTON CYCLE

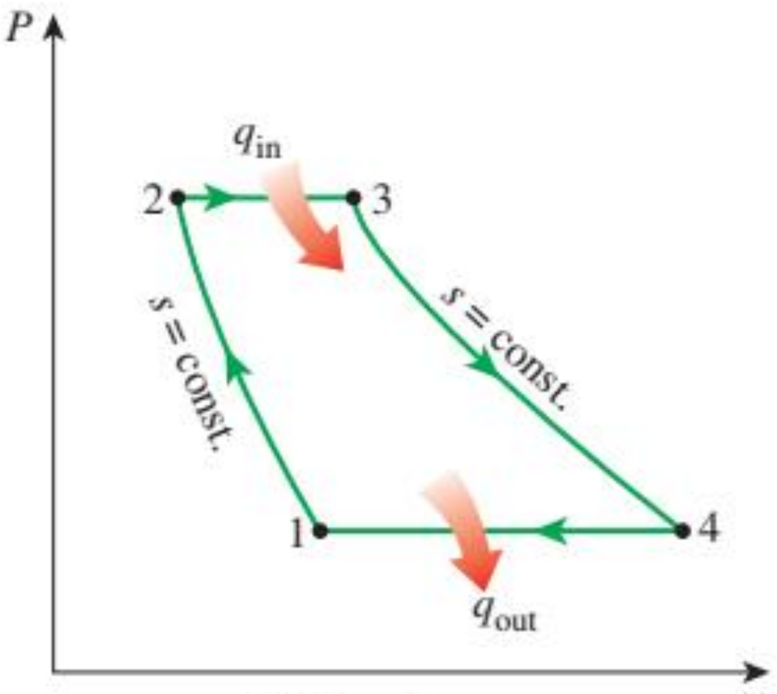
- ✓ The open gas-turbine cycle can be modeled as a *closed cycle,* by utilizing the air-standard assumptions.
- ✓ Compression & expansion processes remain the same.
- ✓ combustion process is replaced by a constant-pressure heat-addition process from an external source.
- ✓ exhaust process is replaced by a constant-pressure heat-rejection process to the ambient air.



P-V DIAGRAM FOR BRAYTON CYCLE

Brayton cycle is made up of four reversible processes:

- ✓ 1-2 Isentropic compression
- ✓ 2-3 Constant-pressure heat addition
- ✓ 3-4 Isentropic expansion
- ✓ 4-1 Constant-pressure heat rejection

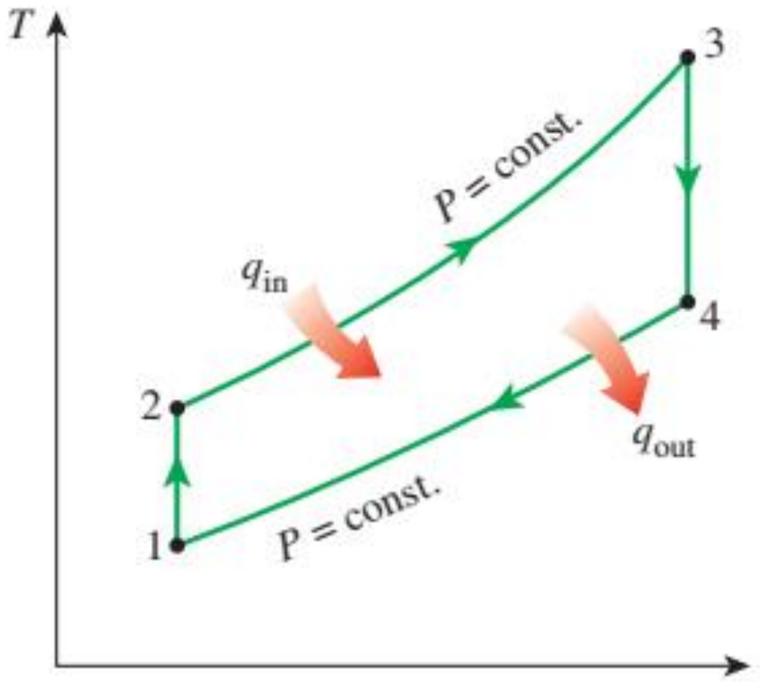


(*b*) *P*-v diagram

T-S DIAGRAM FOR BRAYTON CYCLE

Brayton cycle is made up of four reversible processes:

- ✓ 1-2 Isentropic compression
- ✓ 2-3 Constant-pressure heat addition
- ✓ 3-4 Isentropic expansion
- ✓ 4-1 Constant-pressure heat rejection



(*a*) *T*-*s* diagram

THERMAL EFFICIENCY OF BRAYTON CYCLE

- $q_{out} = c_P(T_4 - T_1)$ and $q_{in} = c_P(T_3 - T_2)$

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

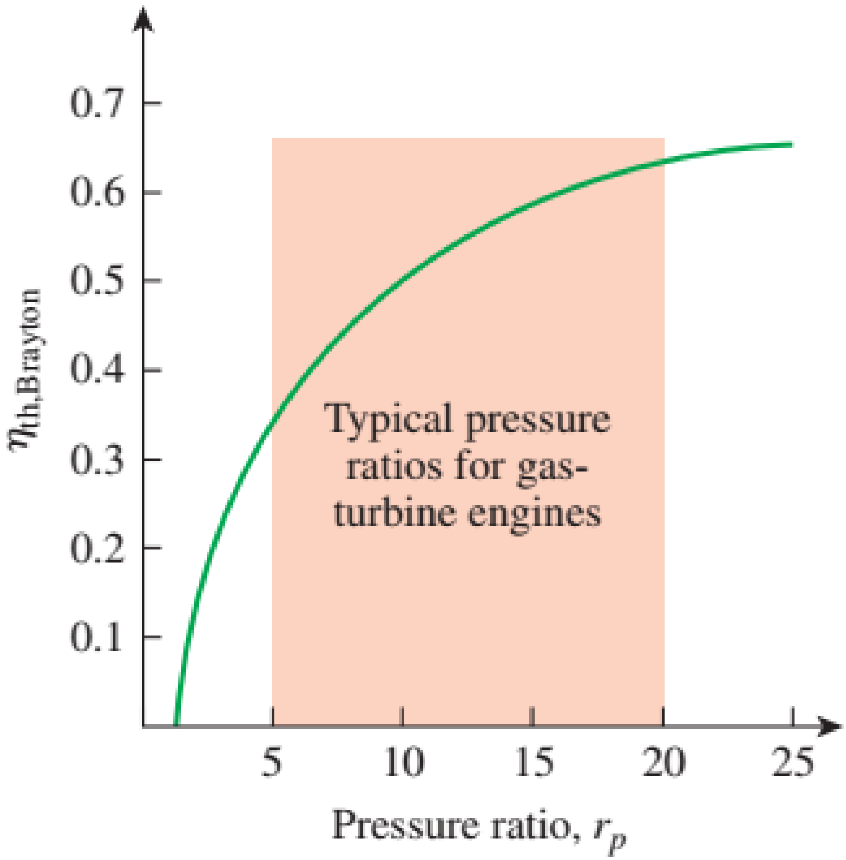
- Processes 1-2 and 3-4 are isentropic, and $P_2 = P_3$ and $P_4 = P_1$.

- $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\gamma-1/\gamma} = \left(\frac{P_3}{P_4}\right)^{\gamma-1/\gamma} = \frac{T_3}{T_4}$

- $\boldsymbol{\eta_{th} = 1 - \frac{1}{r_P^{(\gamma-1)/\gamma}}}$ where r_P=pressure ratio = P_2/P_1

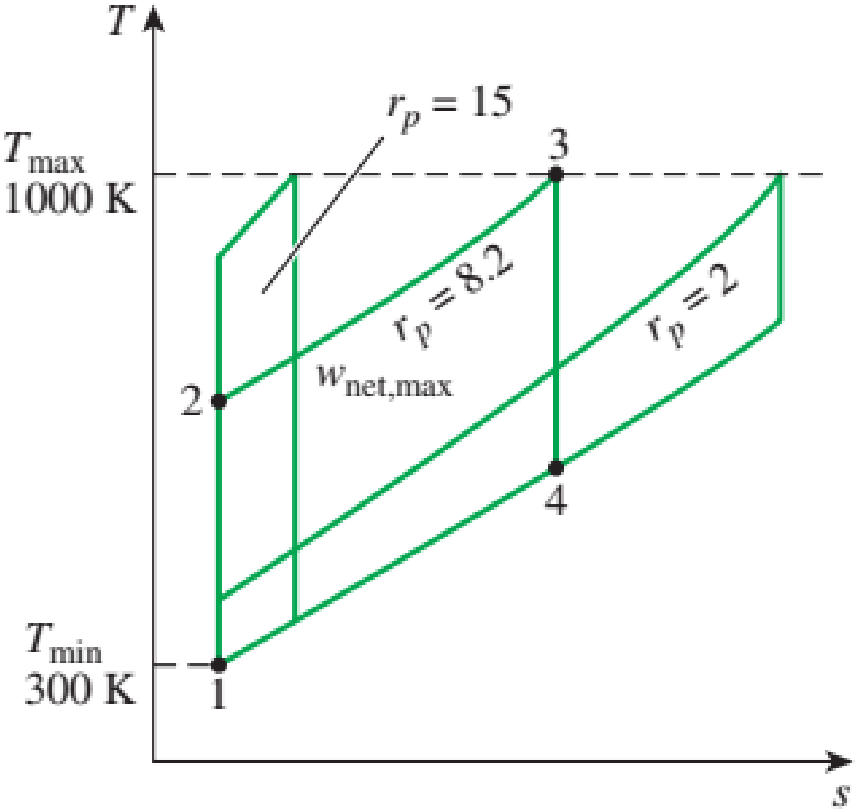
EFFECT OF PRESSURE RATIO

- ✓ The highest temperature in the cycle occurs at the end of the combustion process (state 3), and it is limited by the maximum temperature that the turbine blades can withstand.
- ✓ This also limits the pressure ratios that can be used in cycle.



EFFECT OF PRESSURE RATIO

- ✓ For a fixed turbine inlet temperature T_3, the net work output per cycle increases with the pressure ratio, reaches a maximum, and then starts to decrease.
- ✓ There should be a compromise between the pressure ratio (thus the thermal efficiency) and the net work output.
- ✓ In most common designs, the pressure ratio of gas turbines ranges from about 11-16.



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Residual properties

Lecture - 29/30

The definition for the generic residual property is:

$$M^R = M - M^{ig} \longrightarrow (1)$$

where 'M' is the molar value of any extensive thermodynamic property e.g., V, U, H, S, or G.

Note that 'M' and 'Mig', the actual and ideal-gas properties, are at the same T and P.

The residual volume, for example, is:

$$V^R = V - V^{ig} = V - \frac{RT}{P}$$

Because $V = \frac{ZRT}{P}$, the residual volume and the compressibility factor are related:

$$V^R = \frac{ZRT}{P} - \frac{RT}{P}$$

$$V^R = \frac{RT}{P}(Z-1) \longrightarrow (2)$$

From fundamental property relations for homogeneous fluids of constant composition,

$$dG = Vdp - SdT \longrightarrow (3)$$

Now,

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}dG - \frac{G}{RT^2}dT \longrightarrow (4)$$

using eqn. (3) in eqn. (4),

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}(Vdp - SdT) - \frac{G}{RT^2}dT$$

$$= \frac{V}{RT}dp - \frac{S}{RT}dT - \frac{G}{RT^2}dT$$

$$= \frac{V}{RT}dp - \frac{S}{RT}dT - \frac{(H-TS)}{RT^2}dT$$

$$= \frac{V}{RT}dp - \cancel{\frac{S}{RT}dT} - \frac{H}{RT^2}dT + \cancel{\frac{SdT}{RT}}$$

$$\boxed{d\left(\frac{G}{RT}\right) = \frac{V}{RT}dp - \frac{H}{RT^2}dT} \longrightarrow (5)$$

* The advantage of this equation is that all terms are dimensionless; moreover, in contrast to eqn. (3), the enthalpy rather than entropy appears on the right side.

From eqn, (5),

$$\frac{V}{RT} = \left[\frac{\partial(G/RT)}{\partial P}\right]_T \longrightarrow (6)$$

$$\frac{H}{RT} = -T\left[\frac{\partial(G/RT)}{\partial T}\right]_P \longrightarrow (7)$$

The remaining properties are given by-

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT} \longrightarrow (8)$$

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT} \longrightarrow (9)$$

* When we are given $G/RT = g(T,P)$, we can evaluate all other thermodynamic properties by simple mathematical operations.

* The Gibbs energy when given as a function of T & P, serves as a generating function for the other thermodynamic properties, and implicitly represents complete property information.

Equation (5), written for the special case of an ideal gas, becomes -

$$d\left(\frac{G^{ig}}{RT}\right) = \frac{V^{ig}}{RT}dp - \frac{H^{ig}}{RT^2}dT \longrightarrow (10)$$

Subtracting Eqn. (10) from Eqn. (5) gives -

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}dp - \frac{H^R}{RT^2}dT \longrightarrow (11)$$

Eqn. (11) : This fundamental residual-property relation applies to fluids of constant composition.

other useful forms are :

$$\frac{V^R}{RT} = \left[\frac{\partial(G^R/RT)}{\partial P}\right]_T \longrightarrow (12)$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial(G^R/RT)}{\partial T}\right]_P \longrightarrow (13)$$

From Eqn. (5),

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP \quad \text{(constant temp)}$$

Integration from zero pressure to arbitrary pressure P,

$$\frac{G^R}{RT} = \left(\frac{G^R}{RT}\right)_{P=0} + \int_0^P \frac{V^R}{RT}\,dP \quad \text{(const. T)}$$

For convenience, define

$$\left(\frac{G^R}{RT}\right)_{P=0} \equiv J \equiv \text{constant, independent of } T = \text{May be arbitrarily set equal to zero.}$$

Thus,

$$\frac{G^R}{RT} = \cancel{J}\ \cancel{+}\int_0^P \frac{Z-1}{P}\,dP \quad \text{(using eqn. 2)} \longrightarrow (14)$$

The derivative of this equation in combination with Eq. (13) gives,

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \longrightarrow (15)$$

The defining equation for the Gibbs energy,

$$G = H - TS,$$

may also be written for the special case of an ideal gas, $G^{ig} = H^{ig} - TS^{ig}$; by difference,

$$G^R = H^R - TS^R, \text{ and}$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} \longrightarrow (16)$$

Combining this equation with Eqs. (14) and (15) gives

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \longrightarrow (17)$$

The compressibility factor is defined as $Z = PV/RT$;

* The compressibility factor is defined as $Z = PV/RT$; values of 'Z' and of $(\partial Z/\partial T)_P$ may be calculated from experimental PVT data, and integrals can be evaluated by numerical or graphical methods.

Alternatively, the integrals may be evaluated analytically when 'Z' is expressed as a function of 'T' and 'P' by a volume-explicit equation of state..

Residual properties from the virial Equations of state

The two-term virial equation gives,

$$Z - 1 = \frac{BP}{RT}$$

substituting in Eq^n. (14) reduces it to

$$\frac{G^R}{RT} = \frac{BP}{RT} \longrightarrow (18)$$

From Eq^n. (4 13),

$$\frac{H^R}{RT} = -T\left[\frac{\partial(G^R/RT)}{\partial T}\right]_P$$

$$= -T\frac{\partial}{\partial T}\left[\frac{BP}{RT}\right]_P$$

$$= -T\left(\frac{P}{R}\right)\left[\frac{1}{T}\frac{dB}{dT} - \frac{B}{T^2}\right]$$

$$\frac{H^R}{RT} = \frac{P}{R}\left[\cancel{d}\ \frac{B}{T} - \frac{dB}{dT}\right] \longrightarrow (19)$$

From eq^n. (16),

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} = \frac{P}{R}\left[\frac{B}{T} - \frac{dB}{dT}\right] - \frac{BP}{RT} = -\frac{P}{R}\frac{dB}{dT}$$

$$\frac{S^R}{R} = -\frac{P}{R}\frac{dB}{dT} \longrightarrow (20)$$

* Evaluation of residual enthalpies and residual entropies is straightforward for given values of T, P, provided one has sufficient data to evaluate B and dB/dT.

We have, $PV = ZRT$

$\rho = \frac{1}{V}$ → molar volume

↓ Molar density

In the alternative form,

$$P = Z\rho RT \longrightarrow (21)$$

Differentiation gives:

$$dP = RT(Z\,d\rho + \rho\,dZ) \qquad (\text{const. } T)$$

Dividing by eqn. (21),

$$\frac{dP}{P} = \frac{RT(Z\,d\rho + \rho\,dZ)}{RTZ\rho} = \frac{d\rho}{\rho} + \frac{dZ}{Z}$$

using eqn. (14),

$$\frac{G^R}{RT} = \int (Z-1)\left\{\frac{d\rho}{\rho} + \frac{dZ}{Z}\right\}$$

$$= \int (Z-1)\frac{dZ}{Z} + \int (Z-1)\frac{d\rho}{\rho}$$

$$= \cancel{\int \left(1 - \frac{dZ}{Z}\right)}$$

$$= \int_1^Z \left(1 - \frac{1}{Z}\right) dZ + \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

$$= (Z - \ln Z)_1^Z + \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

$$\boxed{\frac{G^R}{RT} = (Z - \ln Z - 1) + \int_0^\rho (Z-1)\frac{d\rho}{\rho}} \longrightarrow (22)$$

$Z = \frac{PV}{RT}$

$P \to 0;$ $Z \to 1$

$P \to P;$ $Z \to Z$

$\rho \to 0$

$P \to 0$

From eq^n. (11),

$$\frac{H^R}{RT^2}\,dT = \frac{V^R}{RT}\,dp - d\left(\frac{G^R}{RT}\right)$$

$$= (Z-1)\frac{dp}{p} - d\left(\frac{G^R}{RT}\right) \qquad [\text{using eq}^n.\ 2]$$

Division by dT & restriction to constant 'ρ' gives-

$$\Rightarrow \frac{H^R}{RT^2} = \frac{(Z-1)}{P}\left(\frac{\partial P}{\partial T}\right)_\rho - \left[\frac{\partial(G^R/RT)}{\partial T}\right]_\rho \longrightarrow (23)$$

Differentiation of eq^n. (21) provides the first derivative on the right, and differentiation of eq^n. (22) provides

Thus, from eq^n. (21),

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \frac{\partial}{\partial T}(Z\rho RT)_\rho$$

$$= \rho R\left[Z + T\frac{\partial Z}{\partial T}\right]$$

from eq^n. (22),

$$\left[\frac{\partial(G^R/RT)}{\partial T}\right]_\rho = \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} + \frac{\partial Z}{\partial T} - \frac{1}{Z}\frac{\partial Z}{\partial T}$$

on substitution in eq^n. (23),

$$\frac{H^R}{RT^2} = \left(\frac{Z-1}{P}\right)\left(\rho RZ + \rho RT\frac{\partial Z}{\partial T}\right) - \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - \frac{\partial Z}{\partial T} + \frac{1}{Z}\frac{\partial Z}{\partial T}$$

$$\Rightarrow \frac{H^R}{RT} = T(Z-1)\left(\frac{\rho RZ}{P} + \frac{\rho RT}{P}\frac{\partial Z}{\partial T}\right) - T\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= T(Z-1)\left(\frac{\rho R \cancel{Z}}{\cancel{Z}\rho R T} + \frac{\rho R \cancel{T}}{Z\rho R \cancel{T}}\frac{\partial Z}{\partial T}\right) - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= T(Z-1)\left(\frac{1}{T} + \frac{1}{Z}\frac{\partial Z}{\partial T}\right) - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= (TZ-T)\left(\frac{1}{T} + \frac{1}{Z}\frac{\partial Z}{\partial T}\right) - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= Z + \cancel{T\frac{\partial Z}{\partial T}} - 1 - \cancel{\frac{T}{Z}\frac{\partial Z}{\partial T}} - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - \cancel{T\frac{\partial Z}{\partial T}} + \cancel{\frac{T}{Z}\frac{\partial Z}{\partial T}}$$

$$= -T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} + Z - 1$$

Thus,

$$\boxed{\frac{H^R}{RT} = -T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} + Z - 1} \longrightarrow (24)$$

The residual entropy is found from eqn. (16),

$$\frac{S^R}{R} = -T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} + \cancel{Z} - \cancel{1} - \cancel{Z} + \ln Z + \cancel{1} - \int_0^{\rho}(Z-1)\frac{d\rho}{\rho}$$

$$\boxed{\frac{S^R}{R} = \ln Z - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - \int_0^{\rho}(Z-1)\frac{d\rho}{\rho}} \longrightarrow (25)$$

Residual properties by cubic Equation of state

The generic cubic equation of state:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \quad ; \sigma, \epsilon = \text{constants.}$$

Divide by ρRT & substitute $V = 1/\rho$

$$\frac{P}{\rho RT} = \frac{\cancel{RT}}{\rho \cancel{RT}(V-b)} - \frac{a(T)}{\rho RT(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \quad Z = \frac{1}{\rho\left(\frac{1}{\rho}-b\right)} - \frac{a(T)}{\rho RT\left(\frac{1}{\rho}+\epsilon b\right)\left(\frac{1}{\rho}+\sigma b\right)}$$

$$= \frac{1}{(1-b\rho)} - \frac{a(T)}{\cancel{\rho}RT\frac{(1+\epsilon\rho b)}{\cancel{\rho}}\frac{(1+\sigma\rho b)}{\rho}}$$

$$= \frac{1}{(1-b\rho)} - \frac{\rho\, a(T)}{RT(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$q = \frac{a(T)}{bRT}$$

$$\frac{a(T)}{RT} = qb$$

$$Z = \frac{1}{(1-b\rho)} - q\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)} \longrightarrow (26)$$

The two quantities needed for evaluation of G^R, H^R & S^R are $Z-1$ ~~&~~ and $\left(\frac{\partial Z}{\partial T}\right)_\rho$. Thus, from eqn (26),

$$Z-1 = \frac{1}{(1-\rho b)} - 1 - q\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$= \frac{1-1+\rho b}{(1-\rho b)} - q\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$Z-1 = \frac{\rho b}{(1-\rho b)} - q\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)} \longrightarrow (27)$$

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = -\left(\frac{dq}{dT}\right)\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)} \longrightarrow (28)$$

The integrals are evaluated as follows:

$$\int_0^\rho (Z-1)\frac{d\rho}{\rho} = \int_0^\rho \frac{\rho b}{(1-\rho b)}\frac{d(\rho b)}{\rho b} - q\int_0^\rho \frac{d(\rho b)}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} = -\frac{dq}{dT}\int_0^\rho \frac{d(\rho b)}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

These two equations simplify to

$$\int_0^\rho (Z-1)\frac{d\rho}{\rho} = -\ln(1-\rho b) - qI \; ; \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} = -\frac{dq}{dT}I$$

where, $$I = \int_0^{\rho} \frac{d(\rho b)}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

<u>case I</u>: $\epsilon \neq \sigma$

$$I = \frac{1}{\sigma-\epsilon} \ln\left(\frac{1+\sigma\rho b}{1+\epsilon\rho b}\right)$$

we have, $\beta = \frac{bP}{RT}$; $Z = \frac{P}{\rho RT}$

$$\frac{\beta}{Z} = \frac{b\cancel{P}}{\cancel{RT}} \times \frac{\rho \cancel{RT}}{\cancel{P}} = \rho b$$

$$I = \frac{1}{\sigma-\epsilon} \ln\left(\frac{Z+\sigma\beta}{Z+\epsilon\beta}\right) \longrightarrow (29)$$

<u>case II</u>: $\epsilon = \sigma$

$$I = \frac{\rho b}{1+\epsilon\rho b} = \frac{\beta}{Z+\epsilon\beta}$$

using this, we get-

$$\boxed{\frac{G^R}{RT} = Z-1-\ln(Z-\beta)-qI} \rightarrow (30)$$

$$\boxed{\frac{H^R}{RT} = Z-1+\left[\frac{d\ln\alpha(T_r)}{d\ln T_r}-1\right]qI} \rightarrow (31)$$

$$\boxed{\frac{S^R}{R} = \ln(Z-\beta)+\frac{d\ln\alpha(T_r)}{d\ln T_r}qI} \rightarrow (32)$$

JOULE-THOMSON EXPANSION

Lecture No. 32/33

JOULE-THOMSON EXPANSION

Throttling valves

- Throttling valves are any kind of ***flow-restricting devices*** that cause a ***significant pressure drop*** in the fluid.
- Some familiar examples are :

(*a*) An adjustable valve

(*b*) A porous plug

(*c*) A capillary tube

Joule Thomson effect

☐ Unlike turbines, they produce a ***pressure drop without involving any work***.

☐ The ***pressure drop*** in the fluid is often **accompanied** by a large ***drop in temperature***, and for that reason throttling devices are commonly used in refrigeration and air-conditioning applications.

☐ The magnitude of the temperature drop (or, sometimes, the temperature rise) during a throttling process is governed by a property called the ***Joule Thomson coefficient.***

Joule Thomson effect

- Throttling valves are usually small devices, and the flow through them may be assumed to be adiabatic ($q \approx 0$) since there is neither sufficient time nor large enough area for any effective heat transfer to take place.
- Also, there is no work done ($w = 0$), and the change in potential energy, if any, is very small.
- Even though the exit velocity is often considerably higher than the inlet velocity, in many cases, the increase in kinetic energy is insignificant.
- Then the conservation of energy equation for this single-stream steady-flow device reduces to (See Equation 12 of Lecture 9):

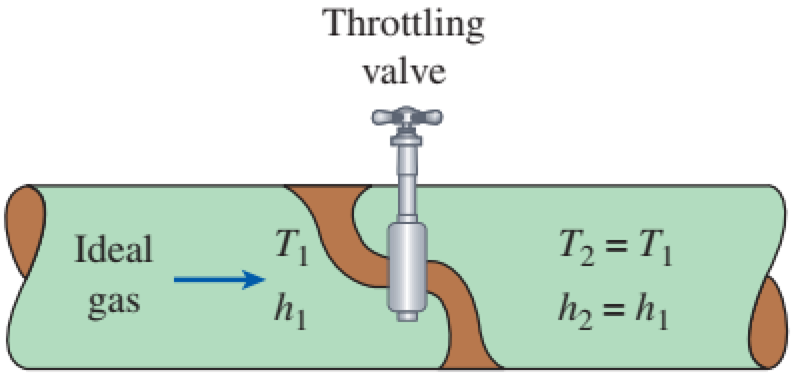
$$h_i = h_{out}$$

Isenthalpic Process

$$h_{in} = h_{out}$$

That is, enthalpy values at the inlet and exit of a throttling valve are the same.

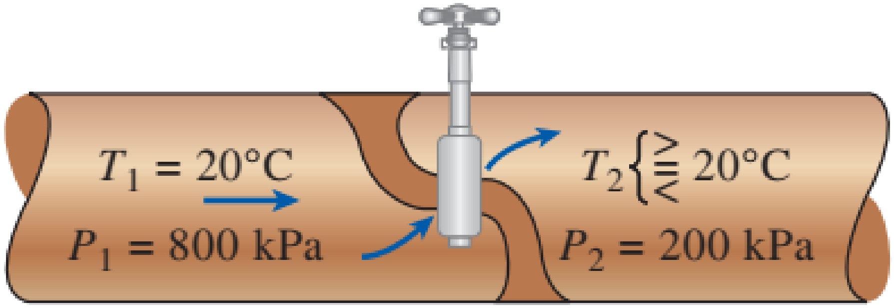
For this reason, a throttling valve is sometimes called an ***isenthalpic device***.



The temperature of an ideal gas does not change during a throttling (h = constant) process since $h = h(T)$

Joule-Thomson coefficient

- Temperature of the fluid may remain unchanged, or it may even increase or decrease during a throttling process.



- The temperature behavior of a fluid during a throttling (h = constant) process is described by the ***Joule-Thomson coefficient***, defined as:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

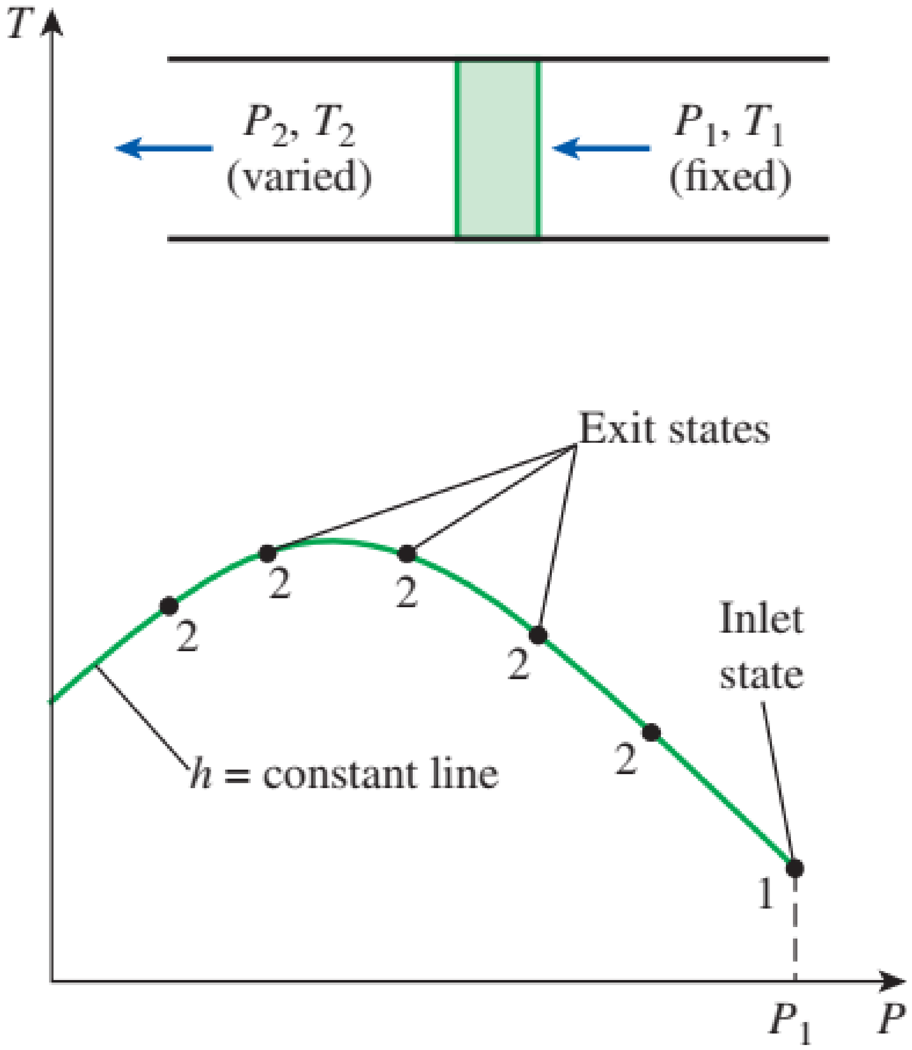
Joule-Thomson coefficient

- ☐ Thus the Joule-Thomson coefficient is a measure of the change in temperature with pressure during a constant-enthalpy process.

- ☐ If

$$\mu_{JT} \begin{cases} < 0 & \text{Temperature increases} \\ = 0 & \text{Temperature remains constant} \\ > 0 & \text{Temperature decreases} \end{cases}$$

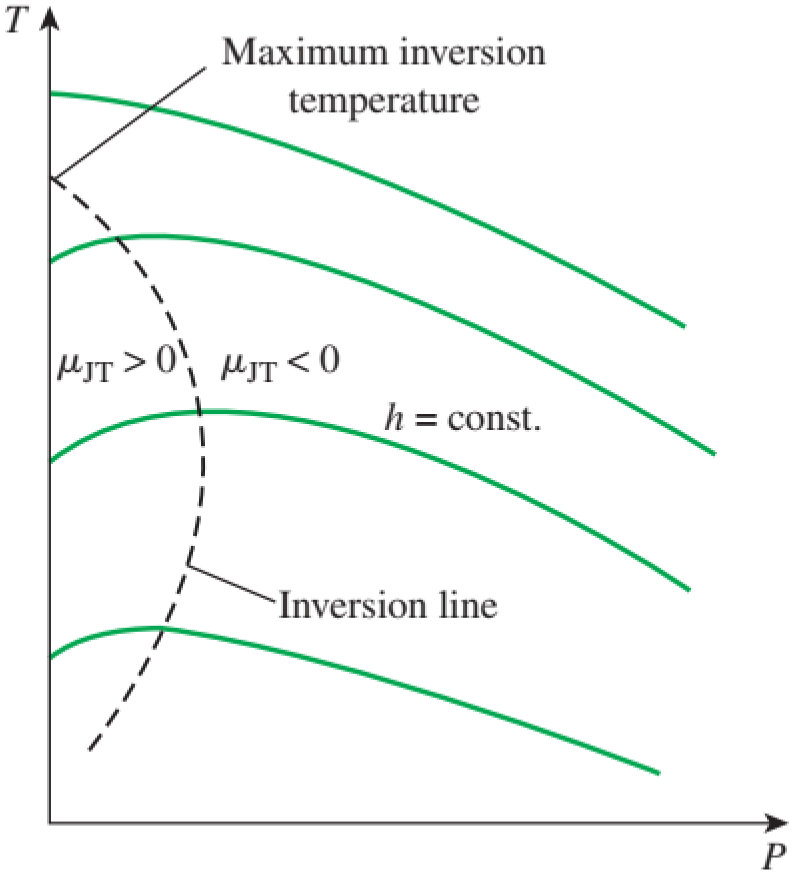
Development of an *h* = constant line on a *P-T* diagram.



Development of an *h* = constant line on a *P-T* diagram.

- ☐ A careful look at its defining equation reveals that the Joule-Thomson coefficient represents the slope of *h* = constant lines on a *T-P* diagram.
- ☐ Such diagrams can be easily constructed from temperature and pressure measurements alone during throttling processes.
- ☐ A fluid at a fixed temperature and pressure T_1 and P_1 (thus fixed enthalpy) is forced to flow through a porous plug, and its temperature and pressure downstream (T_2 and P_2) are measured.
- ☐ The experiment is repeated for different sizes of porous plugs, each giving a different set of T_2 and P_2. Plotting the temperatures against the pressures gives us an *h* = constant line on a *T-P* diagram.

- Repeating the experiment for different sets of inlet pressure and temperature and plotting the results, we can construct a *T-P* diagram for a substance with several *h* = constant lines.



Constant-enthalpy lines of a substance
on a *T-P* diagram

- Some constant-enthalpy lines on the *T-P* diagram pass through a point of zero slope.
- The line that passes through these points is called the inversion line, and the temperature at a point where a constant-enthalpy line intersects the inversion line is called the inversion temperature.
- The temperature at the intersection of the $P = 0$ line (ordinate) and the upper part of the inversion line is called the maximum inversion temperature.
- The slopes of the h = constant lines are negative ($\mu_{JT} < 0$) at states to the right of the inversion line and positive ($\mu_{JT} > 0$) to the left of the inversion line.

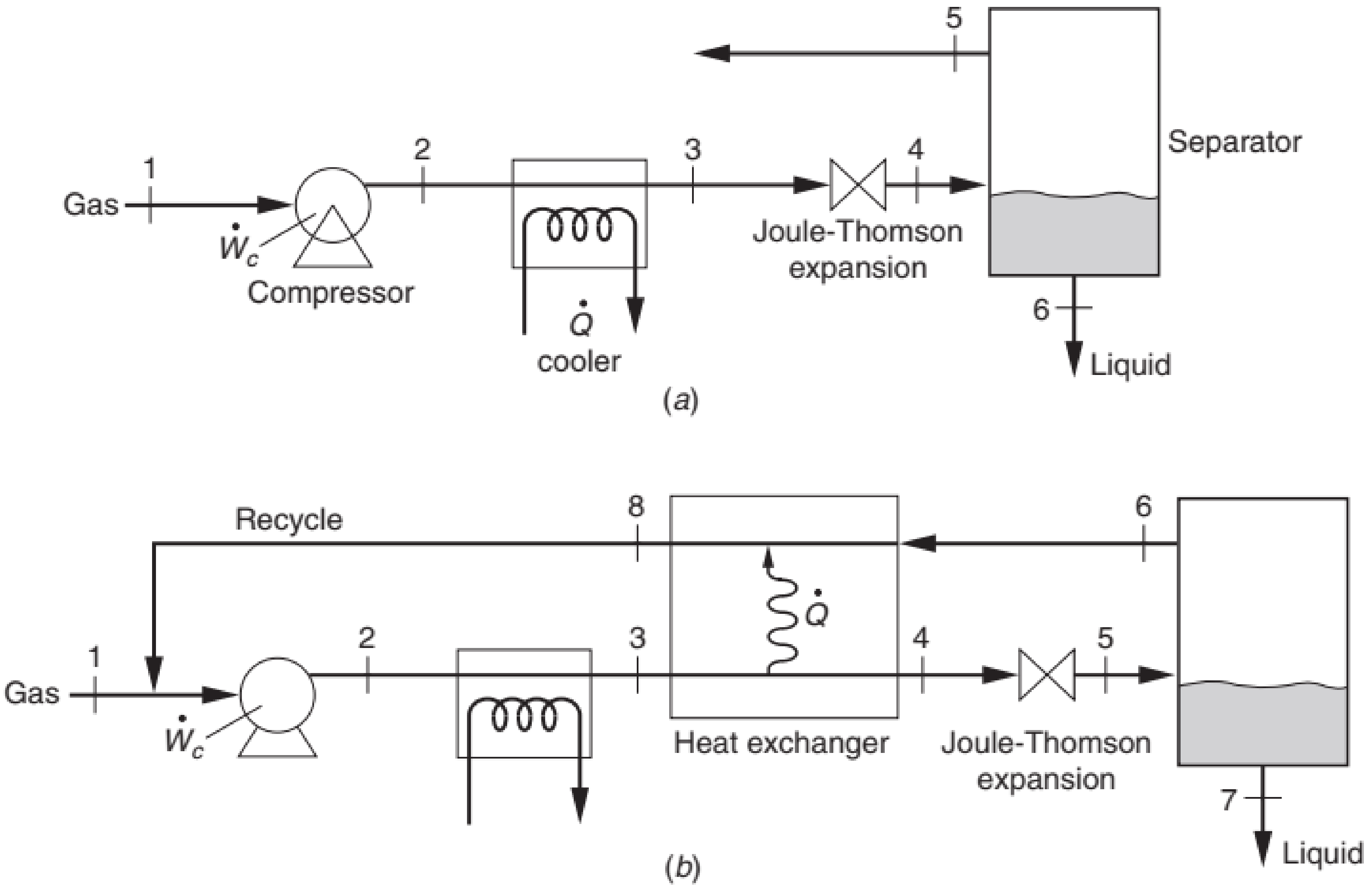
- A throttling process proceeds along a constant-enthalpy line in the direction of decreasing pressure, that is, from right to left.
- Therefore, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line.
- However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line.
- It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature.
- This presents a problem for substances whose maximum inversion temperature is well below room temperature.

- ☐ The decrease in temperature as the pressure drops corresponds to a decrease in molecular kinetic energy, the molecular potential energy must be increasing or else energy conservation would be violated. We can say the molecules are more stable when they are closer together at the higher pressure and, consequently, that attractive forces are dominant in this region. The temperature will increase as pressure decreases, indicating that repulsive forces dominate the behavior in this region.
- ☐ These two regions are separated by the inversion line, where the slope of T vs. P is zero and where attractive and repulsive interactions exactly balance.
- ☐ For a given pressure, the temperature at which these interactions balance is known as the **Boyle temperature**.

Liquefaction

- Joule-Thomson expansion can be used to liquefy gases if it is performed in the region where $\mu_{\mathrm{JT}} > 0$ to the left of the inversion line.
- Liquefaction is an important process industrially (e.g. liquid nitrogen and helium).

(a) Basic liquefaction process using Joule–Thomson expansion
(b) Linde process



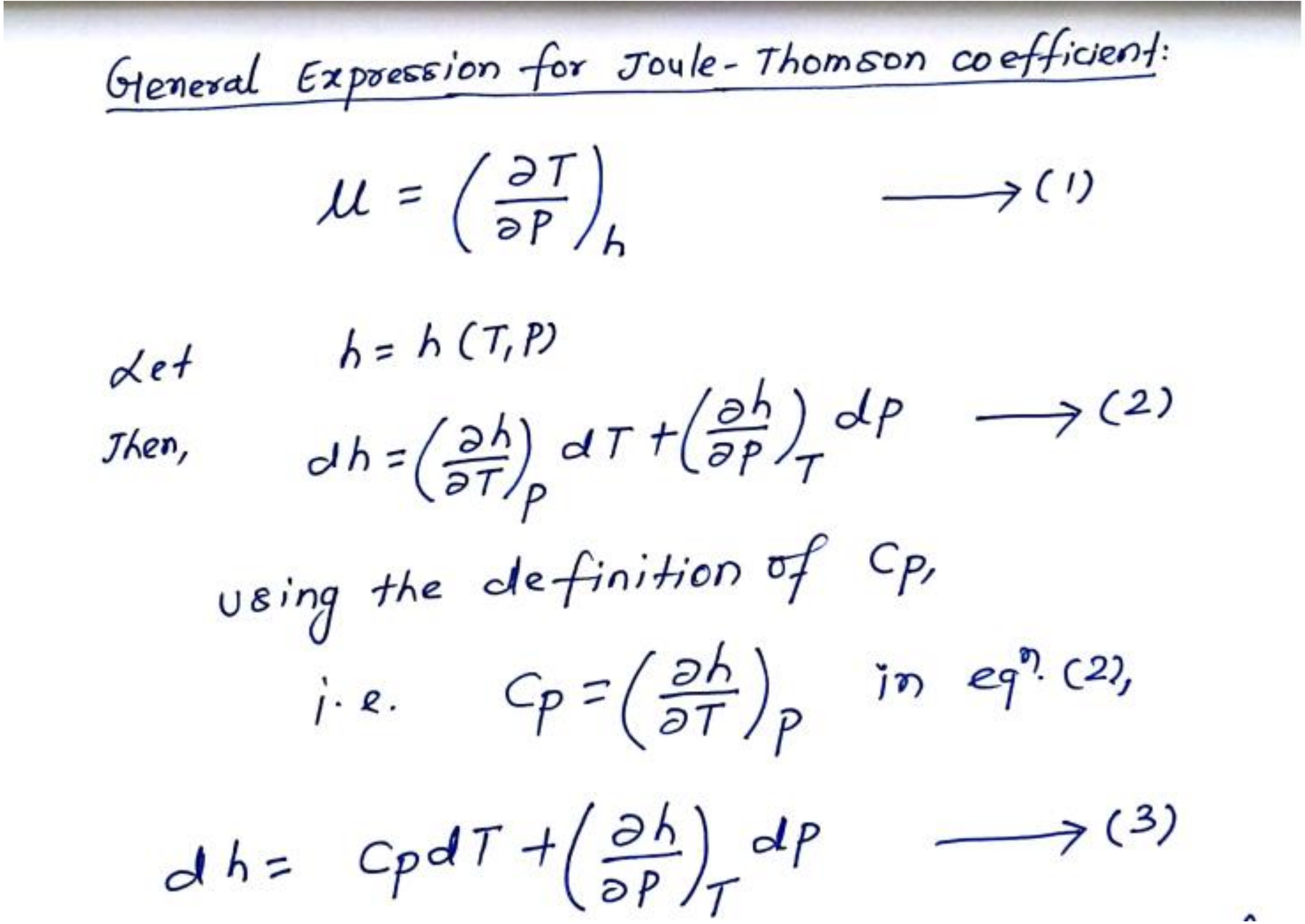
Liquefaction

- The gas is first compressed from state 1 to 2 to increase its pressure. However, during compression, the temperature of the gas also rises. It is then cooled from state 2 to state 3 to lower its temperature.
- These two processes are intended to bring it to the left region of inversion curve and to put it in a state where a throttling process will bring it into the two phase region.
- It now goes through an isenthalpic Joule-Thomson expansion, from state 3 to state 4, where the temperature drops low enough to lead to condensation.
- The vapor and liquid streams at states 5 and 6, respectively, are then separated.

Liquefaction

- ❑ An improvement to the liquefaction process is shown in Figure b. In this process, an additional heat exchanger is employed to recover the energy from the non-condensed gas. This gas is then recycled. The process depicted in Figure b is known as the ***Linde process***.

General Expression for Joule-Thomson Coefficient



General Expression for Joule-Thomson coefficient:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \longrightarrow (1)$$

Let $h = h(T, P)$

Then, $$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \longrightarrow (2)$$

using the definition of C_P,

i.e. $C_P = \left(\frac{\partial h}{\partial T}\right)_P$ in eq^n. (2),

$$dh = C_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \longrightarrow (3)$$

General Expression for Joule-Thomson Coefficient

Now, we choose the entropy to be a function of T and P, i.e. $s = s(T,P)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \longrightarrow (4)$$

Substituting this into

$$dh = Tds + vdp \longrightarrow (5)$$

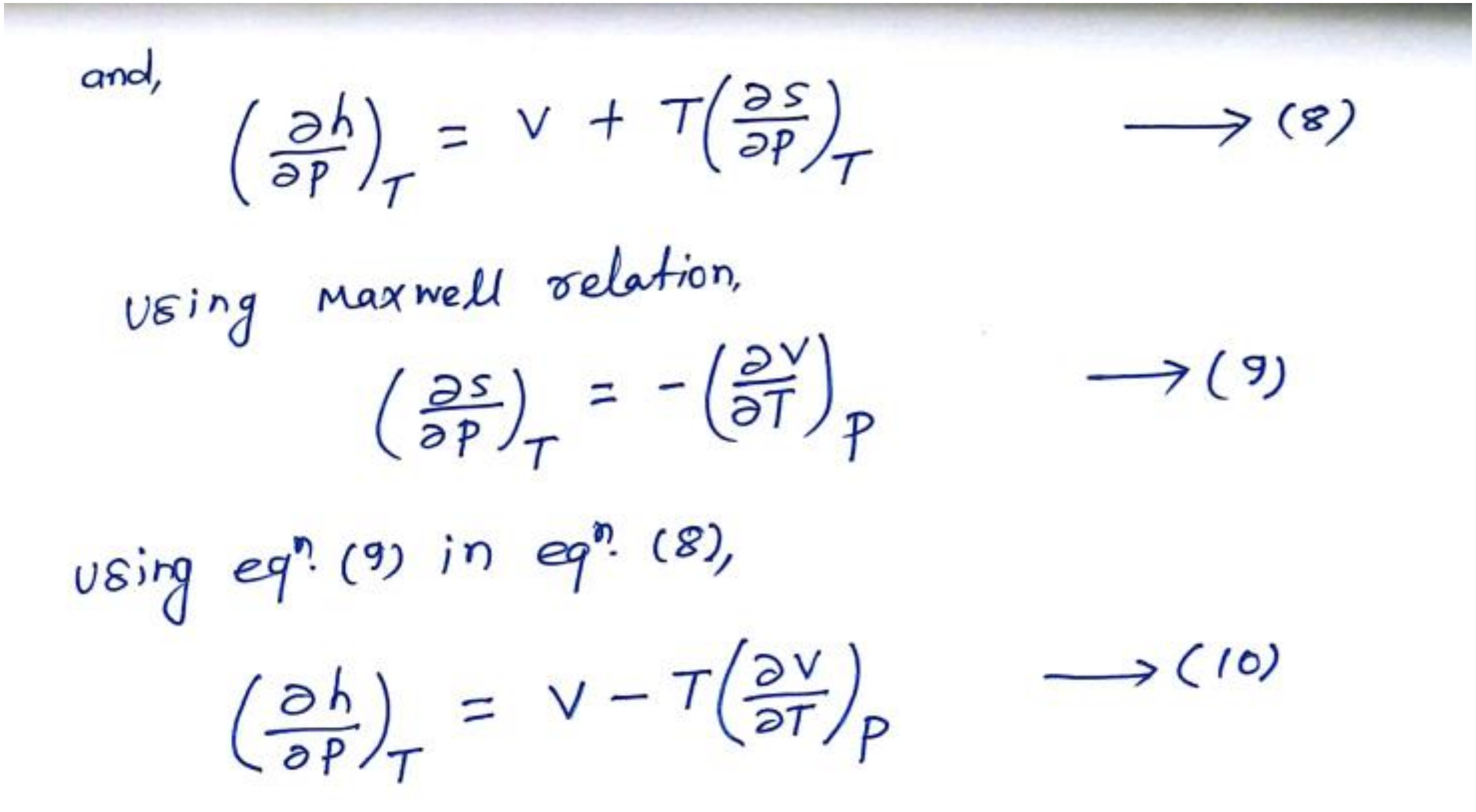
$$\Rightarrow \quad dh = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dp + vdp$$

$$dh = T\left(\frac{\partial s}{\partial T}\right)_P dT + \left[v + T\left(\frac{\partial s}{\partial P}\right)_T\right] dp \longrightarrow (6)$$

Comparing eq^n. (3) and eq^n. (6),

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T} \longrightarrow (7)$$

General Expression for Joule-Thomson Coefficient



and,

$$\left(\frac{\partial h}{\partial p}\right)_T = v + T\left(\frac{\partial s}{\partial p}\right)_T \longrightarrow (8)$$

using maxwell relation,

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \longrightarrow (9)$$

using eqn. (9) in eqn. (8),

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p \longrightarrow (10)$$

General Expression for Joule-Thomson Coefficient

using eq^n. (10) in eq^n. (3),

$$\boxed{dh = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp} \longrightarrow (11)$$

For constant enthalpy process, $h = \text{const.}$; $dh = 0$

Thus,

$$C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp = 0$$

$$\Rightarrow C_p dT = -\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

$$\Rightarrow \boxed{\mu = \left(\frac{\partial T}{\partial p}\right)_h = -\frac{1}{C_p}\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]} \longrightarrow (12)$$

General Expression for Joule-Thomson Coefficient

→

For an ideal gas, $V = \frac{RT}{P}$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

using eq^n (12), $\mu = -\frac{1}{C_p}\left[\frac{RT}{P} - \frac{RT}{P}\right] = 0.$

$\therefore \underline{\mu = 0}$

THANK YOU

THERMODYNAMIC CYCLE

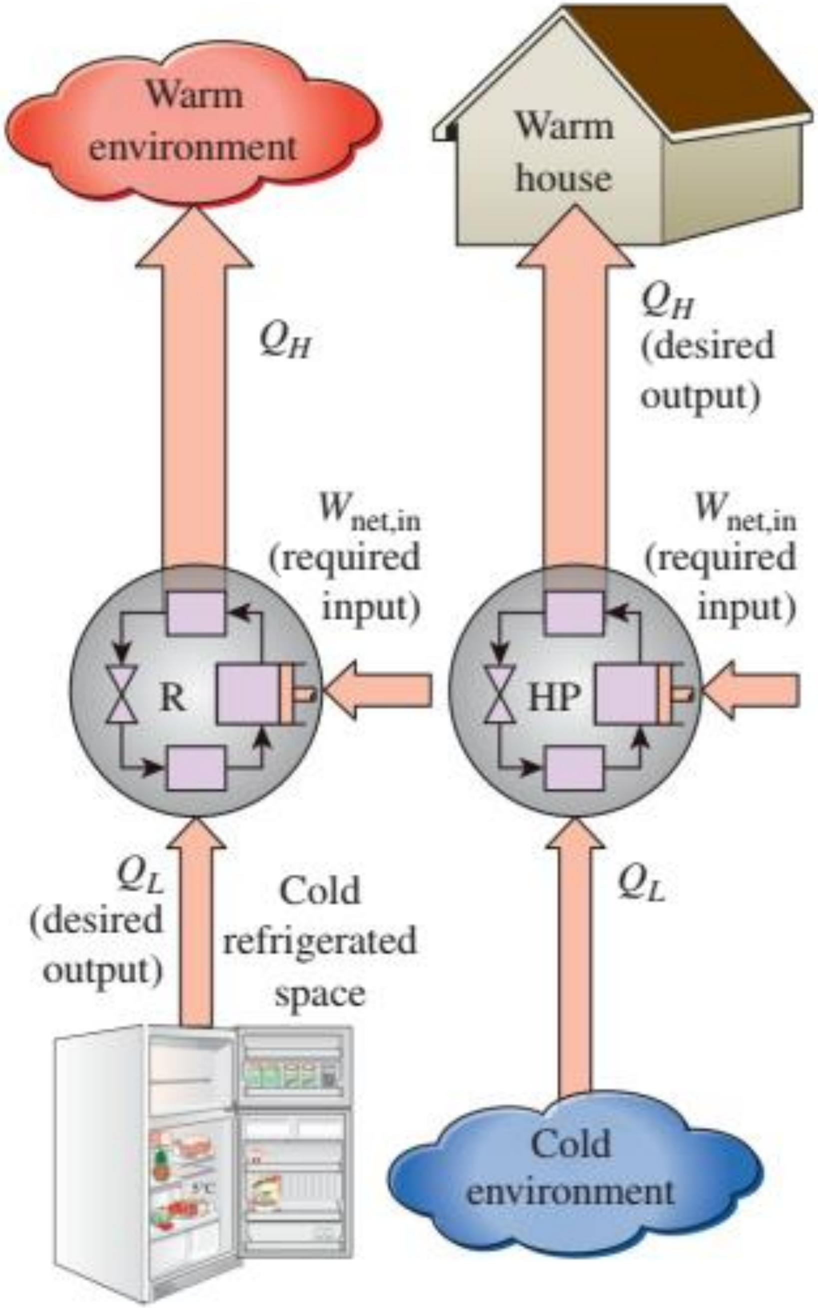
Lecture No. 34/35

REFRIGERATION CYCLES

INTRODUCTION

- Major application area of thermodynamics: ***Transfer of heat from a lower temperature region to a higher temperature one.***
- Devices that produce refrigeration are called ***refrigerators*** and the cycles on which they operate are called ***refrigeration cycles***.
- Most frequently used refrigeration cycle: ***Vapor-compression refrigeration cycle*** in which the refrigerant is vaporized and condensed alternately and is compressed in the vapor phase.
- Another well-known refrigeration cycle is ***absorption refrigeration***, where the refrigerant is dissolved in a liquid before it is compressed.

The objective of a **refrigerator** is to remove heat (Q_L) from the cold medium.



(*a*) Refrigerator (*b*) Heat pump

The objective of a ***heat pump*** is to supply heat (Q_H) to a warm medium.

REFRIGERATORS

- ❑ We all know from experience that heat flows in the direction of decreasing temperature, that is, from high-temperature regions to low-temperature ones. This heat-transfer process occurs in nature without requiring any devices.
- ❑ The reverse process, however, cannot occur by itself. The transfer of heat from a low-temperature region to a high-temperature one requires special devices called ***refrigerators***.
- ❑ Refrigerators are ***cyclic devices***, and the working fluids used in the refrigeration cycles are called ***refrigerants***.

HEAT PUMP

- Another device that transfers heat from a low-temperature medium to a high-temperature one is the ***heat pump***.
- Refrigerators and heat pumps are essentially the same devices; they ***differ in*** their ***objectives*** only.
- ***Objective of a refrigerator***: To maintain the refrigerated space at a low temperature by removing heat from it. Discharging this heat to a higher-temperature medium is merely a necessary part of the operation, not the purpose.
- ***Objective of a heat pump***: To maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low-temperature source & supplying this heat to a warmer medium.

COEFFICIENT OF PERFORMANCE (COP)

- ☐ The performance of refrigerators and heat pumps is expressed in terms of the ***coefficient of performance (COP)***:

$$\mathrm{COP_R} = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Cooling effect}}{\text{Work input}} = \frac{Q_L}{W_{net,in}}$$

$$\mathrm{COP_{HP}} = \frac{\text{Desired output}}{\text{Required input}} = \frac{\text{Heating effect}}{\text{Work input}} = \frac{Q_H}{W_{net,in}}$$

$$\mathrm{COP_{HP}} = \mathrm{COP_R} + 1$$

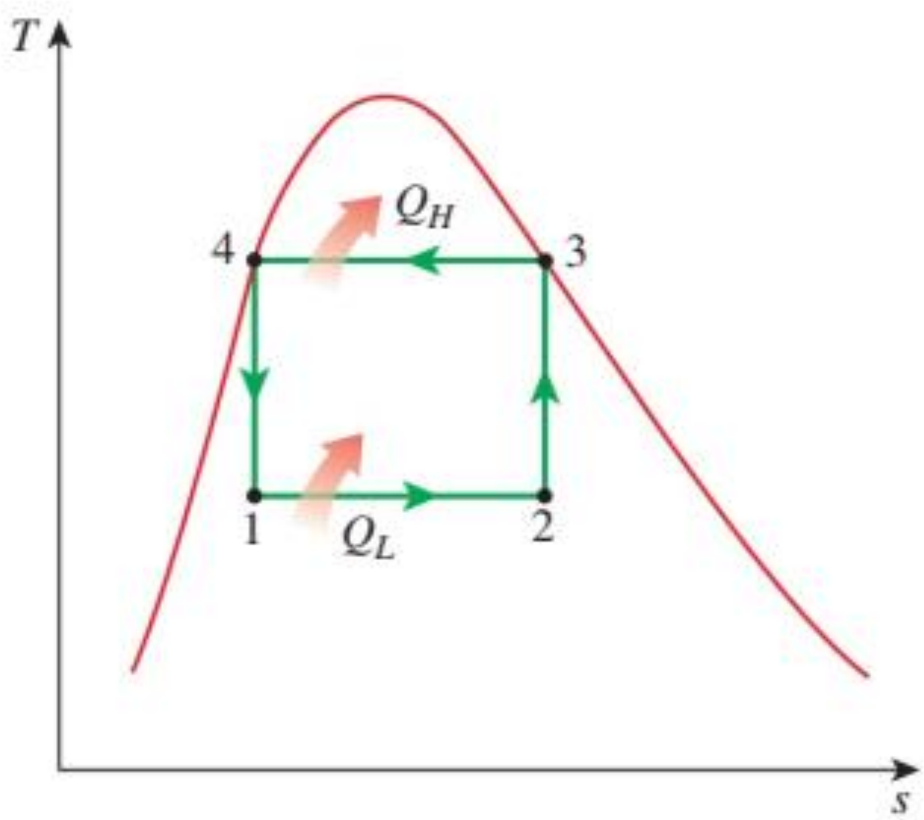
COOLING CAPACITY

- The ***cooling capacity of a refrigeration system***-that is, the rate of heat removal from the refrigerated space-is often expressed in terms of ***tons of refrigeration***.
- The ***capacity of a refrigeration system*** that can freeze 1 ton of liquid water at 0 °C into ice at 0 °C in 24 h is said to be 1 ton.
- One ton of refrigeration is equivalent to 211 kJ/min or 200 Btu/min.

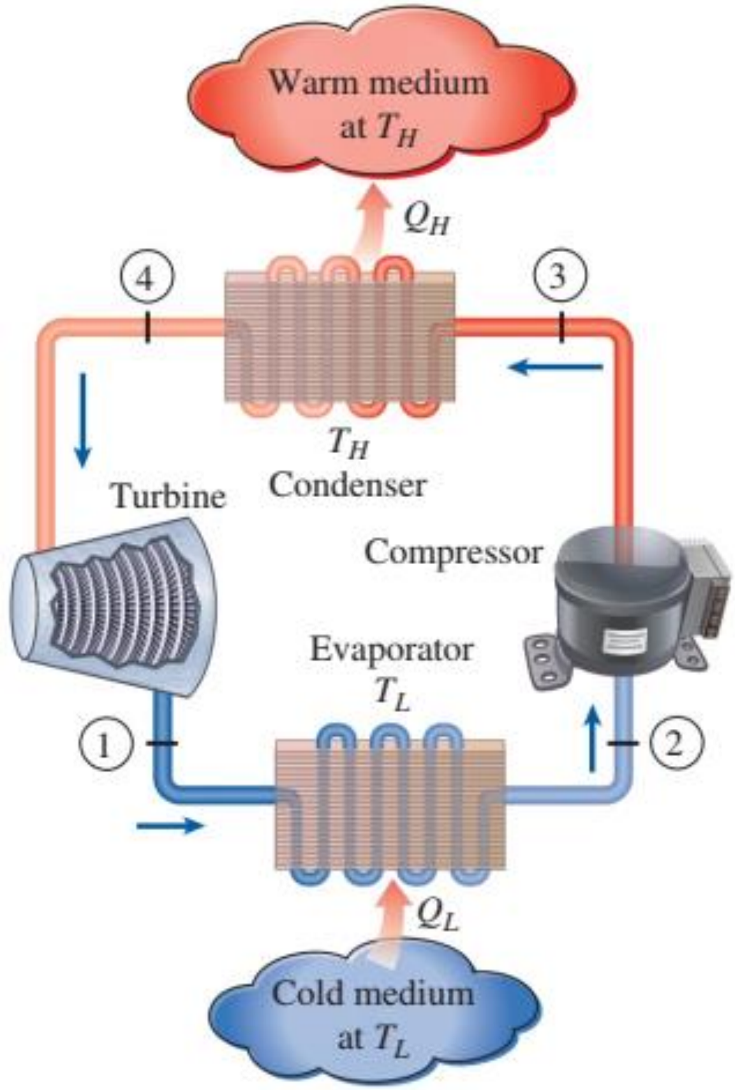
THE REVERSED CARNOT CYCLE

- ***Carnot cycle*** is a totally ***reversible cycle*** that consists of ***two reversible isothermal*** and ***two isentropic processes***. It has the ***maximum thermal efficiency*** for given temperature limits, and it serves as a standard against which actual power cycles can be compared.
- Since it is a reversible cycle, all four processes that comprise the Carnot cycle can be reversed.
- Reversing the cycle does also reverse the directions of any heat and work interactions. The result is a cycle that operates in the counter-clockwise direction on a *T-s* diagram, which is called the ***reversed Carnot cycle***. A refrigerator or heat pump that operates on the reversed Carnot cycle is called a ***Carnot refrigerator or a Carnot heat pump***.

T-s diagram of Reversed Carnot Cycle



Schematic of a Carnot Refrigerator



Reversed Carnot Cycle

Consider a reversed Carnot cycle executed within the saturation dome of a refrigerant. The refrigerant absorbs heat isothermally from a low-temperature source at T_L in the amount of Q_L (process 1-2), is compressed isentropically to state 3 (temperature rises to T_H), rejects heat isothermally to a high-temperature sink at T_H in the amount of Q_H (process 3-4), and expands isentropically to state 1 (temperature drops to T_L). The refrigerant changes from a saturated vapor state to a saturated liquid state in the condenser during process 3-4.

COEFFICIENT OF PERFORMANCE (COP)

- The coefficients of performance of Carnot refrigerators and heat pumps are expressed in terms of temperatures as

$$\mathrm{COP}_{\mathrm{R,\ Carnot}} = \frac{1}{\frac{T_H}{T_L} - 1}$$

$$\mathrm{COP}_{\mathrm{HP,\ Carnot}} = \frac{1}{1-\frac{T_L}{T_H}}$$

- Notice that both COPs increase as the difference between the two temperatures decreases, that is, as T_L rises or T_H falls.

Reversed Carnot Cycle

- The reversed Carnot cycle is the most efficient refrigeration cycle operating between two specified temperature levels.
- Therefore, it is natural to look at it first as a prospective ideal cycle for refrigerators and heat pumps.
- If we could, we certainly would adapt it as the ideal cycle.
- As explained below, however, the reversed Carnot cycle is not a suitable model for refrigeration cycles.

Reversed Carnot Cycle

- The two isothermal heat transfer processes are not difficult to achieve in practice since maintaining a constant pressure automatically fixes the temperature of a two-phase mixture at the saturation value. Therefore, processes 1-2 and 3-4 can be approached closely in actual evaporators and condensers.

- However, processes 2-3 and 4-1 cannot be approximated closely in practice. This is because process 2-3 involves the compression of a liquid-vapor mixture, which requires a compressor that will handle two phases, and process 4-1 involves the expansion of high-moisture-content refrigerant in a turbine.

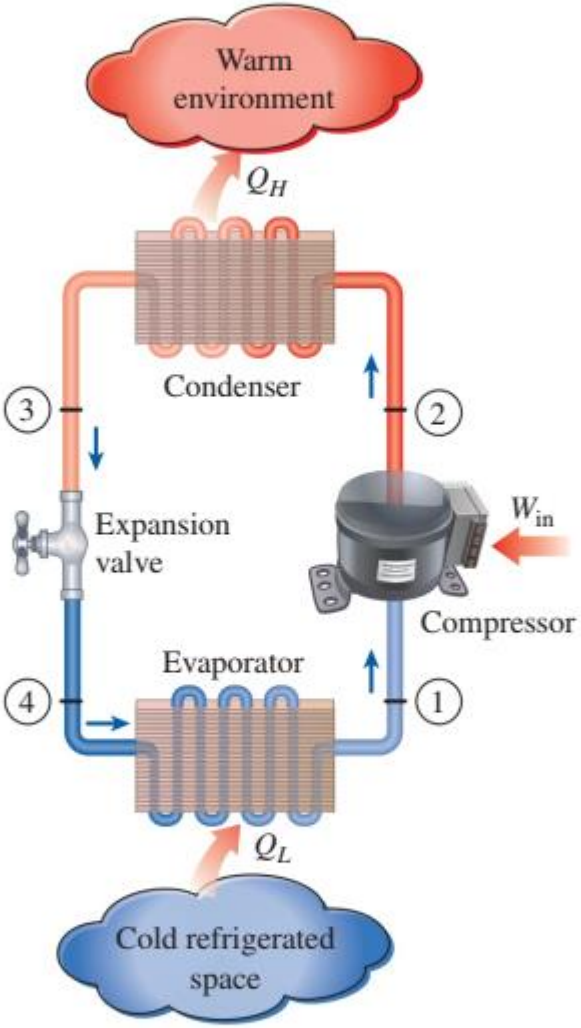
- Therefore, reversed Carnot cycle cannot be approximated in actual devices and is not a realistic model for refrigeration cycles. However, the reversed Carnot cycle can serve as a standard against which actual refrigeration cycles are compared.

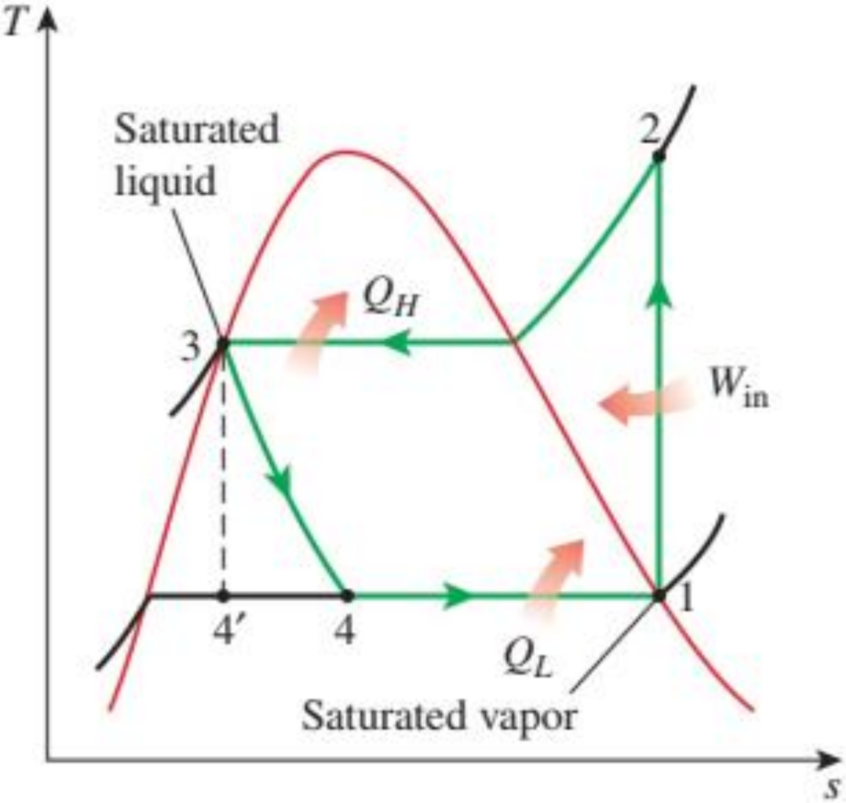
VAPOR-COMPRESSION REFRIGERATION CYCLE

- Many of the impracticalities associated with the reversed Carnot cycle can be eliminated by **vaporizing the refrigerant completely before it is compressed** and ***by replacing the turbine with a throttling device***, such as an expansion valve or capillary tube. The cycle that results is called the ideal ***vapor-compression refrigeration cycle***.

- The vapor-compression refrigeration cycle is the most widely used cycle for refrigerators, air-conditioning systems, and heat pumps.

VAPOR-COMPRESSION REFRIGERATION CYCLE





VAPOR-COMPRESSION REFRIGERATION CYCLE

- It consists of four processes:
  - 1-2 Isentropic compression in a compressor.
  - 2-3 Constant pressure heat rejection in a condenser.
  - 3-4 Throttling in an expansion device.
  - 4-1 Constant pressure heat absorption in an evaporator.

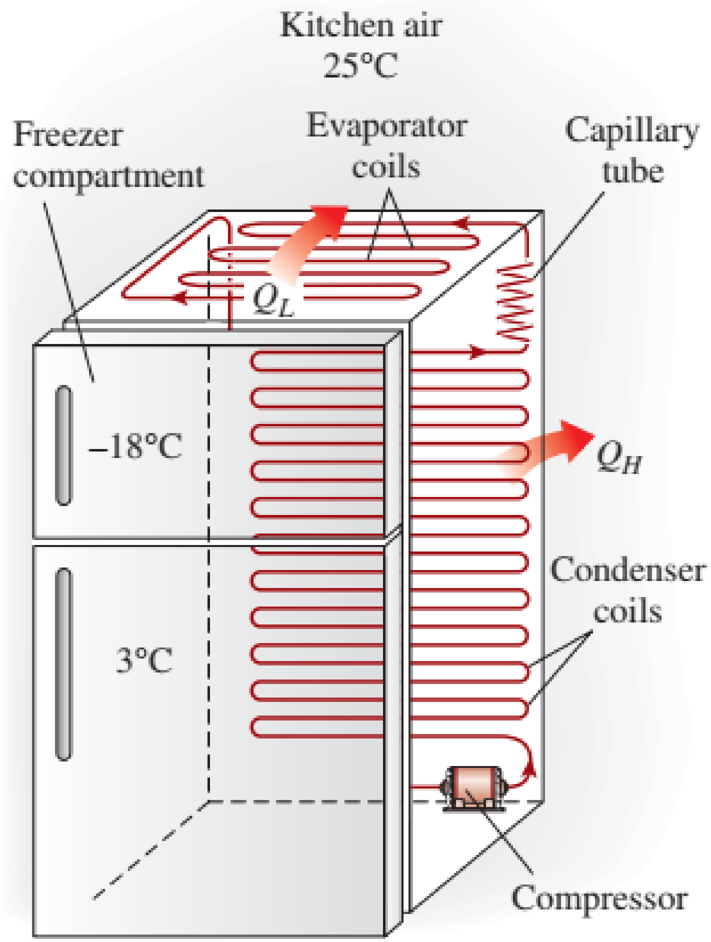
VAPOR-COMPRESSION REFRIGERATION CYCLE

- In vapor-compression refrigeration cycle, the refrigerant enters the compressor at **state 1** as saturated vapor and is compressed isentropically to the condenser pressure. The temperature of the refrigerant increases during this isentropic compression process to well above the temperature of the surrounding medium.
- The refrigerant then enters the condenser as superheated vapor at **state 2** and leaves as saturated liquid at **state 3** as a result of heat rejection to the surroundings. The temperature of the refrigerant at this state is still above the temperature of the surroundings.

VAPOR-COMPRESSION REFRIGERATION CYCLE

- The saturated liquid refrigerant at **state 3** is throttled to the evaporator pressure by passing it through an expansion valve or capillary tube. The temperature of the refrigerant drops below the temperature of the refrigerated space during this process.
- The refrigerant enters the evaporator at **state 4** as a low-quality saturated mixture, and it completely evaporates by absorbing heat from the refrigerated space. The refrigerant leaves the evaporator as saturated vapor and re-enters the compressor, completing the cycle.

VAPOR-COMPRESSION REFRIGERATION CYCLE



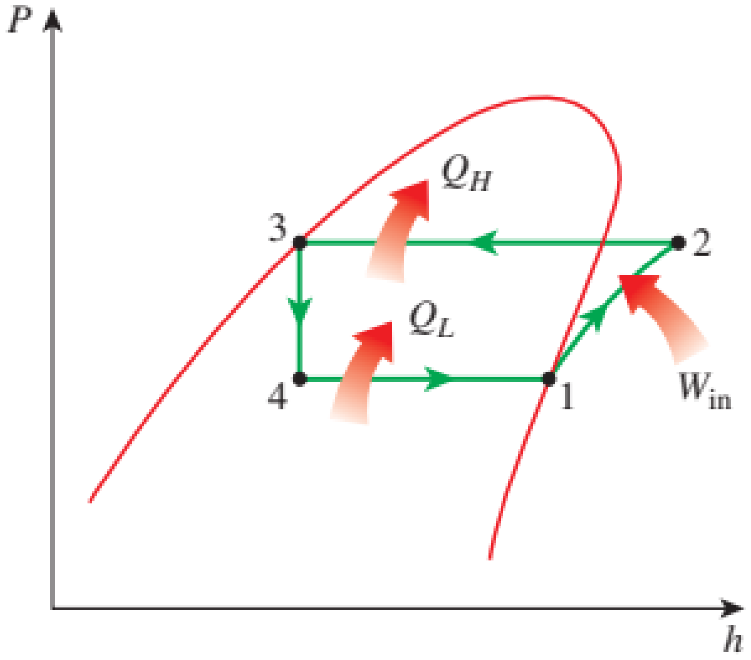
An ordinary household refrigerator

VAPOR-COMPRESSION REFRIGERATION CYCLE

- Area under the process curve on a ***T-s*** diagram represents the heat transfer for internally reversible processes.
- The area under the process curve ***4-1*** represents the heat absorbed by the refrigerant in the evaporator.
- The area under the process curve ***2-3*** represents the heat rejected in the condenser.
- A rule of thumb is that the COP improves by 2 to 4 % for each °C the evaporating temperature is raised or the condensing temperature is lowered.

VAPOR-COMPRESSION REFRIGERATION CYCLE

- ❖ Another diagram frequently used in the analysis of vapor-compression refrigeration cycles is the *P-h* diagram.
- ❖ On this diagram, three of the four processes appear as straight lines.



The *P-h* diagram of an ideal vapor compression refrigeration cycle

VAPOR-COMPRESSION REFRIGERATION CYCLE

- The ideal vapor compression refrigeration cycle is not an internally reversible cycle since it involves an irreversible (throttling) process.
- If the throttling device were replaced by an isentropic turbine, the refrigerant would enter the evaporator at state 4’ instead of state 4.
- To have heat transfer at a reasonable rate, a temperature difference of 5-10 °C should be maintained between the refrigerant and the medium with which it is exchanging heat.
- The lowest pressure in a refrigeration cycle occurs in the evaporator, and this pressure should be above atmospheric pressure to prevent any air leakage into the refrigeration system. Therefore, a refrigerant should have a saturation pressure of 1 atm or higher at -20 °C .

THANK YOU

Entropy Balance for open systems

Just as an energy balance can be written for processes in which fluid enters, exits or flows through a control volume, so too can an entropy balance can be written. There is, however, an important difference: Entropy is not conserved.

The second law states that the total entropy change associated with any process must be positive, with a limiting value of zero for a reversible process. This requirement is taken into account by writing the entropy balance for both the system and its surroundings, considered together, and by including an entropy-generation term to account for the irreversibilities of the process. This term is the sum of three others:

1) one for the difference in entropy between exit and entrance streams,
2) one for the entropy change within the control volume, and
3) one for the entropy change in the surroundings.

If the process is reversible, these three terms sum ~~up~~ to zero, making $\Delta S_{total} = 0$. If the process is irreversible, they sum to a positive quantity, the entropy-generation term.

The statement of balance, expressed as rates, is therefore:

$$\left\{\begin{array}{l}\text{Net rate of}\\ \text{change in}\\ \text{entropy of}\\ \text{flowing streams}\end{array}\right\} + \left\{\begin{array}{l}\text{Time rate of}\\ \text{change of}\\ \text{entropy}\\ \text{in control}\\ \text{volume}\end{array}\right\} + \left\{\begin{array}{l}\text{Time rate}\\ \text{of change}\\ \text{of entropy}\\ \text{in surroundings}\end{array}\right\}$$

$$= \left\{\begin{array}{l}\text{Total rate}\\ \text{of entropy}\\ \text{generation}\end{array}\right\}$$

The equivalent equation of entropy balance is:

$$\Delta(S\dot{m})_{fs} + \frac{d}{dt}(mS)_{cv} + \frac{dS^t_{surr}}{dt} = \dot{S}_G \geqslant 0 \qquad \longrightarrow (1)$$

where $\dot{S}_G$ is the rate of entropy generation.

The first term is simply the net rate of gain in entropy of the flowing streams i.e. the difference between the total entropy transported out by exit streams and the total entropy transported in by entrance streams. The second term is the time rate of change of the total entropy of the fluid contained within the control volume. The third term is the time rate of change of the entropy of the surroundings, resulting from heat transfer between system and surroundings.

Let rate of heat transfer $\dot{Q}_J$ with respect to a particular part of the control surface be associated with $T_{\sigma,j}$ where subscript σ,j denotes a temperature in the surroundings. The rate of entropy change in the surroundings as a ~~resulting~~ result of this transfer is then $\frac{-\dot{Q}_j}{T_{\sigma,j}}$

The third term in Eq. (1) is therefore the sum of all such quantities:

$$\frac{dS^t_{surr}}{dt} = -\sum_j \frac{\dot{Q}_j}{T_{\sigma,j}}$$

Equation (1) is now written:

$$\boxed{\Delta(S\dot{m})_{fs} + \frac{d(mS)_{cv}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0} \longrightarrow (2)$$

For a steady-state flow process

$$\boxed{\Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}_J}{T_{\sigma,j}} = \dot{S}_G \geq 0} \longrightarrow (3)$$

If ~~thee~~ there is one entrance and one exit, with $\dot{m}$ the same for both streams, dividing through by $\dot{m}$ yields,

$$\boxed{\Delta S - \sum_j \frac{Q_j}{T_{\sigma,j}} = S_G \geq 0} \longrightarrow (4)$$

* Each term in eqn. (4) is based on a unit amount of fluid flowing through the control volume.

Calculation of ideal work

For reversible process (from eqn. 3): (written for the uniform surroundings temp. T_σ)

$$\Delta(S\dot{m})_{fs} - \frac{\dot{Q}}{T_\sigma} = 0$$

$$\Rightarrow \quad \dot{Q} = T_\sigma \Delta(S\dot{m})_{fs} \quad \longrightarrow (5)$$

From Energy balance for steady-state flow processes:

$$\Delta\left[\left(H+\tfrac{1}{2}u^2+gz\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}_s \quad \longrightarrow (6)$$

using eqn. (5) in eqn. (6),

$$\Delta\left[\left(H+\tfrac{1}{2}u^2+gz\right)\dot{m}\right]_{fs} = T_\sigma \Delta(S\dot{m})_{fs} + \dot{W}_s(\text{rev})$$

The shaft work, $\dot{W}_s(\text{rev})$, is here the work of a completely reversible process. If $\dot{W}_s(\text{rev})$ is given the name ideal work, $\dot{W}_{ideal}$, the preceding equation may be rewritten:

$$\dot{W}_{ideal} = \Delta\left[\left(H+\tfrac{1}{2}u^2+gz\right)\dot{m}\right]_{fs} - T_\sigma \Delta(S\dot{m})_{fs} \quad \longrightarrow (7)$$

In most applications, the K.E. and P.E. terms are negligible compared with the others; so,

$$\dot{W}_{ideal} = \Delta(H\dot{m})_{fs} - T_\sigma \Delta(S\dot{m})_{fs} \quad \longrightarrow (8)$$

For the special case of a single stream flowing through the control volume, eqn. (8) may be expressed as rates or upon division by $\dot{m}$ on the basis of a unit amount of fluid flowing through the control volume. Thus,

Thus,

$$\dot{W}_{ideal} = \dot{m}\left(\Delta H - T_\sigma \Delta S\right) \longrightarrow (9)$$

$$W_{ideal} = \Delta H - T_\sigma \Delta S \longrightarrow (10)$$

The above equations give the work of a completely reversible process associated with given property changes in the flowing streams.

When the same property changes occur in an actual process, the actual work $\dot{W}_S$ can be compared with the Ideal work.

When $\dot{W}_{ideal}$ is positive, it is the minimum work required to bring about a given change in the properties of the flowing streams, and is smaller than $\dot{W}_S$. In this case a thermodynamic efficiency is defined as the ratio of the ideal work to the actual work:

$$\eta_t \,(\text{work required}) = \frac{\dot{W}_{ideal}}{\dot{W}_S} \longrightarrow (11)$$

When $\dot{W}_{ideal}$ is negative, $|\dot{W}_{ideal}|$ is the maximum work obtainable from a given change in the properties of the flowing streams and is larger than $|\dot{W}_S|$. In this case,

$$\eta_t \,(\text{work produced}) = \frac{\dot{W}_S}{\dot{W}_{ideal}} \longrightarrow (12)$$

Lost Work

Work that is wasted as the result of irreversibilities in a process is called lost work, W_{lost}, and is defined as the difference between the actual work of a process and the ideal work for the process. Thus,

$$W_{lost} = W_S - W_{ideal} \longrightarrow (13)$$

In terms of rates,

$$\dot{W}_{lost} = \dot{W}_S - \dot{W}_{ideal} \longrightarrow (14)$$

Now, $\dot{W}_S = \Delta\left[\left(H + \frac{1}{2}u^2 + gz\right)\dot{m}\right]_{fs} - \dot{Q}$

and $\dot{W}_{ideal} = \Delta\left[\left(H + \frac{1}{2}u^2 + gz\right)\dot{m}\right]_{fs} - T_\sigma \Delta(s\dot{m})_{fs}$

Thus, $$\boxed{\dot{W}_{lost} = T_\sigma \Delta(s\dot{m})_{fs} - \dot{Q}} \longrightarrow (15)$$

For the case of a single surroundings temperature T_σ, Eq^n.(3) becomes

$$\dot{S}_G = \Delta(s\dot{m})_{fs} - \frac{\dot{Q}}{T_\sigma} \longrightarrow (16)$$

or, $$T_\sigma \dot{S}_G = T_\sigma \Delta(s\dot{m})_{fs} - \dot{Q} \longrightarrow (17)$$

comparing eq^n. (15) and eq^n. (17),

$$\boxed{\dot{W}_{lost} = T_\sigma \dot{S}_G} \longrightarrow (18)$$

As a consequence of the second law, $\dot{S}_G \geq 0$; it follows that $\dot{W}_{lost} \geq 0$.

When a process is completely reversible, the equality holds, and $\dot{W}_{lost} = 0$.

For irreversible processes the inequality holds, and $\dot{W}_{lost}$ i.e. the energy that becomes unavailable for work is positive.

The engineering significance of this result is clear: The greater the irreversibility of a process, the greater the rate of entropy production and the greater the amount of energy that becomes unavailable for work.

The Third Law of thermodynamics

The entropy of a perfect crystalline substance is zero at ~~the~~ absolute zero temperature.

→ This allows us to determine the absolute entropy.

→ Entropy for substances are always positive.

$$\lim_{T \to 0} S = 0.$$

⇒ principle of the unattainability of the absolute zero:

It is impossible by any procedure, no matter how idealized, to reduce any assembly to the absolute zero in a finite number of operations. and within a finite time.

⇒ ~~det~~ for any solid, let S_0 be the entropy at 0K and S be the entropy at TK, then

$$\Delta S = S - S_0 = \int_0^T \frac{C_p dT}{T}$$

Since, $S_0 = 0$ @ 0K, from 3rd law of thermo.

$$S = \int_0^T \frac{C_p dT}{T}$$