CHEMICAL ENGINEERING THERMODYNAMICS

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SECOND LAW OF THERMODYNAMICS

DEPARTMENT OF CHEMICAL ENGG.

BITS PILANI K. K. BIRLA GOA CAMPUS

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Introduction and basis for Second law

- The First Law provides a constraint on the total energy contained in a system and its surroundings. It is reasonable to assume that a process must satisfy the first law to occur.

- However, it places no restriction on the direction in which a process will occur

- Take example of some natural / spontaneous processes:
  - Heat always flows from a high temperature body to one at a lower temperature
  - Momentum flow is always prompted in the direction of a pressure gradient
  - Molecules always migrate from a region of higher to lower chemical potential

Introduction and basis for Second law

- Based on these observations of nature, we see that processes can take place in a certain direction and not in the <u>reverse direction</u>

- Relaxation processes act naturally to reduce any temperature and velocity gradients in the system result in conversion of mechanical energy in the form of work or heat

- While the first law gives a quantitative estimate it gives no information on whether a process will occur or not

- Answer to this is provided by the second law

- The <u>reverse processes,</u> if at all they occur spontaneously, end up violating the second law

- For a process / cycle to occur it must satisfy both the laws of thermodynamics

- While the first law discusses **quantity** the second law looks at **quality** and degree of degradation of energy during a process

Heat, Work and Engines

- Although both heat and work are different forms of energy, there is distinction between work (mechanical energy) and heat (thermal energy)

- Heat is a form of energy intrinsically less useful and hence less valuable than an equal quantity of work or mechanical or electrical energy

- All efforts to, devise a process, or development of device (<u>heat</u> <u>engine</u>), for the continuous conversion of heat completely into work have failed

- Much efforts has been spent on developing heat engines of high efficiency that convert as large as a fraction of the heat supplied to useful work as possible

Statements of Second law

▸ The *second law* expressed a general restriction on processes, beyond that imposed by *first law*, by two statements:

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

Statement 1 a: It is impossible by a cyclic process to convert the heat absorbed by a system completely into work done by the system (Kelvin Planck's Statement)

Statement 2: No process is possible which consists solely in the transfer of heat from one temperature level to a higher one (Clausius Statement)

▸ The second law is also used to determine the theoretical limits for performance of various engineering systems as well as predicting the degree of completion of various chemical reactions

Isothermal expansion of gas in piston-cylinder arrangement
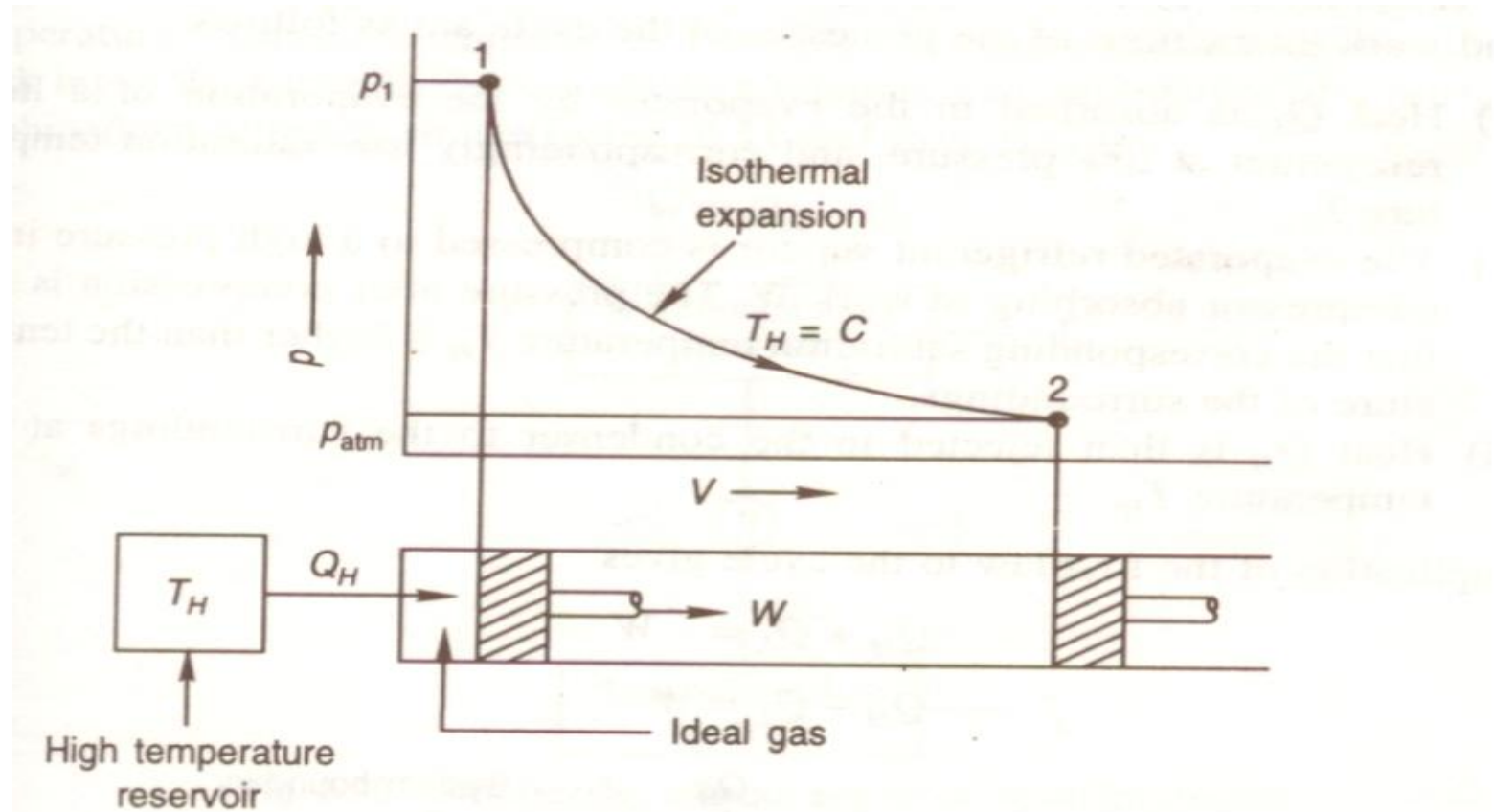
Fig. 6.8 A process: Isothermal expansion of a gas in which $W = Q_H$

Heat Engines

- This a thermodynamic system operating on a cycle to which net positive amount of heat is added and net positive amount of work is obtained

- Note the stress on the word "net" and "operating on a cycle". The later term implies that by operating just in a single process, it is not possible to obtain work continuously

- A heat engine
  - Receive heat from a high temperature (source)
  - Convert part of this heat into work
 - Reject the remaining heat to a low temperature (sink)
  - Operates in a cycle

Heat Reservoir

- It is a body with large heat capacity to and from which heat can be transferred without change in temperature

- Some typical examples in nature are oceans, lakes, rivers, atmosphere etc.

- A two phase system can be modelled as a heat reservoir since it can absorb and release large quantities of heat at constant temperature

- A reservoir that supplies energy in the form of heat is called a **source** and one that absorbs energy in the form on heat is referred to as a **sink**

- These are closed systems with no work interaction

- A heat reservoir is always characterised by its temperature

Illustration of heat engines

- **Steam Power Plant:** Heat enters the heat engine at boiler and leaves at condenser, and the difference between these two equals the work done by turbine

- **Automobile Engines**: Mechanical Engine

- **Thermocouple:** Temperature measuring device consists of two wires (placed in cold reservoir and hot reservoir) of dissimilar metals joined to form a loop. An electromotive force is generated, which cause current to flow, which could be used to operate electric motor

Illustration of heat engines
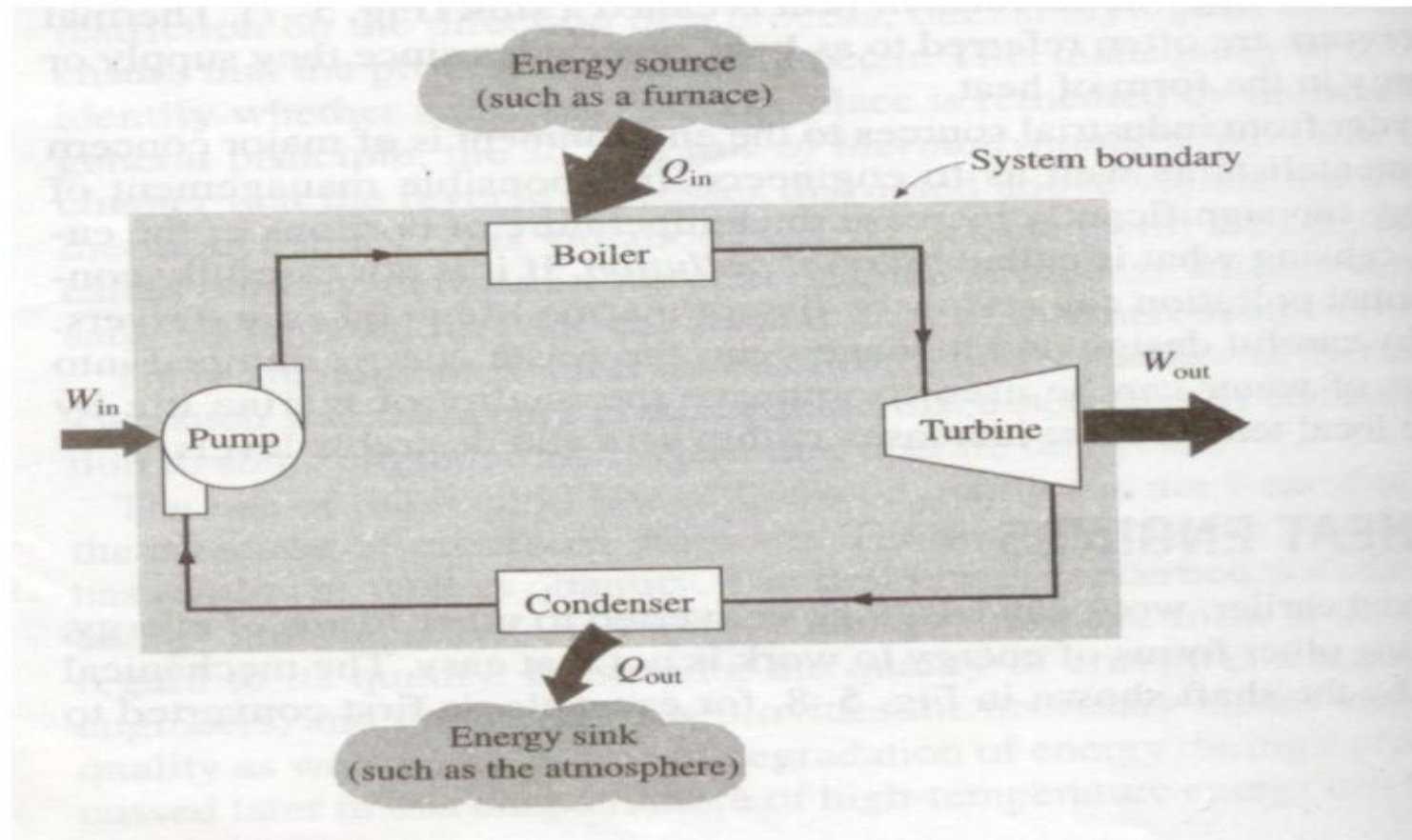
Note: cycle is complete thermodynamically

Ilustration of heat engines (Thermal efficiency)

- Note Q_{out} is the magnitude of energy wasted in the environment in order to complete the cycle, but it can never be equal to zero

- Only a part of the heat input transferred is converted to work

- The fraction of heat input that is converted to work (desired output) is a measure of performance of the heat engine

η_{th} = objective quantity / quantity that costs

= net work output / total heat input

Ilustration of heat engines (Thermal efficiency)

$$\eta_{th} = W_{net\ out} / Q_{in} = 1 - (Q_{out} / Q_{in})$$

- Most devices operate between a high temperature and low temperature reservoir (between temperatures T_H and T_L)

$$\eta_{th} = 1 - (Q_L / Q_H) < 1$$

- Thermal efficiency is a measure of how efficiently an engine converts heat into work

- For large steam power plants η_{th} ~ 40% and that for diesel and petrol engines ~ 35%

Generalized Heat Engine Efficiency

- Second Law states that no heat engine can have an efficiency of 100 %

- If so, then what is the maximum efficiency possible for a heat engine?

- Thermal efficiency of heat engine depend on the degree of reversibility.

- A heat engine working in a completely reversible manner is proposed by Carnot, and is called *Carnot engine*.

- While Carnot's engine has great theoretical utility, it would be most impractical to build and operate.

The Carnot cycle

- The most efficient engine is the one which operates between given high temperature and low temperature reservoirs, does so in a cycle in which every process is reversible

- First proposed by French engineer Sadi Carnot (1824)

- One of Carnot's important accomplishment was to propose a reversible engine cycle whose efficiency could be readily calculated for all temperature levels

- If the cycle is reversed the heat engine becomes a refrigerator or heat pump

Carnot's Theorem

Corollary 1

No heat reservoir operating in a cycle between two constant temperature reservoirs can be more efficient than a reversible engine operating between the same two reservoirs

Corollary 2

All reversible engines operating between the same two reservoirs have the same efficiency irrespective of the substance used

Carnot efficiency

- From the corollaries it is seen that the thermal efficiencies of two reversible heat engines E and E' is the same between same two reservoirs, thus $(\eta_{th})_E = (\eta_{th})_{E'}$

- Therefore $(Q_L / Q_H)_E = (Q_L / Q_H)_{E'}$ (ratio is the same)

- Since a reservoir is characterized by its temperature, (Q_L / Q_H) is a function of t_L and t_H only

- Therefore $(\eta_{th})_{max} = (\eta_{th})_{Carnot} = f(t_H, t_L)$. Same logic applies for Carnot COP

- Thus both Carnot efficiency and COP are independent of working substance used

Thermodynamic temperature scale

- Efficiency of a Carnot cycle as seen is independent of the working substance and depends only on temperatures of source and sink

- This fact provides a basis for an absolute temperature scale also known as thermodynamic scale of temperature.

- This approach involves the use of a reversible, heat engine as thermometer
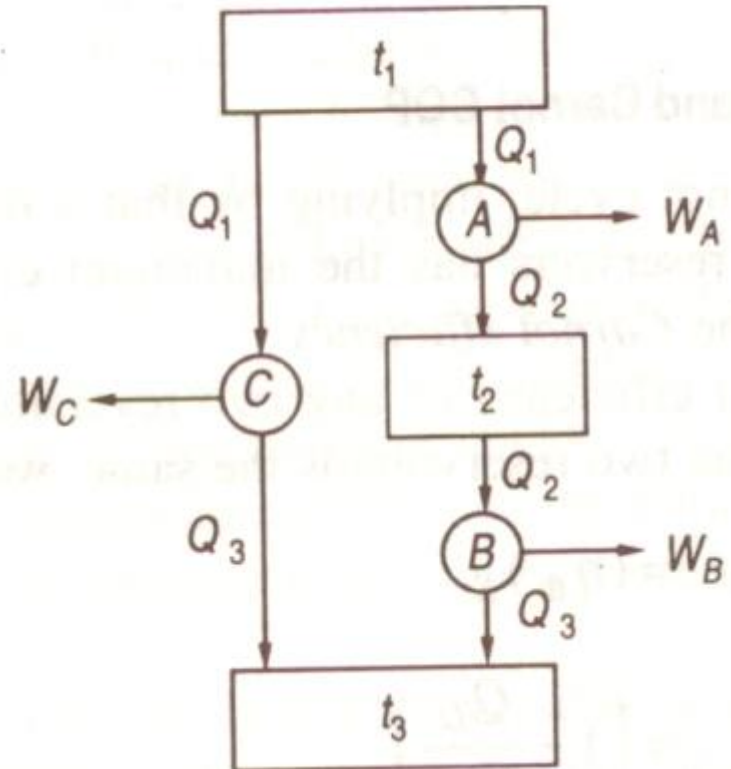
Thermodynamic or the absolute temperature scale

- **Efficiency is a function of temperature for a Carnot cycle** $\longrightarrow$
$$\eta_{\text{thermal}} = 1 - \frac{Q_L}{Q_H} = 1 - \psi(t_L, t_H)$$

$$\frac{Q_1}{Q_2} = \psi(t_1, t_2)$$

$$\frac{Q_2}{Q_3} = \psi(t_2, t_3)$$

Therefore $\qquad \dfrac{Q_1}{Q_3} = \psi(t_1, t_3)$

Thermodynamic or the absolute temperature scale

- **Since** $\dfrac{Q_1}{Q_3} = \dfrac{Q_1 Q_2}{Q_2 Q_3}$

$$\psi(t_1, t_3) = \psi(t_1, t_2) \times \psi(t_2, t_3)$$

$$\psi(t_1, t_2) = \frac{f(t_1)}{f(t_2)} \qquad \psi(t_2, t_3) = \frac{f(t_2)}{f(t_3)}$$

$$\frac{Q_1}{Q_3} = \psi(t_1, t_3) = \frac{f(t_1)}{f(t_3)} \qquad \frac{Q_H}{Q_L} = \psi(t_H, t_L) = \frac{f(t_H)}{f(t_L)}$$

Thermodynamic or the absolute temperature scale

- There are several number of functional relationships that will satisfy the equation

- The one proposed by Kelvin was

$$\frac{Q_H}{Q_L} = \psi(t_H, t_L) = \frac{f(t_H)}{f(t_L)} = \frac{t_H + C}{t_L + C} = \frac{T_H}{T_L}$$

- This function makes the absolute scale coincides with the ideal gas temperature scale developed earlier with an assigned value of 273.16 K for triple point of water

- The validity of the relation can be theoretically demonstrated by using an ideal gas as the working fluid in a reversible cycle

The Carnot cycle (salient features)

Composed of four reversible processes, regardless of the working substance

- **a →b** Adiabatic compression until the temperature rises from T_C to T_H.

- **b →c** Isothermal expansion to point c with absorption of heat $|Q_H|$.

- **c →d** Adiabatic expansion until the temperature decreases to T_C.

- **d →a** Isothermal compression to the initial state with rejection of heat $|Q_C|$.
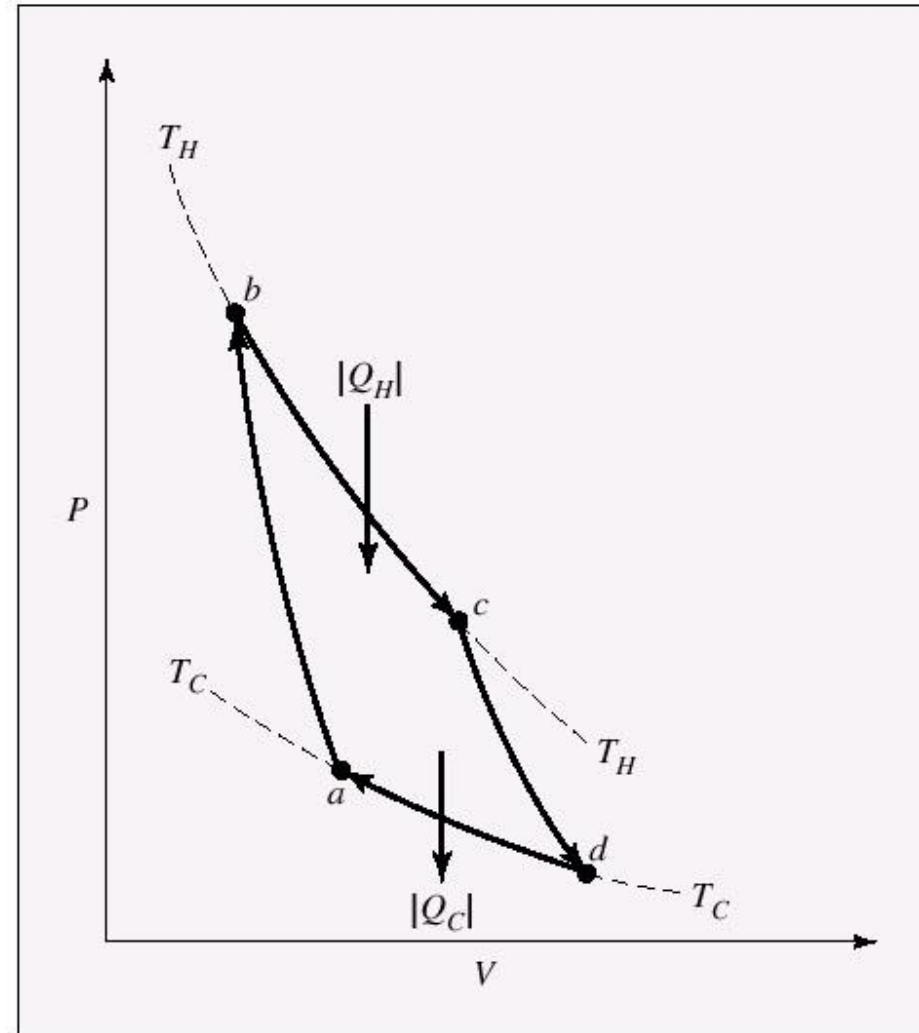
The Carnot cycle : Ideal gas

- Consider a Carnot engine consists of a cylinder fitted with a frictionless piston, enclosing an ideal gas as working substance.

- The engine is undergoing a cyclic process consists of $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$ (shown on figure in previous page)

- The work and heat effects of four steps in cycle are presented in table below:

Process	Heat absorbed by gas	Work done by gas	Remark
a-b	0	$C_v (T_H - T_C)$	$\int_{T_C}^{T_H} \frac{C_V}{R} \frac{dT}{T} = -\ln \frac{V_b}{V_a}$
b-c	$Q_H = RT_H \ln (V_c/V_b)$	$RT_H \ln (V_c/V_b)$	$\Delta U = 0$
c-d	0	$-C_v (T_H - T_C)$	$\int_{T_H}^{T_C} \frac{C_V}{R} \frac{dT}{T} = -\ln \frac{V_d}{V_c}$
d-a	$Q_C = RT_C \ln (V_a/V_d)$	$RT_C \ln (V_a/V_d)$	$\Delta U = 0$

Thermodynamic or the absolute temperature scale

- With absolute temperatures defined thus, the thermal efficiency of a Carnot engine cycle can be expressed as

$$\eta_{th} = 1 - (Q_L / Q_H) = 1 - (T_L / T_H)$$

- The COPs of a Carnot refrigerator and a Carnot pump

$$COP_R = Q_L / (Q_H - Q_L) = T_L / (T_H - T_L)$$
$$COP_H = Q_H / (Q_H - Q_L) = T_H / (T_H - T_L)$$

Effect of temperature T_H and T_L

- For high thermal efficiency it is seen that the temperature of the heat source should be as high as possible

- For high thermal efficiency the temperature of the low temperature reservoir or sink must be as low as possible

- Steam Power plant source at 450 ^{o}C and sink at 45 ^{o}C gives an efficiency of 0.44 (not more than 40 % with irreversibility)

- For a solar source at at 150 ^{o}C and sink at 40 ^{o}C, efficiency is 0.26 (not more than 10% with irreversibility)

Absolute zero

- This exists in the thermodynamic scale and corresponds to –273.15 ^{o}C on the Celsius scale
- Achieved by considering a combination of reversible heat engines operating between a high temperature reservoir and low temperature reservoirs such that T_L tends to zero
- In such a case work output becomes equal to heat input and thermal efficiency tends to 1
- In practice there is no heat reservoir existing at absolute zero temperature
- The thermal efficiency is governed by the lowest possible temperature of heat rejection in the surroundings

The quality of energy

- We know the thermal efficiency decreases as the source temperature drops. For example at a source temperature of 925 K, 67.2 % of it gets converted to work, while at 500 K, the efficiency drops to 39.4 %

- Energy thus has quality. Higher the temperature, higher is the quality

- Work has higher quality since 100% of it can be converted to heat. Heat when degraded, gets converted to work, only a fraction of it though

Clausius Equality

- Carnot equation can be written as

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

Heat quantities refers to the working fluid of the engine, Q_H is positive and Q_L is negative

or

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

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$$

$$\frac{dQ_H}{T_H} + \frac{dQ_C}{T_C} = \oint \frac{dQ_{rev}}{T} = 0 \qquad \textbf{Clausius Equality}$$

For a irreversible process $\oint \dfrac{dQ_{rev}}{T} < 0$ **Clausius Inequality**

Entropy for reversible process

- Clausius equality is also applies to other reversible cycles

- The figure shows an arbitrary reversible cycle for arbitrary fluid

- Divide the area by a series of reversible adiabatic curves and connect adjacent adiabatic curves by two short reversible isotherms

- When the separation becomes very small, each pair of adiabatic and isothermal curves represent Carnot cycle and summation leads to
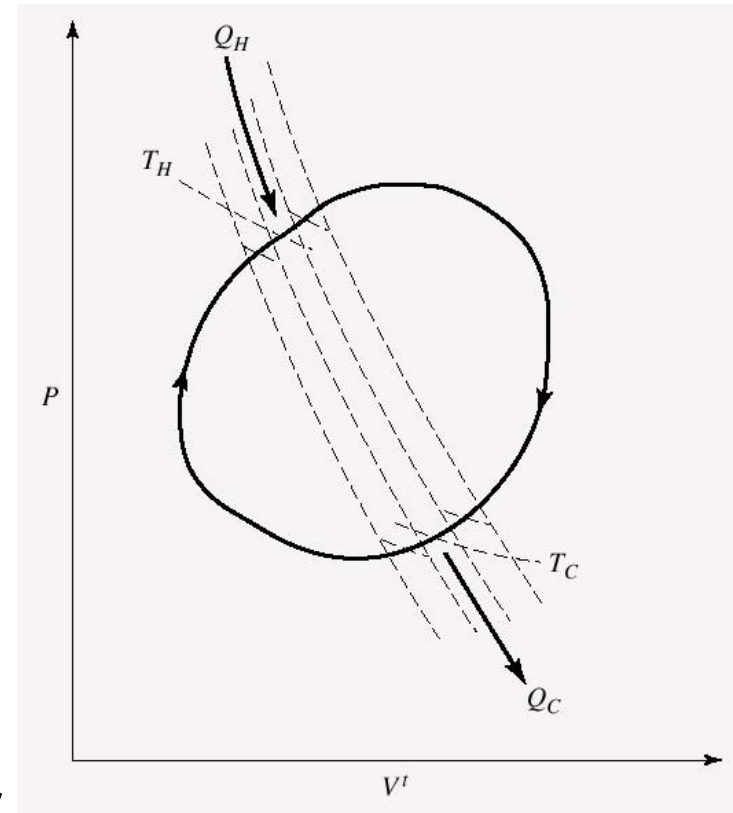
$$\oint \frac{dQ_{rev}}{T} = 0$$

Entropy a thermodynamic property

- It is proved that the equality of Clausius holds good for reversible cycles and suggest a characteristic property

  (Remember the cyclic integral of heat and work is not zero, but that of internal energy it is zero and internal energy is a property)

- Therefore a quantity whose cyclic integral is zero depends on state only and not the path and is therefore a property,

- Clausius called this property ENTROPY

$$dS^t = \left(\frac{\delta Q_{rev}}{T} \right)$$

- S^t is total entropy of the system (extensive property)

Entropy for reversible process in a closed system

- Once the process is evaluated it applies to any process (reversible or irreversible)

- This is because the difference of a property between two given state points is independent of the manner of reaching one state from another

- Note that the integral along an irreversible path is not a property and different values will be obtained when integration is carried out along different irreversible paths

- Even for an irreversible process, the integration must be carried out along some convenient imaginary reversible path between specified states

Entropy changes of an ideal gas

For unit mole (or mass) of ideal gas undergoing reversible process in a closed system, entropy as:

- Volume Explicit form

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln \frac{P}{P_0}$$

These equations relates properties only, therefore represent a general equation for the calculation of entropy change of an ideal gas

- Pressure Explicit form

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_V^{ig}}{R} \frac{dT}{T} + \ln \frac{V}{V_0}$$

Mathematical Statement of Second Law

Consider a system exchanging heat |Q| between two heat reservoirs, one at temperature T_H and other at T_C (lower)

The entropy changes of the reservoirs at T_H and T_C are:

Total entropy change :

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

$$\Delta S_{total} = \Delta S_H^t + \Delta S_C^t = \frac{-|Q|}{T_H} + \frac{|Q|}{T_C} = |Q| \left(\frac{T_H - T_C}{T_H T_C} \right)$$

Since $T_H > T_C$, the total entropy change for irreversible process is always positive.

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

Entropy and Second Law

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

- Mathematical statement of second Law:
  - Every process proceeds in such a direction that the total entropy change associates with it is positive
  - The limiting value of zero being attained by a reversible process
  - No process is possible for which the total entropy decreases
- The entropy change for an irreversible process may be positive, negative or zero.
- For an irreversible process, the sum of the entropy changes of the system plus surroundings is always greater than zero. This is also called the **Clausius inequality**.

Work from Heat Engine

Again consider a heat engine that takes heat $|Q_H|$ from a reservoir at T_H and discards the heat $|Q_C|$ from a reservoir at T_C

The total entropy change of the heat reservoirs:

$$\Delta S_{\text{total}} = \frac{-|Q_H|}{T_H} + \frac{|Q_C|}{T_C}$$

The work produced by engine is $|W| = |Q_H| - |Q_C|$

The general equation for work of a heat engine:

$$|W| = -T_C\,\Delta S_{\text{total}} + |Q_H|\left(1 - \frac{T_C}{T_H}\right)$$

- For minimum work output (W=0), process degenerates into simple irreversible heat transfer
- Maximum work is obtained when ΔS=0 reversible process

Entropy Balance for Open Systems

- The second law states that the total entropy change associated with any process must be positive, with a limiting value of <u>zero for a reversible process</u>

- For entropy balance on open system for both system and surroundings, an ***entropy-generation*** term is added to account for irreversibilities of the process

- General rate form of the entropy balance

$$
\begin{Bmatrix} \text{Net rate of change} \\ \text{in entropy of flowing} \\ \text{stream} \end{Bmatrix} + \begin{Bmatrix} \text{Time rate of change} \\ \text{of entropy in control} \\ \text{volume} \end{Bmatrix} + \begin{Bmatrix} \text{Time rate of change} \\ \text{of entropy in} \\ \text{surroundings} \end{Bmatrix} = \begin{Bmatrix} \text{Total rate of} \\ \text{entropy change} \end{Bmatrix}
$$

$$
\Delta(S\dot{m})_{fs} + \frac{d(mS)_{CV}}{dt} + \frac{dS^{t}_{surr}}{dt} = \dot{S}_{G} \geq 0 \quad \longleftarrow \text{Entropy generation}
$$

- Considering rate of change of entropy in surroundings

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

- For a steady-state flow process the mass an entropy of the fluid in the control volume are constant,

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

- For one entrance and exit, with same mass flow rate

$$\Delta S - \sum_j \frac{Q_j}{T_{\sigma,j}} = S_G \geq 0$$

Ideal work in a flow system

Ideal work obtains when the processes associated with the open system are both internally and externally reversible

$$\dot{m}(\Delta S)_{fs} - \frac{\dot{Q}}{T_\sigma} = \dot{S}_G = 0 \qquad \text{SS Flow process}$$

Thus, $\quad \dot{Q} = T_\sigma \, \dot{m}(\Delta S)_{fs}$

From the first law applied to ideal cases,

$$\Delta\left[\left(H + \frac{1}{2}(u^2/g_c) + z(g/g_c)\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}_{ideal}$$

Simplifying and assuming negligible PE and KE changes

$$\dot{W}_{ideal} = \Delta\left[H\dot{m}\right]_{fs} - T_\sigma \Delta(S\dot{m})_{fs} \qquad \boxed{W_{ideal} = \Delta H - T_\sigma \Delta S}$$

Lost work in a flow system

In real processes however, actual work involved will depend on the extent of associated irreversibilities; hence we define *lost work as follows:*

$$\dot{W}_{lost} = \dot{W}_{actual} - \dot{W}_{ideal}$$

For an actual process

$$\Delta\left[H\,\dot{m}\right]_{fs} = \dot{Q}_{actual} + \dot{W}_{actual}$$

$$\dot{W}_{lost} = T_\sigma \Delta(S\,\dot{m})_{fs} - \dot{Q}_{actual}$$

Entropy balance for a real process $\quad \dot{m}(\Delta S)_{fs} - \dfrac{\dot{Q}_{actual}}{T_\sigma} = \dot{S}_G$

Lost Work → $\boxed{\dot{W}_{lost} = T_\sigma \dot{S}_G}$ From second law, $\dot{S}_G \geq 0$, it follows that $\dot{W}_{lost} \geq 0$

Entropy change of pure substances

- In engineering thermodynamics, only entropy changes are required and if at one state which can be taken as reference, entropy is assigned zero value, the entropy value for the substance can be evaluated

- According to Nernst, the entropy of a substance approaches zero as the temperature approaches absolute zero

- Entropy evaluated with absolute zero represents absolute value of entropy

$$S = \int_0^{T_f} \frac{(C_P)_S}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{Tv} \frac{(C_P)_l}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_{vf}}^{T} \frac{(C_P)_g}{T} dT$$

The Third Law of Thermodynamics

The entropy of all substances in the perfect crystalline state (for solids) or the perfect liquid state (e.g., Helium) is zero at the absolute zero of temperature (0 K)

- Here "perfect" means without any disturbance in the arrangement of the atoms
- A more correct statement is that all substances in the perfect state should have the same entropy value at 0 K
- It is for convenience for preparation of thermodynamics table that entropy of zero at 0 K is chosen