Chapter 3

Second Law of Thermodynamics

Introduction:

The second law helps us to determine the direction in which energy can be transferred. It also helps us to predict whether a given process or a chemical reaction can occur spontaneously. It introduces a new concept of entropy. It also helps us to know the equilibrium conditions.

Statement of the Second Law of Thermodynamics :

1. "Heat cannot spontaneously pass from a colder to a warmer body." (**R.J.E calusius**).
2. "In an adiabatic process the entropy either increases or remains unchanged, $\Delta S \geq 0$
   where the inequality sign referes to the irreversible process whereas the equality sign refers to the reversible case. (**P.S. Epstein**).
3. ***"Work can always be completely converted into heat but heat can't be completely converted into work without leaving a permanent change in the system or surroundings. Only a fraction of heat can be converted into useful work & the rest remains unavailable & unconverted.***
4. "In any irreversible process the total entropy of all bodies concerned is increased." (**G.N. Lewis**)

Carnot cycle or Carnot reversible heat engine:

The Carnot cycle is a theoretical, ideal and reversible cyclic process, devised by a french engineer Sadi Carnot (1824), to demonstrate the maximum convertibility of heat into work. An ideal machine to demonstrate this cycle is called carnot heat engine.

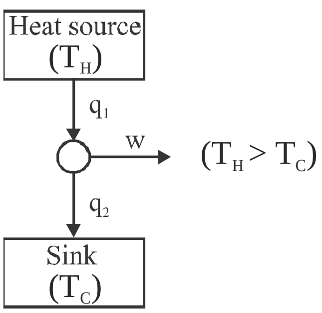
The work done in a carnot cycle is maximum because the various steps involved are reversible and the reversible work is the maximum work which a system can do.

Carnot engine consist of :

(i) Source of heat (A), at high temperature T_H.
(ii) Sink (B) , at lower temperature T_C
(iii) System or working substance (C)

Operations involved in Carnot cycle:

This cycle involves four operations. These are as follows.



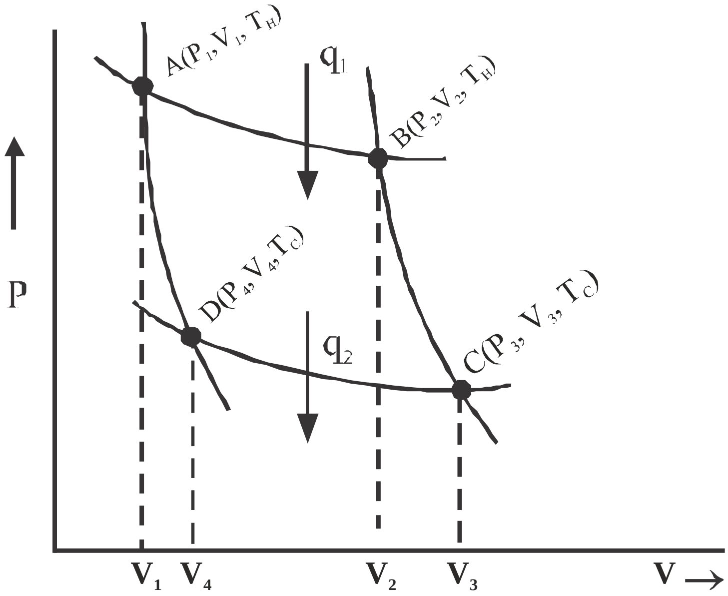


Diagram of Carnot Cycle

Step 1: Isothermal and reversible expansion of working substance:

System is placed in the source and load on the piston of the system is decreased. The system expands isothermally and absorbed heat equal to q_1.

T_H = constant $\quad\quad \therefore \quad \Delta U = 0$

According to the first law, $q_1 = -w_1 = RT_H \ell n \dfrac{V_2}{V_1}$

Step 2: Adiabatic reversible expansion of working substance:

System is removed from the source put in the sink having perfectly insulating walls. Load is further decreased to cause expansion of working substance adiabatically.

$\therefore \quad q = 0 \quad\quad$ (From first law)

$$w_2 = -\frac{nR}{1-\gamma}\left(T_C - T_H\right)$$

Step 3: Isothermal and reversible compression of substance:

Insulated walls of the system is removed and the load on the piston is inreased . System is compressed isothermally releasing heat equal to q_2.

$$q_2 = -w_3 = RT_C \ell n \frac{V_4}{V_3}$$

Step 4: Adiabatic reversible compression of substance:

System is now placed in source having insulated walls and load on the piston is increased. System now, undergoes adiabatic compression increasing the temperature of the system to T_H.

$$w_4 = -\frac{nR}{1-\gamma}\left(T_H - T_C\right)$$

Thus net work done during one complete cycle,

$$w_{Total} = w_1 + w_2 + w_3 + w_4$$

$$= -RT_H \ell n \frac{V_2}{V_1} - \frac{nR}{1-\gamma}\left(T_C - T_H\right) - RT_C \ell n \frac{V_4}{V_3} - \frac{nR}{1-\gamma}\left(T_H - T_C\right)$$

$$= -RT_H \ell n\frac{V_2}{V_1} - \frac{nR}{1-\gamma}(T_C - T_H) - RT_C \ell n\frac{V_4}{V_3} + \frac{nR}{1-\gamma}(T_C - T_H)$$

$$\therefore \quad w_{Total} = -RT_H \ell n\frac{V_2}{V_1} - RT_C \ell n\frac{V_4}{V_3} \qquad \text{... (1)}$$

For adiabatic curve BC, $T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1}$

$$\therefore \quad \frac{T_C}{T_H} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \text{... (2)}$$

For adiabatic curve DA, $T_C V_4^{\gamma-1} = T_H V_1^{\gamma-1}$

$$\therefore \quad \frac{T_C}{T_H} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \text{... (3)}$$

from equation (2) and (3)

$$\left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$$

$$\therefore \quad \frac{V_2}{V_1} = \frac{V_3}{V_4} \qquad \text{... (4)}$$

Substituting the value of equation (4) in equation (1)

$$w_{Total} = -RT_H \ell n\frac{V_2}{V_1} - RT_C \ell n\frac{V_1}{V_2} = -RT_H \ell n\frac{V_2}{V_1} + RT_C \ell n\frac{V_2}{V_1}$$

$$w_{Total} = -R\ell n\frac{V_2}{V_1}(T_H - T_C)$$

Efficiency (η) of Carnot heat engine:

It is defined as the ratio of work done by the system to the amount of heat absorbed by the system from the source.

$$\eta = \frac{|w_{Total}|}{q_1} = \frac{|q_2 + q_1|}{q_1} = 1 + \frac{q_2}{q_1}$$

Absorbed heat $q_1 = RT_H \ell n\frac{V_2}{V_1}$

$$\therefore \quad \eta = \frac{|w|}{q_1} = \frac{\left|R\ell n\frac{V_2}{V_1}(T_H - T_C)\right|}{RT_H \ell n\frac{V_2}{V_1}}$$

$$\Rightarrow \quad \eta = \frac{T_H - T_C}{T_H}$$

Characteristics of efficiency of Carnot engine:

(i) η does not depend on the working substance used.
(ii) η depends only on the ratio of sink to source temperature
(iii) η is always less than one.

(iv) η is one only when $\frac{T_C}{T_H}$ is zero. i.e. when $T_C = 0K$ or $T_H = \infty K$. Both these temperature are impossible to obtain. Therefore, the efficiency of an engine can never be one or 100%. That is heat can't be transformed completely into work.

(v) For all reversible cycle operating between the same source and sink temperature, the efficiency is the same.

Comparison of efficiencies of reversible and irreversible engine.

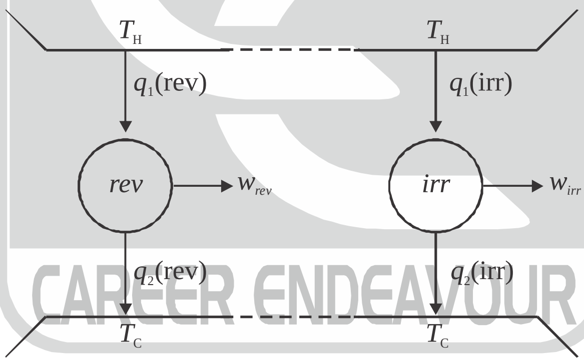
The efficiency of a reversible Carnot cycle is the theoretically possible maximum value which an engine can have. Since the various processes of this type of engine are to be carried out reversibly, therefore, such type of an engine does not have any realistic basis because reversible processes are idealized concepts which can never be realized. A real heat engine, which is irreversible in nature, will have efficiency smaller than the reversible heat engine.

Let us have two cycles, one operating reversibly and the other irreversibly. Let both of them operate between the same two temperature T_C and T_H and involve ideal gas as the working substance. These two cycles along with q values, are shown in the figure below.

(A) Isothermal expansion form volume V_1 to V_2. The expressions for the work involved are

$$-w_1(rev) = q_1(rev) = RT_H \ln\frac{V_2}{V_1}$$

And $\quad -w_1(irr) = q_1(irr) = p_{opp}(V_2 - V_1)$



Since we know that $|w_1(rev)| > |w_1(irr)|$, therefore,

$$q_1(rev) > q_1(irr)$$

(B) Isothermal compression from volume V_3 to V_4. The expressions for the work involved are

$$-w_3(rev) = q_2(rev) = RT_C \ln\frac{V_4}{V_3}$$

$$-w_3(irr) = q_2(irr) = P'_{ext}(V_4 - V_3)$$

Now, since in the irreversible process, more work is done as compared to that in the reversible process, we have

$$w_3(irr) > w_3(rev)$$

It follows that

$$|q_2(irr)| > |q_2(rev)|$$

Now the efficiencies of the two cycles are

$$\eta(rev) = \frac{q_1(rev) + q_2(rev)}{q_1(rev)} = 1 - \frac{|q_2(rev)|}{q_1(rev)}$$

$$\eta(irr) = \frac{q_1(irr) + q_2(irr)}{q_1(irr)} = 1 - \frac{|q_2(irr)|}{q_1(irr)}$$

Now since $q_1(rev) > q_1(irr)$ and $|q_2(rev)| < |q_2(irr)|$, therefore, it follows that

$$\frac{|q_2(rev)|}{q_1(rev)} < \frac{|q_2(irr)|}{q_1(irr)} \quad \text{or} \quad \left\{1 - \frac{|q_2(rev)|}{q_1(rev)}\right\} > \left\{1 - \frac{|q_2(irr)|}{q_1(irr)}\right\}$$

i.e. $\eta(rev) > \eta(irr)$

Basic Conclusion from Efficiency of a Carnot Cycle :

For a reversible Carnot cycle operating between two temperatures T_H and T_C, the efficiency is given as

$$\eta = \frac{q_1 + q_2}{q_1} = \frac{T_H - T_C}{T_H}$$

where q_1 and q_2 are the heats exchanged with the thermal reservoirs at temperatures T_H and T_C, respectively. Rewriting the above expression, we have

Or, $\quad 1 + \dfrac{q_2}{q_1} = 1 - \dfrac{T_C}{T_H} \quad$ or $\quad \dfrac{q_2}{q_1} = -\dfrac{T_C}{T_H}$

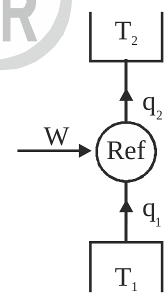
Or, $\quad \dfrac{q_1}{T_H} + \dfrac{q_2}{T_C} = 0$

that is, the sum of the ratios of the heat involved and the corresponding temperature is zero for a Carnot cycle.

Carnot Refrigerator:

It is the reverse of Carnot engine i.e. the energy flow from low temperature body to a high temperature body by providing energy in the form of work to the system. It is the energy transfer device therefore, the ratio of its output to input is represented by coefficient of performance which can be greater than 1.

In case of Carnot refrigerator system absorbed heat from low temperature body and transfer it to the high temeprature body. In carnot engine heat is input work is output. In refrigerator heat is output and work is input.



Co-efficient of performance (β) of Carnot refrigerator:

It is defined as the ratio of heat transferred from a lower temperature to a higher temperature to the work done on the system, i.e. $\beta = \dfrac{|q_C|}{w}$

The lesser the work done the more efficient the operation and greater the coefficient of performance.

$$\beta = \frac{|q_C|}{|q_h| - |q_C|} = \frac{T_C}{T_H - T_C}$$

At $T_C \to 0K$, $\beta = 0$

$\therefore \quad w = \dfrac{|q_C|}{\beta} = \dfrac{(q_C)}{0} = \infty$

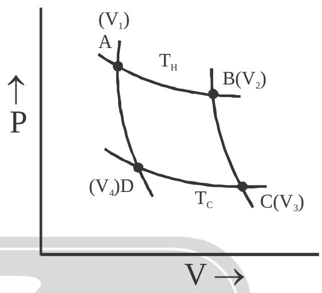
Thus as the temperature of a system is lowered the amount of work required to lower the temperature further increases rapidly and approaches infinity as the zero kelvin temperature is attained.

Efficiency of Carnot cycle $(\eta) = 1 - \dfrac{T_C}{T_H}$

For adiabatic curve $TV^{\gamma-1}$

$\therefore \quad T_H V_2^{(\gamma-1)} = T_C V_3^{(\gamma-1)}$

$$\frac{T_C}{T_H} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \Rightarrow \frac{T_C}{T_H} = \frac{1}{\left(\frac{V_2}{V_3}\right)^{\gamma-1}} = \frac{1}{(\rho)^{\gamma-1}}$$



$\therefore \quad \eta = 1 - \left(\dfrac{1}{\rho}\right)^{\gamma-1} \quad \left\{\text{where, } \rho = \dfrac{V_3}{V_2} = \dfrac{V_4}{V_1}\right\}$

Relation between η and β :

$\because \quad \beta = \dfrac{T_C}{T_H - T_C} \qquad T_H > T_C$

Again. $\eta = \dfrac{T_H - T_C}{T_H} \Rightarrow \dfrac{1}{\eta} = \dfrac{T_H}{T_H - T_C} \Rightarrow \dfrac{1}{\eta} - 1 = \dfrac{T_H}{T_H - T_C} - 1 \Rightarrow \dfrac{1-\eta}{\eta} = \dfrac{T_H - T_H + 1}{T_H - T_C} = \dfrac{T_C}{T_H - T_C}$

$$\beta = \frac{1-\eta}{\eta} \quad \text{or} \quad \eta = \frac{1}{\beta + 1}$$

Problem-1: A certain engine which operates in a Carnot cycle absorbs 4 kJ at 527ºC how much work is done on the engine per cycle and how much heat is evolved at 127ºC in each cycle?

Soln. The efficiency of the Carnot cycle is given by

$$\eta = \frac{T_H - T_C}{T_H} = \frac{q_1 + q_2}{q_1}$$

Thus, $-\dfrac{T_C}{T_H} = \dfrac{q_2}{q_1}$ and hence $q_2 = -\left(\dfrac{T_C}{T_H}\right) q_1$

Thus, the heat evolved in the present case is

$$q_2 = -\left(\frac{400K}{800K}\right)(4kJ) = -2kJ$$

and the work done on the engine is

$$w = -(q_1 + q_2) = -4 + 2 = -2kJ$$

The negative sign indicates that the work is actually done by the engine.