Lecture Notes Dated: Sep 07-08, 2012

Carnot Refrigerator

Since a Carnot cycle consists of reversible processes, it may be performed in either direction. When it is performed in a direction opposite to that shown in the examples of Carnot cycle, then this cycle is known as a ***refrigeration cycle*** and the system is called a ***Carnot refrigerator*** which is represented symbolically in Figure 7.

Figure 7 *(a) Carnot engine* *(b) Carnot Refrigerator.*

The important feature of a Carnot refrigeration cycle, which separate it from any other reversible engine cycle, is that the heat given to heat reservoir Q_1, heat extracted from heat sink Q_2 and work done on the working substance W are numerically equal to those quantities when the cycle is performed in the opposite direction, i.e., in Carnot engine.

Thus, the cycle working in the reverse direction will act as an ideal refrigerator in which heat is taken from the heat sink and transferred to the heat reservoir.

The ***efficiency*** or ***coefficient of performance*** for a refrigerator is defined as

$$\omega = \frac{\text{heat taken fromthe sink}}{\text{work input}}$$

$$\omega = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} \qquad (35)$$

The ω can be much greater than unity.

Carnot Theorem

Carnot's theorem is stated as follows; *No heat engine operating between two given reservoirs can be more efficient than a Carnot engine operating between the same reservoirs.* In other words; *All heat engines working between the same temperatures, the reversibile Carnot engine has the maximum efficiency.* We now proceed to prove this important theorem with the help of ***the second law of thermodynamics***.

Imagine a Carnot engine R (shown in figure 8), which is reversible, and any other engine I, which is irreversible, working between the same two reservoirs (i.e., heat reservoir and heat sink) and adjusted so that they both deliver the same amount of work W. Thus

Carnot Engine *R*	**Irreversible Engine *I***
◆ Absorb heat Q_1, from the heat reservoir.	Absorb heat Q'_1 form the heat reservoir.
◆ Performs work *W*.	Performs work *W*.
◆ Reject heat Q_1 - *W* to heat sink.	Reject heat Q'_1 - *W* to the heat sink.
◆ Efficiency $\eta_R = \frac{W}{Q_1}$	Efficiency $\eta_I = \frac{W}{Q'_1}$

Let us assume that the efficiency of the engine *I* is greater than that of *R*. Thus

$$\eta_I > \eta_R$$

or,
$$\frac{W}{Q'_1} > \frac{W}{Q_1}$$

so,
$$Q_1 > Q'_1$$

Now, let the engine *I* drive the Carnot engine *R* backward as a Carnot Refrigerator. The engine *I* and the refrigerator *R* coupled together in this way form a self-contained machine, since all the work needed to operate the refrigerator is supplied by the engine.

Figure 8 *Irreversible engine I operating a Carnot refrigerator R.*

The net heat extracted from the heat sink is $\Rightarrow (Q_1 - W) - (Q'_1 - W) = Q_1 - Q'_1$

The net heat delivered to the heat reservoir is also $\Rightarrow Q_1 - Q'_1$

Therefore, the effect of this self-contained machine is to transfer (Q_1 - Q'_1) heat from heat sink to a heat reservoir without work being done by the surrounding. Since the machine violets ***the second law of thermodynamics***, our original assumption that $\eta_I > \eta_R$ is false and Carnot theorem is proved. We may express this result as

$$\eta_I \le \eta_R \qquad (36)$$

Hence proved.

Corollary to Carnot Theorem

According to the corollary to Carnot theorem; All Carnot engine operating between the same two reservoir have the same efficiency. We now proceed to prove this corollary;

Consider two Carnot engine R_1 and R_2, operating between the same two reservoirs. If we imagine R_1 driving R_2 backward, then Carnot theorem states that

$$\eta_{R_1} \leq \eta_{R_2}$$

If R_2 drives R_1 backward, then

$$\eta_{R_2} \leq \eta_{R_1}$$

But the efficiency of the first reversible engine cannot be both less than or equal to as well as greater than or equal to the efficiency of the second reversible engine. Therefore, it follows that the efficiencies can only be equal.

$$\eta_{R_1} = \eta_{R_2} \qquad (37)$$

Hence proved.

Clausius-Clapeyron Equation

The Clausius Clapeyron equation may be derived from a study of a Carnot engine. Consider a Carnot engine operating in the two phase region of the water vapour region, as shown in figure 9. In the reversible cycle shown, processes *AB* and *CD* are adiabatic and processes *BC* and *DA* are isothermal and isobaric. During the process *BC*, at temperature $T + dT$, n moles of liquid are converted to vapour at pressure $p + dp$; while during process *DA*, at temperature T, n moles of vapour are converted back to liquid at pressure p. Thus from eq. (34)

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or

$$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2} \qquad (38)$$

The heat absorbed by the system during the isothermal process *BC* is, $Q_1 = n(L + dL)$ and

The heat liberated by the system during the isothermal process *DA* is, $Q_2 = nL$ respectively, where L and $(L + dL)$ are the molar latent heat of vaporization at temperature T and $(T + dT)$ respectively. Thus,

$$T_1 - T_2 = (T + dT) - T = dT$$

The work done by the system during the Carnot cycle is the area enclosed by the cycle *ABCD*, which is almost a rectangle of width dp and length $n\Delta v$, where Δv is the change in molar volume at temperature T. Thus,

$$W = area\ \boldsymbol{ABCD} = (dp)(n\,\Delta v)$$

Therefore, eq. (38) becomes

$$\frac{W}{Q_2} = \frac{dT}{T} \qquad (39)$$

$$\frac{(dp)(n\,\Delta v)}{nL} = \frac{dT}{T}$$

or, within the coexistence region,

$$\frac{dp}{dT} = \frac{L}{T \Delta v} \quad (40)$$

This equation is known as ***Clausius Clapeyron equation***, which shows how the melting point and boiling point changes with temperature. Some times it is called ***the first latent heat equation of Clausius***.

Figure 9 *pV diagram showing a Carnot cycle in the liquid-vapour region.*

Clausius Equation: Specific Heat of Saturated Vapour

Let C_1 denotes the molar specific heat of liquid in contact with its saturated vapours and C_2 the molar specific heat of saturated vapours in contact with its liquid. Let us consider *n* moles of the substance is taken one Carnot cycle *ABCD*. Then

1. The quantity of heat absorbed during *AB* reversible adiabatic process, when its temperature rises by *dT* is equal to $Q_1' = nC_1 dT$.
2. The heat absorbed by the system during the isothermal and isobaric process *BC* in which liquid changes into saturated vapour at temperature $T + dT$ is equal to $Q_1 = n(L + dL)$.
3. The quantity of heat liberated during *CD* reversible adiabatic process, when its temperature falls by *dT* is equal to $Q_2' = nC_2 dT$.
4. The heat liberated by the system during the isothermal and isobaric process *DA* in which saturated vapour changes into liquid at temperature *T* is equal to $Q_2 = nL$.

The net amount of heat absorbed during the cycle *ABCD* must be equal to the work done by the system during the Carnot cycle, thus

$$W = Q_1' + Q_1 - Q_2' - Q_2$$

$$W = nC_1 dT + n(L + dL) - nC_2 dT - nL$$

$$W = n(C_1 - C_2) dT + ndL \quad (41)$$

From eq. (39), $$\frac{W}{Q_2} = \frac{dT}{T} \quad (39)$$

$$\frac{n(C_1 - C_2) dT + ndL}{nL} = \frac{dT}{T}$$

or, $$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T} \quad (42)$$

This is ***the second latent heat equation of Clausius***, it gives the variation of latent heat of a substance with temperature and connects it with the specific heat of the substance in the two states.