Quadrant II – Transcript and Related Materials

Programme : **Bachelor of Science (First Year)**
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Unit 4 : **Second Law of Thermodynamics**
Module Name : **Calpeyron Latent Heat Equation and its Applications**
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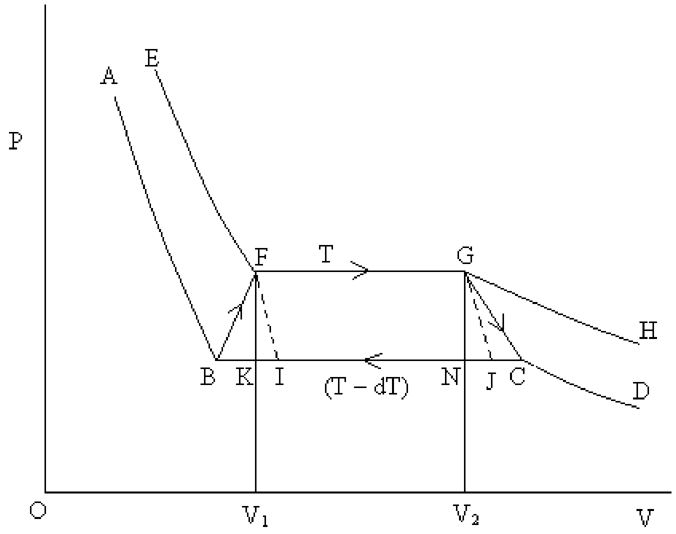
Notes

Clausius – Clapeyron or the First Latent Heat Equation:

Consider a unit mass of a gas taken through a Carnot's cycle working between temperatures T°K and (T – dT)°K where both temperatures are below the critical temperature. ABCD and EFGH are two isothermals corresponding to temperatures (T – dT) and T respectively, as shown in fig.



Let FI and GJ be the adiabatic curves drawn through F and G to meet BC. If dT is very small, the differences BI and JC can be neglected.

At F the substance is entirely in the liquid state and at G it is just completely in the vapour state. The amount of heat taken in by the substance in passing from F to G is L – the latent heat.

The work done by the substance in one cycle can be expressed in two ways:

(i) Work = efficiency x heat taken in at higher temperature.
(ii) Work = area of loop

From the theory of Carnot's cycle;

$$Efficiency;\ \eta = \frac{T_1 - T_2}{T_1} = \frac{T-(T-dT)}{T}$$

$$\therefore \eta = \frac{dT}{T}$$

Hence the work done per cycle,

$$W = \frac{dT}{T}.L ----------------------(1)$$

Again, using the second method:

W = Area of loop FGJI

W $\approx$ Area of rectangle FGNK

$\therefore$ W = dP . ($V_2 - V_1$) --(2)

Since, FG = $V_2 - V_1$ and FK = dP

Equating the RHS of equations (1) and (2)

$$\mathrm{dP}\ .\ \left(\mathrm{V}_2\ -\ \mathrm{V}_1\right)\ =\frac{dT}{T}.L$$

$$\therefore \frac{dP}{dT}=\frac{L}{T(V_2-V_1)}-----------------------(3)$$

This is the Clausius – Clapeyron equation or the first latent heat equation.

The above equation which is derived for the liquid and vapour phases can also be applied to the change of phase from a solid to a liquid state.

(a) In the case of a change of phase from liquid to vapour, V_1 corresponds to liquid phase and V_2 corresponds to vapour phase.

(b) In case of a change of phase from solid to a liquid state, V_1 and V_2 are specific volumes of the substance in solid and liquid state respectively.

If the first latent heat equation is applied to the melting of a solid at the melting point,

(i) In the case of the substances such as ice that contract on melting, i.e. $V_2 < V_1$, dP/dT is negative, hence melting point of the solid (or freezing point of the liquid) decreases with increase in pressure.

(ii) In the case of the substances that expand on melting ($V_2 > V_1$), the melting point increases with increase in pressure. Similar considerations apply to the change of boiling point with pressure in the case of phase from liquid to the vapour state. In almost all such cases, the boiling point increases with pressure.

Second Latent Heat Equation:

Consider a unit mass of substance taken in a Carnot cycle between the temperatures T and (T – dT) as in the previous case. Starting from the point F at which the substance is entirely in the liquid state, it may be taken in a cycle represented by FGCB in above fig. If dT is very small we can assume that the parts of the cycle shown by GC and BF almost coincide with adiabatics GJ and IF respectively.

Let L and (L – dL) be the latent heat of vaporization at T°K and (T – dT)°K respectively. Starting from the point F,

(i) The heat (absorbed) taken in along FG is L

(ii) The heat given out along GC is equal to (C_2dT) where C_2 is the specific heat of saturated vapour.

(iii) The heat given out along CB is (L – dL), and

(iv) The heat absorbed along BF is C_1dT, where C_1 is the specific heat of the liquid. Therefore, the net heat absorbed in a cycle is;

$Q = L - C_2dT - (L - dL) + C_1dT$

$Q = dL + (C_1 - C_2)\, dT$ --(1)

This is equal to the work done per the cycle, i.e. $W = dL + (C_1 - C_2)\, dT$

The heat taken in at higher temperature is L. The expression for the efficiency of the Carnot's engine;

$$\eta = \frac{dT}{T}$$

The work done per cycle is;

W = η . heat taken in at higher temperature

$$W = \frac{dT}{T}.L ------------------------(2)$$

Equating RHS of equation (1) and (2);

$$dL + (C_1 - C_2)\, dT = \frac{dT}{T}.L$$

$$\therefore \frac{dL}{dT} - \frac{L}{T} = C_2 - C_1 ----------------(3)$$

This is the second latent heat equation or Clausius latent heat equation.

In the case of water at 100°C.

$$\frac{dL}{dT} = -0.64, \qquad L = 540\ cal.$$

T = 370°K and C_1 = 1cal.

$\therefore$ C_2 = 1 – 0.64 $-\frac{540}{373}$ = - 1.087 cal.

Thus, the specific heat of saturated steam is 100°C is negative.

Explanation of the negative specific heat of saturated steam:

Consider one gram of saturated steam at 100°C. The specific heat is the quantity of heat required to raise its temperature by 1°C, i.e., from 100°C to 101°C. When the temperature is raised the steam become unsaturated, to keep it saturated at 101°C it has to be compressed and in this process the temperature rises above 101°C. Therefore, heat has to be taken out of steam to keep it saturated. The heat taken out happens to be greater than the heat supplied to steam in raising its temperature from 100°C to 101°C at the same time keeping it saturated. Thus, the specific heat of saturated steam at 100°C is negative.