THIRD LAW OF THERMODYNAMICS

The entropy change associated with any isóthermal reversible process of a condensed system approaches zero as the temperature approaches to zero is called third law of thermodynamics by Fowler and Guggenheim. Planck added further that not only entropy change is zero but also entropy itself is zero for solids at 0 K.

EXPLANATION

The Helmholtz free energy of a system is defined as

$$F = U - TS \qquad \text{--------- (1)}$$

For an infinitesimal reversible process

$$dF = dU - TdS - S\,dT$$

First law is $dQ = dU + PdV$

$$dF = dQ - P\,dV - TdS - S\,dT$$

Second law is $dQ = TdS$

$$dF = TdS - P\,dV - TdS - S\,dT$$

$$\mathbf{dF = -P\,dV - S\,dT} \qquad \text{--------- (2)}$$

Regarding F as function of V and T

$$F = F(V, T)$$

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT \qquad \text{--------- (3)}$$

Comparing eq(2) and eq(3)

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

Hence eq(1) can be written as

$$F = U - T\left(\frac{\partial F}{\partial T}\right)_v \quad \text{.........(4)}$$

or

$$F_1 - F_2 = U_1 - U_2 + T\left[\left(\frac{\partial F_1}{\partial T}\right)_v - \left(\frac{\partial F2}{\partial T}\right)_v\right]$$

Experiments show that if we go on decreasing the temperature, the value of $(F_1 - F_2)$ becomes more and more nearly equal to $(U_1 - U_2)$ provided we keep pressure and volume almost unchanged. Hence above relation can be written as

$$\underset{T\to 0}{\text{Limit}}\,[F_1(T) - F_2(T)] = \underset{T\to 0}{\text{Limit}}\,[U_1(T) - U_2(T)]$$

It shows that differences of the functions F and U tend to become equal as T approaches to zero. This conclusion was first noticed by Nernst. Plank went a step further and assumed that the functions F and U themselves tend to become equal as T approaches zero.

$$\underset{T\to 0}{\text{Limit}}\, F(T) = \underset{T\to 0}{\text{Limit}}\, U(T)$$

$$\underset{T\to 0}{\text{Limit}}\left(\frac{\partial F}{\partial T}\right)_v = \underset{T\to 0}{\text{Limit}}\left(\frac{\partial U}{\partial T}\right)_v$$

This Nernst–plank hypothesis leads us to a very important result concerning the entropy of pure solids and liquids at absolute zero. If we put $F - U = \beta$, then above relations can be written as

$$\underset{T\to 0}{\text{Limit}}\,(F - U) = 0$$

$$\underset{T\to 0}{\text{Limit}}\,\beta = 0$$

And

$$\underset{T\to 0}{\text{Limit}}\left(\frac{\partial (F - U)}{\partial T}\right)_v = 0$$

$$\underset{T\to 0}{\text{Limit}}\left(\frac{\partial (\beta)}{\partial T}\right)_v = 0$$

As

$$\beta = F - U$$

$$\frac{\partial \beta}{\partial T} = \frac{\partial F}{\partial T} - \frac{\partial U}{\partial T} \quad \text{.........(5)}$$

From eq(4)

$$F - U = T\left(\frac{\partial F}{\partial T}\right)_v$$

$$\beta = T\left(\frac{\partial F}{\partial T}\right)_v$$

$$\frac{\beta}{T} = \frac{\partial F}{\partial T} \quad \text{..........(6)}$$

Put eq(6) in eq(5)

$$\frac{\partial \beta}{\partial T} = \frac{\beta}{T} - \frac{\partial U}{\partial T}$$

$$\frac{\partial \beta}{\partial T} - \frac{\beta}{T} = -\frac{\partial U}{\partial T} \quad \text{..........(7)}$$

When T becomes small, β also becomes small and so we can take T equal to ∂T and β equal to ∂β. Thus

$$\underset{T \to 0}{\text{Limit}} \left(\frac{\partial \beta}{\partial T}\right) = \underset{T \to 0}{\text{Limit}} \left(\frac{\beta}{T}\right)$$

Using eq(7)

$$\underset{T \to 0}{\text{Limit}} \left(\frac{\partial U}{\partial T}\right)_V = 0$$

Thus $\underset{T \to 0}{\text{Limit}} \left(\frac{\partial F}{\partial T}\right)_V$ also zero

$$\underset{T \to 0}{\text{Limit}} \left(\frac{\partial F}{\partial T}\right)_V = 0$$

Since $\left(\frac{\partial F}{\partial T}\right)_V = -S$

$$\underset{T \to 0}{\text{Limit}}\ S = 0$$

The entropy of pure solid or liquid is zero at the absolute zero of temperature. This is one method of describing the Nernst heat theorem and also called third law of thermodynamics. The theorem applies to only pure substances in the liquid or solid state.

For mixtures, the total entropy cannot be zero even at T = 0 as there must be some term representing the increase of entropy accompanying the process of mixing. A refrigerator enables us to lower the temperature of a body. If the refrigerator goes on working, the temperature also goes on falling. But experience shows that the process of cooling becomes extremely slow as the temperature of the cooling body approaches the absolute zero of temperature.

In other words a body cannot be cooled to the absolute zero of temperature by a finite number of cycles. The refrigerator must perform an infinite number of cycles in order to attain the absolute zero of temperature.