Third Law of Thermodynamics (Nernst Heat Theorem, Determination of Absolute Entropy, Unattainability of Absolute Zero) And Its Limitation

The third law of thermodynamics states that the entropy of a system approaches a constant value as its temperature approaches absolute zero.

In order to understand the abovementioned statement fully, we need to discuss some very important concepts and consequences of third law thermodynamics first such as “Nernst heat theorem” or “absolute entropies” etc.

**Nernst Heat Theorem**

In 1906, Walther Nernst, a German chemist, studied the variation of enthalpy change and free energy change as a function of temperature. His results gained very much popularity as “Nernst heat theorem” in chemistry and built the foundation of many other discoveries. For detailed picture, recall the Gibbs-Helmholtz equation i.e.

\[
\Delta G = \Delta H + T \left( \frac{\partial (\Delta G)}{\partial T} \right)_P
\]

(68)

It is obvious from the above equation that the free energy change will become equal to the enthalpy change when the temperature is reduced to absolute zero i.e. \( \Delta G = \Delta H \) at \( T = 0 \). Besides, Nernst also noted that the magnitude of \( \frac{\partial (\Delta G)}{\partial T} \) declines gradually and approaches the zero with the decrease of temperature.
In other words, W. Nernst observed that as the temperature is decreased continuously, the Gibbs free energy change was decreasing while the enthalpy change was increasing gradually with the same magnitude. Therefore, the change in slope in both curves must become zero near absolute zero i.e.

\[
\lim_{T \to 0} \frac{\partial (\Delta G)}{\partial T} = \lim_{T \to 0} \frac{\partial (\Delta H)}{\partial T} = 0
\]  

(69)

Which is the mathematical form of Nernst heat theorem. The pictorial representation of these observations is also given below for a more clear perspective.

It is also worthy to mention that though we have shown \( \Delta G \) greater than \( \Delta H \) when the temperature is set greater than zero, the reverse may also be possible because \( \frac{\partial (\Delta G)}{\partial T} \) can have positive as well as negative values.

Furthermore, we also know that variation of free energy change with the temperature at constant pressure is equal to the negative of entropy change i.e.

\[
\left( \frac{\partial (\Delta G)}{\partial T} \right)_P = -\Delta S
\]  

(70)

Also, from the definition of change in the heat capacity, we have

\[
\left( \frac{\partial (\Delta H)}{\partial T} \right)_P = \Delta C_P
\]  

(71)
After putting the values of equation (70, 71) in equation (69), we get

$$\lim_{T \to 0} (\Delta S) = 0 \quad \text{and} \quad \lim_{T \to 0} \Delta C_p = 0$$  \hspace{1cm} (72)

Now because, no gas or liquid at or in the vicinity of absolute zero, we can apply the Nernst heat theorem to solids only.

The right-hand side result given in equation (72) is extremely important as far as the third law of thermodynamics is concerned. Actually, we can say that the “third law of thermodynamics” follows from the results obtained by the Nernst heat theorem. In order to understand it more clearly, recall one of two results of Nernst heat theorem i.e.

$$\lim_{T \to 0} \Delta C_p = 0$$  \hspace{1cm} (73)

This means that as we approach absolute zero, the heat capacity of reactants becomes equal to the heat capacity of the product. In other words, we can say that the heat capacities of all substances are equal at absolute zero. Mathematically, it can be formulated as

$$\lim_{T \to 0} C_p(\text{product}) = \lim_{T \to 0} C_p(\text{reactant})$$  \hspace{1cm} (74)

Since the results of the quantum mechanics say that the heat capacity of tends to zero as the temperature approaches absolute zero, the above equation takes the form

$$\lim_{T \to 0} \Delta C_p = 0$$  \hspace{1cm} (75)

Similarly recalling the second result of Nernst heat theorem i.e.

$$\lim_{T \to 0} (\Delta S) = 0$$  \hspace{1cm} (76)

Which means that as we approach absolute zero, the entropy of reactants becomes equal to the entropy of the product. In other words, we can say that the entropy of all substances are equal at absolute zero. Mathematically, it can be formulated as

$$\lim_{T \to 0} S_{\text{product}} = \lim_{T \to 0} S_{\text{reactant}}$$  \hspace{1cm} (77)

Using the same argument as in case of heat capacity, the above equation takes the form

$$\lim_{T \to 0} S = 0$$  \hspace{1cm} (78)

Therefore, the entropy of all crystalline substances can be taken as zero at absolute zero, which is the general statement of the third law of thermodynamics.
Determination of Absolute Entropy

One of the most interesting and important applications of the third law of thermodynamics (or the Nernst heat theorem) is that it can be used to determine the absolute entropies of different substances at any temperature. The procedure employs the fact that we can calculate the entropy change easily and if the entropy of the initial state is zero then this difference will simply be equal to the absolute entropy i.e.

\[ \Delta S = S_T - S_0 \]  \hspace{1cm} (79)

Where \( S_T \) and \( S_0 \) are the entropies at temperatures \( T \) and 0K, respectively. Since we know from the third law of thermodynamics that \( S_0 = 0 \), the equation (79) takes the form

\[ \Delta S = S_T - 0 = S_T \]  \hspace{1cm} (80)

Before we proceed further, we must remember that a substance may change phase when it supplied with heat. Therefore, we need to discuss the absolute entropies in solid, liquid and gases separately.

1. Absolute entropies in case of solids: To calculate the absolute entropy of a solid at any temperature, we just need to find the total entropy change in shifting the absolute zero state to that temperature. The very small entropy change is given by

\[ dS = \frac{\delta q}{T} \]  \hspace{1cm} (81)

However, the general expression for heat capacity is

\[ C_P = \frac{\delta q}{dT} \]  \hspace{1cm} (82)

\[ \delta q = C_P \, dT \]  \hspace{1cm} (83)

After putting the value of \( \delta q \) from equation (83) into equation (81), we have

\[ dS = \frac{C_P \, dT}{T} \]  \hspace{1cm} (84)

In order to find the total entropy change in the same phase (solid in this case) when the temperature is raised from 0 to \( T \), we need to integrate the above equation over the range of interest i.e.

\[ \int_0^T dS = \int_0^T \frac{C_P \, dT}{T} \]  \hspace{1cm} (85)

\[ S_T - S_0 = \int_0^T C_P \, d\ln T \]  \hspace{1cm} (86)

Since \( S_0 = 0 \), the above equation becomes
Thus, the entropy of any solid at temperature $T$ can be obtained by heat capacity at many temperature points between 0K to $T$. The total integral of equation (87) can be obtained by measuring the area under the plot of $C_P$ vs $\ln T$.

\[ S_T = \int_0^T C_P \, d \ln T \]  

(87)

**2. Absolute entropies in case of liquids:** To calculate the absolute entropy of a liquid at any temperature, we just need to find the total entropy change in shifting the absolute zero state to that temperature. The whole process can be divided into three steps; one in heating up the solid phase from 0K to its melting or fusion point, then phase change from solid to liquid at fusion temperature, and the last step in which liquid is heated up to temperature $T$.

i) Entropy change from 0K to $T_f$:

\[ \Delta S_1 = \int_0^{T_f} C_P(s) \, d \ln T \]  

(88)

ii) Entropy change of fusion at $T_f$:

\[ \Delta S_2 = \frac{\Delta H_f}{T_f} \]  

(89)
iii) Entropy change from $T_f$ to $T$ :

$$\Delta S_3 = \int_{T_f}^{T} C_p(l) \, d \ln T$$  \hspace{1cm} (90)

The total entropy change for the process can be obtained by simply adding equations (88–90) i.e.

$$S_T - S_0 = \Delta S_1 + \Delta S_2 + \Delta S_3$$  \hspace{1cm} (91)

$$S_T = \int_0^{T_f} C_p(s) d \ln T + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T} C_p(l) \, d \ln T$$  \hspace{1cm} (92)

Where $C_p(s)$ and $C_p(l)$ are the heat capacities for solid and liquid phases, respectively. The symbol $\Delta H_f$ represents the latent heat of fusion.

3. Absolute entropy in case of gases: To calculate the absolute entropy of a gas at any temperature, we just need to find the total entropy change in shifting the absolute zero state to that temperature. The whole process can be divided into five steps; one in heating up the solid phase from 0K to it melting or the fusion point, then phase change from solid to liquid at fusion temperature, followed by the raising the temperature from $T_f$ to $T_b$.

The fourth step includes the vaporization of liquid phase to gaseous phase at boiling point followed by the last step in which the temperature must be raised from $T_b$ to the required temperature $T$.

i) Entropy change from 0K to $T_f$ :

$$\Delta S_1 = \int_0^{T_f} C_p(s) \, d \ln T$$  \hspace{1cm} (93)

ii) Entropy change of fusion at $T_f$ :

$$\Delta S_2 = \frac{\Delta H_f}{T_f}$$  \hspace{1cm} (94)

iii) Entropy change from $T_f$ to $T_b$ :

$$\Delta S_3 = \int_{T_f}^{T_b} C_p(l) \, d \ln T$$  \hspace{1cm} (95)

iv) Entropy change of vaporization at $T_b$ :

$$\Delta S_4 = \frac{\Delta H_{vap}}{T_b}$$  \hspace{1cm} (96)
v) Entropy change from $T_b$ to $T$:

$$\Delta S = \int_{T_b}^{T} C_P(g) \, d \ln T$$

(97)

The total entropy change for the process can be obtained by simply adding equations (88–90) i.e.

$$S_T - S_0 = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

(98)

$$S_T = \int_{0}^{T_f} C_P(s) \, d \ln T + \int_{T_f}^{T_b} C_P(l) \, d \ln T + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_b}^{T} C_P(g) \, d \ln T$$

(99)

Where $C_P(s)$, $C_P(l)$ and $C_P(g)$ are the heat capacities for solid, liquid and gas phases, respectively. The symbol $\Delta H_{\text{vap}}$ represents the latent heat of vaporization.

The unattainability of Absolute Zero

One more statement of the third law of thermodynamics is that the lowering of the temperature of a material body to the absolute zero is impossible in the finite number of steps. To understand this claim, recall the concept of Carnot refrigerator first. A Carnot refrigerator is basically just the reverse of the Carnot heat engine i.e. Carnot heat engine working in reverse cycle. Since a Carnot heat engine provides work through reversible isothermal-adiabatic compressions and expansions, a net amount of work must be done in Carnot refrigerator making it electricity consumer.

Let $q_1$ be the amount of heat absorbed by a Carnot refrigerator from a body at lower temperature $T_1$ and $q_2$ as the amount of heat rejected by the same refrigerator to a body at higher temperature $T_2$. The coefficient of performance ($\beta$) of the reversible Carnot refrigerator can be given by the following relation.

$$\beta = \frac{q_2}{q_1} - 1$$

(100)

Since for a Carnot cycle, we know that

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}$$

(101)

or

$$\frac{q_2}{q_1} = \frac{T_2}{T_1}$$

(102)

After using the value of $q_2/q_1$ from equation (102) in equation (100), we get

$$\beta = \frac{1}{T_2/T_1 - 1}$$

(103)
Furthermore, we also know that the coefficient of performance of an ideal Carnot refrigerator is simply the ratio of the cooling effect to the work done i.e.

$$\beta = \frac{q_1}{w}$$  \hspace{1cm} (104)

Which means that how much heat is removed from the body at lower temperature per unit of work done. Now from equation (103) and equation (104), we have

$$\frac{q_1}{w} = \frac{1}{T_2/T_1 - 1}$$  \hspace{1cm} (105)

$$\frac{q_1}{w} = \frac{T_1}{T_2 - T_1}$$  \hspace{1cm} (106)

Taking reciprocal of the above result, we get

$$w = \frac{T_2 - T_1}{T_1}$$ \hspace{1cm} (107)

Thus, it is obvious from the above equation that as the lower temperature $T_1$ approaches zero, more and more work will be needed to remove the same amount of heat ($w$ is inversely proportional to $T_1$), which is the unattainability of the absolute zero.

**Limitation of Third Law of Thermodynamics**

Although the third law of thermodynamics is very useful in determining various thermodynamic properties of various substances, there are some limitations of the same. The reason being is the fact that entropies obtained using the third law of thermodynamics are thermal entropies and are somewhat smaller than the entropy values obtained using statistical mechanics. This deviation is typically in range of $3–5 \text{JK}^{-1}\text{mol}^{-1}$.

From this, we may conclude that there is some entropy present even at the 0K temperature. This entropy is called as “residual entropy” and can be obtained using the following relation.

$$S = k \ln W$$  \hspace{1cm} (108)

Where $k$ is Boltzmann constant and the $W$ is the thermodynamic probability which represents the number of equally probable orientations of the molecule under consideration. For instance, consider a sample of $N$ number of carbon monoxide molecules. Since each molecule can have two orientations that are equally probable (CO CO OC CO OC OC), the thermodynamic probability will be $W = 2^N$. The residual entropy is

$$S = k \ln W = k \ln 2^N = kN \ln 2$$  \hspace{1cm} (109)

For one mole of sample $kN = R$, the above equation takes the form

$$S = R \ln 2 = 2.303R \log 2 = 5.85 \text{JK}^{-1}\text{mol}^{-1}$$  \hspace{1cm} (110)
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