Third Law of Thermodynamics: Unattainability of Absolute Zero:

Basically in thermodynamics, third law of thermodynamics is based on the non occurrence of absolute zero temperature. This third law actually states that - it is impossible to attain absolute zero temperature by any finite sequence of thermodynamic process.

On the basis of Nernst heat theorem, the development of the idea of this third law appears in thermodynamic culture.

It was discovered experimentally by Nernst who observed that change in entropy in a system is indeed very small when one proceeds from one low temperature equilibrium state to another.

From several experimental observations, it was decided that – the limit of equilibrium entropies of all thermodynamic systems and also the limit of entropy changes of a thermodynamic system in all reversible isothermal processes between equilibrium states tend to zero as the temperature tends to absolute zero.

So mathematically, $\lim_{T\to 0} S \to 0$ and thus $\lim_{T\to 0} \Delta S \to 0$

At that time, before Nernst, another scientist Richards obtains experimentally that at very low temperature, i.e. at neighbour of absolute zero, $\lim_{T\to 0} \Delta G = \Delta H$

where G and H are two thermodynamic potentials, respectively known as Gibbs potential and Enthalpy of a thermodynamic system.

In thermodynamics, we should actually have

$$G = U + PV - TS = H - TS \quad \text{where } H = U + PV.$$

And we should also have Gibbs – Helmholtz equation $\Delta G = \Delta H + T\frac{\partial}{\partial T}(\Delta G)$.

So if we take Richards observation, $\lim_{T\to 0} \Delta G = \Delta H$, we should have from the above equation, $\lim_{T\to 0} T\frac{\partial}{\partial T}(\Delta G) \to 0$.

Here for this equation, we can conclude that since absolute zero temperature cannot be reached, we should have for the validity of this equation, $\lim_{T\to 0} \frac{\partial}{\partial T}(\Delta G) \to 0$

Again as we have $G = U + PV - TS$

$$\Rightarrow \Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T = T\Delta S + V\Delta P - T\Delta S - S\Delta T = V\Delta P - S\Delta T$$

For this equation we can say that $(\frac{\Delta G}{\Delta T})_P = -S \Rightarrow (\frac{\partial G}{\partial T})_P = -S \Rightarrow [\frac{\partial}{\partial T}(\Delta G)]_P = -\Delta S$.

So finally from Richards equation, $\lim_{T\to 0} \frac{\partial}{\partial T}(\Delta G) \to 0$ i.e. $\lim_{T\to 0} \Delta S \to 0$

This gives that at a temperature close to absolute zero, $\Delta S = 0 \Rightarrow S_f = S_i$ i.e. in the neighbourhood of absolute zero, all processes would occur without change in entropy.

Again in that situation, based on Nernst heat theorem, Planck has made another enunciation – the entropy of a solid or a liquid is zero at the absolute zero temperature i.e. $\lim_{T\to 0} S \to 0$

This Nernst heat theorem actually supports third law of thermodynamics i.e. unattainability of absolute zero temperature. Because if absolute zero temperature can be achieved, then at that situation, entropy of the system will be zero or change of entropy will be zero.

This basically gives the non occurrence of several physical processes. Thus consequences sharply indicate the unattainability of absolute zero temperature. Let us now discuss a few consequences of this third law of thermodynamics.

i) We have change in entropy $\Delta S = S_2 - S_1 = \int \frac{dQ}{T} = mc_v \int_{T_1}^{T_2} \frac{dT}{T}$.

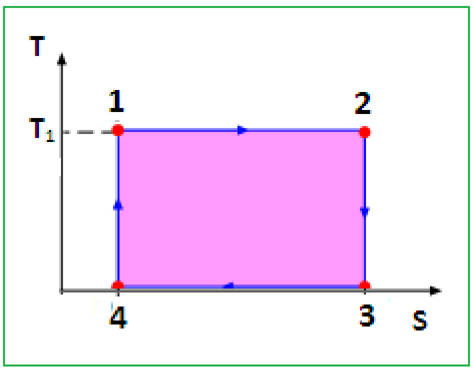
Since we have $\lim_{T\to 0} \Delta S \to 0$ we have $\lim_{T\to 0} c_v \to 0$ which is impossible in classical physics. Thus third law of thermodynamics cannot be explained in the frame work of classical physics.

ii) We have thermal expansivity, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. But by Maxwell's equation, $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ [which we will establish later on], we get, $\alpha = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T$

But we have as $\lim_{T\to 0} \Delta S \to 0$, we get $\lim_{T\to 0}\left(\frac{\Delta S}{\Delta P}\right) \to 0$ and this gives $\lim_{T\to 0} \alpha \to 0$ which is again impossible for a classical system.

iii) We have the entropy of an ideal gas $S = C_V.\ln T + R.\ln V + K$ where the symbols have their usual meanings. But here we get at $T \to 0, S \to -\infty$ which is physically meaningless. This again gives unattainability of absolute zero temperature.

iv) Suppose absolute zero temperature is possible. A Carnot engine works between source at higher temperature T_1 and sink at lower temperature T_2 where the temperature of the sink is taken as absolute zero temperature, i.e. $T_2 = 0$



At this condition, the presentation of Carnot cycle is taken in T-S diagram as shown in figure. Since Carnot cycle is a reversible cycle, we have from Clausius inequality, $\Delta S = \oint_{rev} \frac{dQ}{T} = 0$

But here we have from $T - S$ diagram, the entropy

change in Carnot cycle is

$$\Delta S]_{\text{Carnot}} = \Delta S]_{12} + \Delta S]_{23} + \Delta S]_{34} + \Delta S]_{41} = \frac{Q}{T_1} + 0 + \lim_{T\to 0} \Delta S_{34} + 0$$

But since $\lim_{T\to 0} \Delta S_{34} \to 0$ **, we finally get** $\Delta S]_{\text{Carnot}} = \frac{Q}{T_1} \neq 0$ **which violets Clausius inequality i.e. second law of thermodynamics.**

All these confirm unattainability of absolute zero temperature and supports third law of thermodynamics.