Dr L.K. Mishra
Deptt of Chemistry

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Deg III Chem. Hons, Paper - V

Topic :- Thermodynamics

The third Law of Thermodynamics

Nerst heat theorem has formed the basis of new law called the third law of Thermodynamics as shown in equation (2)

Conclusion from Nerst heat theorem

$$\lim_{T=0} \Delta S = 0 \quad \text{——— (1)}$$

$$\lim_{T=0} \Delta Cp = 0 \quad \text{——— (2)}$$

ΔCp tends to approach zero at $0^{\circ}K$. This means that at absolute zero, the heat capacity of products and reactant become identical.

This has led to the suggestion that at absolute zero, all substances have the same heat capacity.

The Quantum theory as applied to heat capacity of solid has shown that heat capacity of solids should tend to become zero at $0^{\circ}K$.

Further equation (1) of the Nerst Theorem states that for solids ΔS become zero at absolute Zero ie entropy change of a reaction becomes zero at $0^{o}K$

In other words the absolute entropy of products and reactants in solid state are identical. It is highly Probable therefore that in the solid state all Substances have the same entropy at absolute Zero.

The entropy of Pure solids and liquid approach zero at the absolute Zero

$$\lim_{T=0} S = 0$$

This statement which is true for solid but not always for liquid has led to the enunciation of the third Law of Thermodynamics which states

"At absolute zero of temperature, the entropy of every substance may become zero and does become zero in the case of perfectly crystalline structure".

In a Perfect crystal at absolute zero temperature each atom must be at a crystal lattice Point and it must have lowest energy. This means that this particular state is of Perfect order of zero entropy.

The variation of entropy with temperature at Constant Pressure is

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Now for a Pure crystalline substance absolute entropy $S=0$ at $T=0$

Therefore we may write

$$\int_{S=0}^{S=S} dS = \int_{T=0}^{T=T} C_P \frac{dT}{T}$$

$$S_T = \int_0^T C_P \, d(\log T)$$

Where S_T is the absolute entropy of the Crystalline Solid under examination at the temperature T. In order to Calculate its Value it is necessary to know the Value of heat capacity at Constant Pressure C_P from temperature $T=0$ to any desired temperature.