SUBJECT – CHEMISTRY
CLASS – B.Sc(Hons) PART-III
PAPER – V
TOPIC – Absolute entropy of a Solid:

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Q How the 3rd law of thermodyanamics is useful to determine the absolute entropy of a Solid?

Ans Absolute entropy of a Solid:

We know that -

$$H = E + PV$$

$$\therefore dH = dE + PdV + VdP$$

$$= dq + VdP \quad [\because dq = dE + PdV]$$

$$= TdS + VdP \quad \left[\because \frac{dq_{rev}}{T} = dS\right]$$

or $dH = TdS + VdP$

At Constant P,

$$dH = TdS \quad \text{---------- (i)}$$

$$\therefore C_P = \left(\frac{dH}{dT}\right)_P \quad \therefore dH = C_P dT \quad \text{---(ii)}$$

At Constant P, $dP = 0$, hence from (i) & (ii), we get -

$$\therefore TdS = C_P dT \quad \text{or} \quad dS = C_P \frac{dT}{T}$$

$$\int_{S_0}^{S_T} dS = \int_0^T C_P \frac{dT}{T} = \int_0^T C_P d\ln T$$

$$\text{or } S_T - S_0 = \int_0^T C_P d\ln T$$

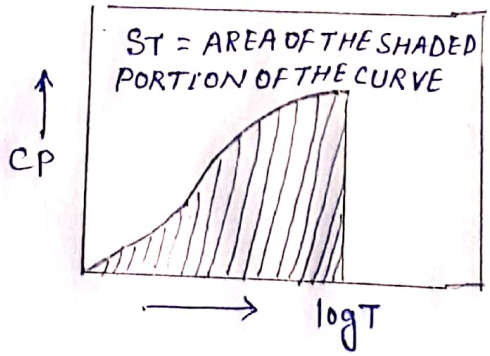
Where S_0 and S_T are entropies of a Solid at 0K and TK respectively

Applying the 3rd law i.e $S_0 = 0$ at $T = 0$ we get

$$S_T = \int_0^T C_P d\ln T$$

The integral can be evaluated graphically by plotting usually Cp Vs. log T. The area under the curve gives the S_T value of a solid between T = 0 to any temperature T. This entropy is called the thermal or absolute entropy. for plotting the curve, Cp values are obtained experimentally at various temperatures, from required temperature TK to 0K. But Cp determination at low temperature is very difficult and also inaccurate. So, Cp is determined at as low a temperature as possible usually 10 to 15K and values of Cp at temperature below that are determined by the following Debye's T^3 laws –

$$C_v = 464.4 (T/\theta)^3 \text{ cal/deg/mole.}$$



The characteristic temperature θ can be determined from the known C_v values at low temperatures once θ is known. C_v values at any temperature can be determined At low temperatures,

$$C_p - C_v = 0 \quad \text{or} \quad C_p = C_v$$

Hence C_v values can be taken as Cp values at low temperatures.