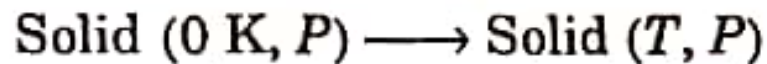


Third law of Thermodynamics : It is

impossible by any method no matter how idealised, to reduce the temperature of system to absolute zero in a finite number of operations. The absolute entropies of products and reactants in solid state are identical. Hence we can conclude that at absolute zero, all solid substances have same entropy.

Planck's statement : Let a solid at a constant pressure be heated from 0K to some temperature T below melting point, *i.e.*,



The entropy change in the above process is given by

$$\Delta S = S_T - S_{0 \text{ K}} = \int_{0 \text{ K}}^T \frac{C_P}{T} dT$$

or

$$S_T = S_{0 \text{ K}} + \int_{0 \text{ K}}^T \frac{C_P}{T} dT$$

As the entropy function increases with temperature, it may be expected that it has a minimum value of 0K. Max Planck (1913) suggest that this *minimum entropy may be assigned a zero value for a pure perfectly crystalline substance*. This suggestion is known as the third law of thermodynamics.

Lewis and Randall stated the third law as, "*every substance has a finite positive entropy, but at absolute zero of temperature the entropy may become zero and does so become in the case of perfectly crystalline substances.*"

This statement of the third law of thermodynamics is similar to the heat theorem proposed by W. Nernst (1906). Nernst asserted that the entropy change for reactions between pure crystalline substances at absolute zero is equal to zero.