

Theories of specific heat of Solids :

First and foremost theory of specific heat of solids was proposed by Dulong and Petit. According to them, molar specific heat of all metals is 6.4. This law was purely empirical and applied only to metals at high temperatures. At low temperatures, specific heat decreases and at and near 0 Kelvin it becomes zero.

$$C_v = 0$$

This was experimentally proved by Verriest.

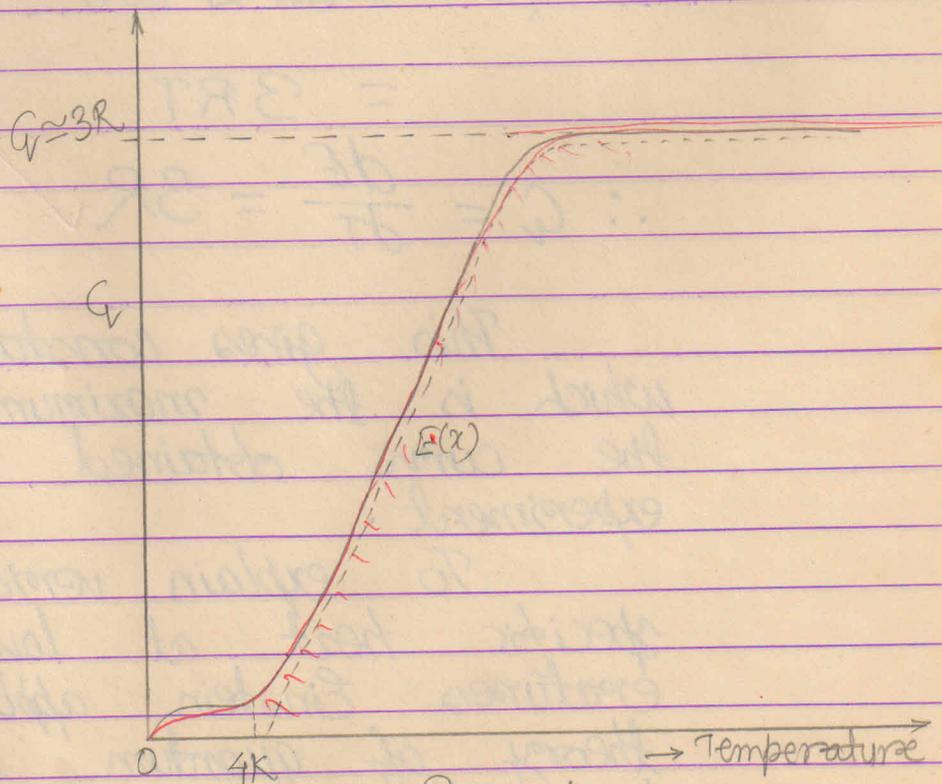


Figure-1

The experimental result is indicated in figure 1 which shows very slow increase of specific heat with temperature up to nearly 4 Kelvin. Above this there is rapid increase up to laboratory temperature (300K).

Beyond this, there is constant specific heat value $3R$.

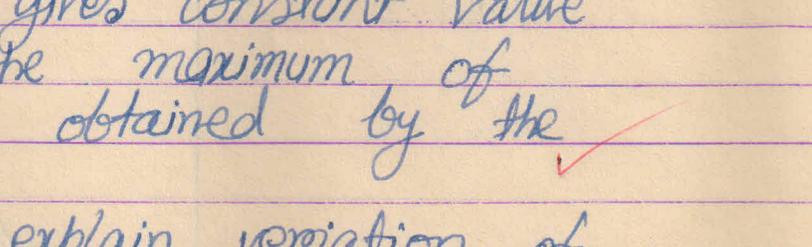
At this point, Maxwell's equipartition theory was applied where each atom of solid was supposed to possess 6 degrees of freedom like diatomic gas molecule.

Therefore, molar energy

$$E = 6 \cdot \frac{1}{2} K \cdot T \cdot N.$$

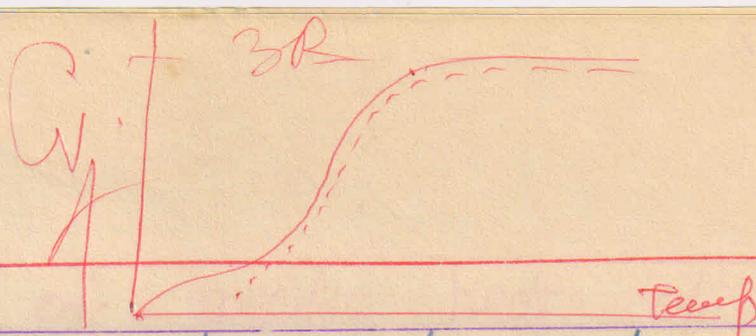
$$= 3RT$$

$$\therefore C_v = \frac{dE}{dT} = 3R \checkmark$$

This gives constant value which is the maximum of the curve obtained by the experiment. 

To explain variation of specific heat at lower temperatures Einstein applied Planck's theory of quantum to specific heat theory.

Accordingly the average



energy for vibrational mode is given by Planck's average

$$E_{av} = \frac{h\nu}{e^{h\nu/KT} - 1}$$

According to Einstein's theory, the nature of experimental curve is explained above $4K$ where $C_v = 0$. This means there is some deficiency.

Debye said that lower value of Einstein is due to single vibrational mode of the atomic vibrators. Actually, there are three — one longitudinal and two transverse. Applying this modification to Planck's average energy Debye's theory tallies well with experimental result.