Sp. Heat of Solid-Dulong and Petit Law.

Solids are characterised by the assembly of atoms are bounded together by chemical bond which might be ionic, covalent or any other type. The atoms are situated at the lattice point and vibrating about its mean position. These vibrations are transmitted from one atom to another atom throughout the crystal lattice.

At low temperatures, the displacement of atoms about their mean position is very small in comparison to the interatomic distance and so the oscillations can be considered to be harmonic.

At high temperatures, however, these displacements might become appreciable and so the motion becomes enharmonic. It is these enharmonic motions at high temperatures which are responsible for the melting of lattice. At ordinary temperatures we can consider the vibration of the lattice to be harmonic. Lattice vibrations can be compared to the sound waves, which are mechanical waves propagating in an elastic medium. Just as the electromagnetic field can be quantised and each quantum called a phonon, the sound waves can be quantised into phonons. Phonons are, therefore, the quantum of the field of sound waves. The acoustic phonons correspond to ordinary waves.

Classically each atom of the solid was considered to be a harmonic oscillator vibrating independently of other similar harmonic oscillators. The total energy of N independent harmonic oscillators in three dimensions for a given gram-mole of the substance was given to be

E = 3NkT= 3RT

and

$$C_{v} = \left(\frac{\partial E}{\partial T}\right)_{v}$$
$$C_{v} = 3R$$

R= constant = Nk_B = 8.3 x 10³ $\frac{J K^{-1}}{Kilo mole}$

In CGS unit

$$C_v = 3R = \frac{8.3x3}{4.18} = 5.96$$
 Calorie/ degree mole.

According to this law the specific heat of solid must be a constant quantity independent of temperature. This is essentially true at high temperature for many solids including metals. Experimental measurements on the specific heat of solid show that at low temperature the specific heat falls rapidly and approaches to zero at absolute zero temperature.



Fig. 1

For most of the solids the sp. heat at very low temperature (Liquid Helium- Debye model to determine sp. heat i.e) is found to be proportional to T^3 . Thus the Dulong –Petit law fails to explain the fall in the value of specific heat at low temperature. This discrepancy is essentially removed when quantum theory is used, as in the Einstein model. T^3
