

Specific Heat

Specific heat: It is the amount of heat required to change the temperature of unit mass of substance by unit degree temperature.

Classical Theory of Specific heat of a solid

Solid molecules have 6 degrees of freedom (3 translational and 3 vibrational).

According to law of equipartition of energy theorem,

Energy associated with each degree of freedom = $\frac{1}{2} k T$

$$\begin{aligned}\therefore \text{Energy associated with one molecule} &= 6 \times \frac{1}{2} k T \\ &= 3 k T\end{aligned}$$

\therefore Total energy associated with one mole of solid, $U = 3 N_A k T$

$$\text{But } N_A k = R \quad \left(\because k = \frac{R}{N_A} \right)$$

$$\therefore U = 3 R T \dots\dots\dots(1)$$

Now the specific heat at constant volume,

$$C_V = \frac{dU}{dT}$$

$$\therefore C_V = \frac{d}{dT} (3 R T)$$

$$\therefore C_V = 3 R$$

Einstein's Theory of Specific heat of a solid

In Einstein's theory, the crystal lattice structure of a solid comprising N atoms can be treated as an assembly of 3N distinguishable one-dimensional oscillators. This assumption is based on that each atom is free to move in three dimensions.

The energy level of harmonic oscillator is

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega$$

$$\text{Where } \hbar = \frac{h}{2\pi} \text{ and } n = 0, 1, 2 \dots \dots \dots$$

Using Maxwell- Boltzmann distribution of energy

$$E = \frac{\int_0^\infty E_n e^{-\frac{E_n}{kT}} dE}{\int_0^\infty e^{-\frac{E_n}{kT}} dE}$$

$$\text{Or } E = \frac{\sum_0^\infty E_n e^{-\frac{E_n}{kT}}}{\sum_0^\infty e^{-\frac{E_n}{kT}}}$$

$$E = \frac{\sum_0^\infty \left(n + \frac{1}{2} \right) \hbar \omega e^{-\left(n + \frac{1}{2} \right) \frac{\hbar \omega}{kT}}}{\sum_0^\infty e^{-\left(n + \frac{1}{2} \right) \frac{\hbar \omega}{kT}}}$$

$$\text{Let } x = -\frac{\hbar \omega}{kT}$$

$$\text{Then, } E = \frac{\hbar \omega \sum_0^\infty \left(n + \frac{1}{2} \right) e^{\left(n + \frac{1}{2} \right) x}}{\sum_0^\infty e^{\left(n + \frac{1}{2} \right) x}}$$

$$E = \hbar\omega \frac{\left(\frac{1}{2}e^{\frac{x}{2}} + \frac{3}{2}e^{\frac{3x}{2}} + \frac{5}{2}e^{\frac{5x}{2}} + \dots\right)}{\left(e^{\frac{x}{2}} + e^{\frac{3x}{2}} + e^{\frac{5x}{2}} + \dots\right)}$$

$$E = \hbar\omega \frac{d}{dx} \left[\ln \left(e^{\frac{x}{2}} + e^{\frac{3x}{2}} + e^{\frac{5x}{2}} + \dots \right) \right]$$

$$E = \hbar\omega \frac{d}{dx} \left[\ln e^{\frac{x}{2}} (1 + e^x + e^{2x} + \dots) \right]$$

$$\text{Since } \ln(1 + e^x + e^{2x} + \dots) = -\ln(1 - e^x)$$

$$\therefore E = \hbar\omega \frac{d}{dx} \left[\ln e^{\frac{x}{2}} - \ln(1 - e^x) \right]$$

$$E = \hbar\omega \frac{d}{dx} \left[\frac{x}{2} - \ln(1 - e^x) \right]$$

$$E = \hbar\omega \left[\frac{1}{2} + \frac{e^x}{1 - e^x} \right]$$

$$E = \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{-x} - 1} \right]$$

$$\text{since } x = -\frac{\hbar\omega}{kT}$$

$$\therefore E = \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1} \right]$$

For one mole, the total energy of system is given by

$$U = 3 N_A E = 3 N_A \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1} \right]$$

\therefore The molar specific heat is given by

$$C_v = \left(\frac{dU}{dT} \right)_v = 3 N_A \hbar\omega \left[0 - \frac{1}{\left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^2} \right] \times -e^{\frac{\hbar\omega}{kT}} \frac{\hbar\omega}{kT^2}$$

$$C_v = 3 N_A k \left(\frac{\hbar\omega}{kT} \right)^2 \left[\frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^2} \right]$$

$$C_v = 3 R \left(\frac{\hbar\omega}{kT} \right)^2 \left[\frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^2} \right]$$

Here $\frac{\hbar\omega}{k} = \theta_E$, called as Einstein temperature

$$\therefore C_v = 3 R \left(\frac{\theta_E}{T} \right)^2 \left[\frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1 \right)^2} \right]$$

Case I : $T \gg \theta_E$

$$\frac{\theta_E}{T} \ll 1$$

$$\therefore e^{\frac{\theta_E}{T}} \rightarrow 1$$

$$e^{\frac{\theta_E}{T}} - 1 \approx 1 + \frac{1}{2!} \left(\frac{\theta_E}{T} \right)^2 + \dots - 1 \approx \frac{\theta_E^2}{T^2}$$

$$\therefore C_v = 3 R \left(\frac{\theta_E}{T} \right)^2 \left[\frac{1}{\left(\frac{\theta_E}{T} \right)^2} \right] = 3R$$

Case I : $T \ll \theta_E$

$$\frac{\theta_E}{T} \gg 1$$

$$\therefore e^{\frac{\theta_E}{T}} - 1 \approx e^{\frac{\theta_E}{T}}$$

$$\therefore C_v = 3R \left(\frac{\theta_E}{T} \right)^2 \left[\frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} \right)^2} \right]$$

$$\therefore C_v = 3R \left(\frac{\theta_E}{T} \right)^2 \left[\frac{1}{e^{\frac{\theta_E}{T}}} \right]$$

In above equation, As $T \rightarrow \infty$, $\frac{\theta_E}{T}$ reaches zero faster than $e^{\frac{\theta_E}{T}}$.
Hence at high temperature $C_v = 0$

Debye's theory of the specific heat of a solid

The main problem of Einstein theory lies in the assumption that a single frequency of vibration characterizes all $3N$ oscillators.

In Debye's theory a solid is viewed as a phonon gas. Vibrational waves are matter waves, each with its own de Broglie wavelength and associated particle. Debye considered the vibration of crystal as whole.

In a vibrating solid, there are three types of waves. After considering one longitudinal and two transverse waves (two states of polarisation),

$$f(v) dv = 4\pi \left(\frac{1}{C_l^3} + \frac{1}{C_t^3} \right) v^2 dv \dots (1)$$

Where C_l & C_t are velocities of longitudinal and transverse wave respectively.

Since each oscillator of the assembly vibrates with its own frequency, and we are considering an assembly of $3N$ linear oscillators, there must be an upper limit to the frequency, so that

$$\begin{aligned} 3N &= \int_0^{v_m} f(v) dv \\ \therefore 3N &= \int_0^{v_m} 4\pi \left(\frac{1}{C_l^3} + \frac{1}{C_t^3} \right) v^2 dv \\ \therefore 3N &= 4\pi \left(\frac{1}{C_l^3} + \frac{1}{C_t^3} \right) \int_0^{v_m} v^2 dv \\ \therefore 3N &= 4\pi \left(\frac{1}{C_l^3} + \frac{1}{C_t^3} \right) \frac{1}{3} v_m^3 \\ \therefore \frac{9N}{v_m^3} &= 4\pi \left(\frac{1}{C_l^3} + \frac{1}{C_t^3} \right) \dots (2) \end{aligned}$$

From eqⁿ (1) and (2), we get

$$f(v) dv = \frac{9Nv^2}{v_m^3} dv$$

According to the quantum theory energy associated with each degree of freedom is

$$\frac{h\nu}{e^{h\nu/kT} - 1}$$

The internal energy of the assembly is given by

$$U = \int_0^{\nu_m} N(\nu) d\nu$$

$$\therefore U = \int_0^{\nu_m} f(\nu) d\nu \frac{h\nu}{e^{h\nu/kT} - 1}$$

$$\therefore U = \int_0^{\nu_m} \frac{9N\nu^2}{\nu_m^3} \frac{h\nu}{e^{h\nu/kT} - 1} d\nu$$

$$\therefore U = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu$$

We know, $C_v = \left(\frac{dU}{dT}\right)_v$

$$\therefore C_v = \left(\frac{dU}{dT}\right)_v = \frac{9N}{\nu_m^3} \int_0^{\nu_m} h\nu^3 \frac{d\left(\frac{1}{e^{h\nu/kT} - 1}\right)}{dT} d\nu$$

$$\therefore C_v = \frac{9N}{\nu_m^3} \int_0^{\nu_m} h\nu^3 \frac{\partial\left(\frac{1}{e^{h\nu/kT} - 1}\right)}{\partial T} d\nu$$

$$\therefore C_v = \frac{9N}{\nu_m^3} \int_0^{\nu_m} h\nu^3 \frac{e^{h\nu/kT} \frac{h\nu}{kT^2}}{\left(e^{h\nu/kT} - 1\right)^2} d\nu$$

$$\therefore C_v = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h^2}{kT^2} \frac{\nu^4 e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2} d\nu$$

$$\therefore C_v = \frac{9N}{\nu_m^3} \frac{h^2}{kT^2} \int_0^{\nu_m} \frac{\nu^4 e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2} d\nu$$

Here $\frac{h\nu_m}{k} = \theta_D$, called as Debye's temperature

Let $x = \frac{h\nu}{kT}$ and $x_m = \frac{h\nu_m}{kT} = \frac{\theta_D}{T}$

$$\therefore C_v = \frac{9N}{\nu_m^3} \frac{h^2}{kT^2} \int_0^{x_m} \frac{\left(\frac{kT}{h} x\right)^4 e^x}{(e^x - 1)^2} \left(\frac{kT}{h} dx\right)$$

$$\therefore C_v = \frac{9N}{\nu_m^3} X \frac{h^2}{kT^2} X \frac{k^5 T^5}{h^5} \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$\therefore C_v = 9Nk X \frac{k^3 T^3}{h^3 \nu_m^3} \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$\therefore C_v = 9Nk \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} dx \dots \dots (1)$$

Case I : At high temperature,

$$\frac{\theta_D}{T} \ll 1, x \ll 1 \text{ and } e^x \approx 1$$

$$\therefore e^x - 1 \approx x$$

Eqⁿ (1) becomes,

$$\therefore C_v = 9Nk \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 \times 1}{x^2} dx$$

$$\therefore C_v = 9Nk \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} x^2 dx$$

$$\therefore C_v = 9Nk \left(\frac{T}{\theta_D}\right)^3 \left[\frac{x^3}{3}\right]_0^{\frac{\theta_D}{T}}$$

$$\therefore C_v = 3Nk \left(\frac{T}{\theta_D}\right)^3 \left(\frac{\theta_D}{T}\right)^3$$

$$\therefore C_v = 3Nk = 3R \quad \because Nk = R$$

Case II : At low temperature,

$$\frac{\theta_D}{T} \gg 1, x \gg 1$$

Eqⁿ (1) becomes,

$$\therefore C_v = 9Nk \left(\frac{T}{\theta_D}\right)^3 \left[\frac{4}{15}\pi^2\right]$$

$$\therefore C_v \propto T^3$$