B.Sc Part I (Physics Hons)
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Question:- Obtain an expression for the specific heat of a solid according to Einstein's theory. Discuss its limitation.

Ans:- **Einstein theory of specific heats of Solid**:→

Einstein assumed that the atoms in a crystal vibrate independently of each other about fixed lattice points. These vibrations are all assumed to be simple harmonic all with the same frequency. The vibrations of any one atom can be splits into three independent vibrations are along each other co-ordinate axes. Hence a solid containing N atoms is equivalent to 3N harmonic oscillators vibrating independently of each other all with the same frequency ν. The value of this frequency depends on the strength of the restoring force.

According to quantum mechanics a stage harmonic oscillator can only exist in certain descrete energy state which can be lebelled 0, 1, 2, ... r. In the state r be energy of oscillations is given by

$$E_r = h\nu\left(r+\frac{1}{2}\right) \qquad \text{--- (1)}$$

Assuming Maxwell's destribution law the number of oscillion is given by

$$N_r = N_0 e^{-h\nu\left(r+\frac{1}{2}\right)/KT}$$

$$= N_0 y^{\left(r+\frac{1}{2}\right)} \qquad \text{--- (2)}$$

where $y = e^{-h\nu/KT}$

The total number of oscillations given by

$$N = N_0 + N_1 + N_2 + N_3 + \ldots + N_r$$

$$= N_0 y^{\frac{1}{2}} + N_0 y^{\frac{3}{2}} + N_0 y^{5/2} + \ldots + N_0 y^{\left(r+\frac{1}{2}\right)} + \ldots$$

$$= N_0 y^{\frac{1}{2}}\left(1 + y^2 + y^3 + y^4 + \ldots + y^r \ldots\right)$$

$$= N_0 y^{\frac{1}{2}}\left(\frac{1}{1-y}\right) = \frac{N_0 y^{1/2}}{1-y} \qquad \text{--- (3)}$$

∴ Total energy of all oscillators

$$E = N_0 h\nu \times \frac{1}{2} + N_1 h\nu\left(1+\frac{1}{2}\right) + N_2 h\nu\left(2+\frac{1}{2}\right) + N_3 h\nu\left(1+\frac{1}{2}\right) + \ldots + N_r h\nu\left(r+\frac{1}{2}\right) + \ldots$$

$$= N_0 h\nu\left[\frac{1}{2}y^{1/2} + \frac{3}{2}y^{3/2} + \frac{5}{2}y^{5/2} + \ldots + \left(r+\frac{1}{2}\right)y^{\left(r+\frac{1}{2}\right)} + \ldots\right]$$

$$= \frac{N_0 h\nu}{2}\left[y^{1/2} + 3y^{3/2} + 5y^{5/2} + \ldots + r y^{\left(r+\frac{1}{2}\right)} + \ldots\right]$$

= [illegible] --- (4)

Hence mean energy per oscillator

$$\epsilon = \frac{E}{N} = \frac{N_0 h\nu y^{1/2}}{2}\left(\frac{1}{1-y} + \frac{2y}{(1-y)^2}\right)\frac{1-y}{N_0 y^{1/2}}$$

$$= \frac{h\nu}{2} + \frac{h\nu y}{1-y} = \frac{h\nu}{2} + \frac{h\nu e^{-h\nu/KT}}{1-e^{-h\nu/KT}}$$

$$= \frac{h\nu}{2} + \frac{h\nu}{e^{\frac{h\nu}{KT}}-1} \quad \text{-------} \quad (5)$$

The first term $\frac{h\nu}{2}$ is the zero point energy which the oscillator prosseses even at the absolute zero of temp. If the Solid contain N atoms it has a total of $3N$ degrees of freedom. Hence the total energy of solid is

$$U = 3N\epsilon = 3N\left[\frac{h\nu}{2} + \frac{h\nu}{e^{\frac{h\nu}{KT}}-1}\right] \quad \text{-------} \quad (6)$$

The frequency ν depends on the restoring force acting on the vibrating atoms. The restoring force in turns depends on the mean interatomic distance. At constant volume we may assume that the lattice spacing is constant. Hence diffrentiating eqn (6) w.r.to T keeping ν constant, we get the specific heat capacity at constant volume as

$$C_V = \left(\frac{du}{dT}\right)_V = 3NK\left(\frac{h\nu}{KT}\right)^2 \cdot \frac{e^{\frac{h\nu}{KT}}}{e^{\frac{h\nu}{KT}}-1}$$

or $$C_V = 3NK\frac{x^2 e^x}{(e^x-1)^2} \quad \text{-------} \quad (7)$$

where $x = \frac{h\nu}{KT} = \frac{\theta}{T}$ and $\theta = \frac{h\nu}{K}$

Eqn (7) is Einstein equation for the atomic heat capacity of a solid at constant volume. 'θ' is called Einsteins temperature. This parameter θ is choosen emperically for each solid in such a way that the predictions eqn (7) agree with experiments.

Limitations :-

As C_V depends on the temp. we have consider two cases.

Case I :- High temperature limit :-

If $T >> \theta$, i.e $x << 1$, then

$$e^x = 1 + x = 1 + \frac{h\nu}{KT}$$

from eq^n (7)

$$C_V = 3NK \cdot \frac{x^2(1+x)}{(1+x-1)^2} = 3NK$$

But $NK = R$, the universal gas constant

$$C_V = 3R \quad \ldots \quad (8)$$

This is in agreement with Dulong and Petit law which agrees with experiment at high temp. Thus at sufficiently high temp. Einsteins result reduces to Dulong and Petit's law

(11) Low temp. limit :-

If $T << \Theta$, i.e. $x >> 1$, then e from eq^n (7)

$$C_V = 3R\left(\frac{\Theta}{T}\right)^2 e^{-\left(\frac{\Theta}{T}\right)} \quad \ldots \quad (9)$$

This shows that as T decreases, the specific heat decreases. It becomes zero as $T \to 0$ as required by the third law of thermodynamics.

Einsteins formula explains the specific heat ~~cur~~ curve up to a certain point. But it fails completely at very low temp. For it predicts an exponential fall whereas decreases is according to the T^3 law. A weak point about Einsteins formula is the emperical nature of the Einstein temp. The nature of this parameter can not be ~~varied~~ verefied by any other physical data.