Unit-II Section A.

Q.1 a) Define Molar specific heat at
i) Constant Pressure and.
ii) Constant Volume.
and.
b) Lattic Heat capacity in solids.

Solution:-

Whenever heat is given to a system it is used in
a) To raise the temp. of body &
b) Rest in doing external work.

$$dQ = dU + dW \quad \text{—— (1)(a)}$$

$$\begin{pmatrix}\text{Heat absorbed}\\ \text{by system}\end{pmatrix} = \begin{pmatrix}\text{Increase}\\ \text{in internal}\\ \text{energy}\end{pmatrix} + \begin{pmatrix}\text{External}\\ \text{Work done}\end{pmatrix}$$

If pressure remains constant and dV is change in volume then $dW = PdV$

$$\therefore dQ = dU + PdV \quad \text{—— (1)(b)}$$

If dT is corresponding increase in temperature then $\left(\frac{dQ}{dT}\right) \rightarrow$ Specific Heat.

There are two types of Specific heats
a) Specific heat at constant Pressure &
b) Specific heat at constant Volume.

In detail

a) Now Molar Specific heat.
It is the amount of heat required (dQ) to raise the temperature of one kilo-mole of a substance through dT °C keeping pressure constant.

$$\therefore \left(\frac{dQ}{dT}\right)_P = C_P = \text{Molar specific heat at constant pressure}$$

Similarly

$$\left(\frac{dQ}{dT}\right)_{C_V} = C_V = \text{Molar specific heat at constant Volume.}$$

* **Imp discussion**

In case of solids at low temperatures both the specific heats are similar. Also as volume expansion of solids is small (negligible) hence in case of Solids we generally apply Specific heat at constant volume. #1
ie $dV = 0. \Rightarrow dQ = dU$ (from eq 1)(b)

$$\text{or } C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

ⓑ Lattice Heat capacity

Now in case of solids the increase in internal energy (dU) takes place in two ways.
i) In crystals it is exhibited by vibrations of atoms (assumed to be free) about their ≡m position.
& ii) In metals and semiconductors in form of thermal excitation of atoms to heigher energy states.

Thus.

$$U = U_{lattice} + U_{elect}$$

$$C_V = \left(\frac{dU}{dT}\right)_V = \frac{d}{dt}(U_{lattice}) + \frac{d}{dt}(U_{elect})$$

$$C_V = C_{lattice} + C_{elect}.$$

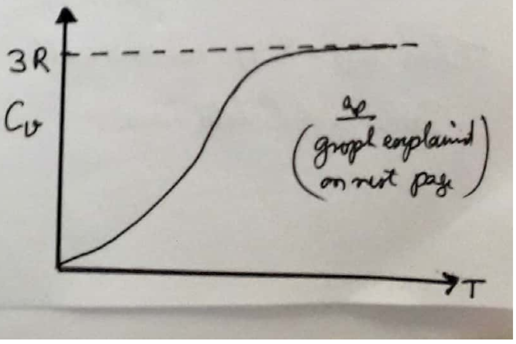
The quantity

$C_{lattice} \rightarrow$ Lattice Specific heat
OR
Lattice heat capacity

In case of crystalline solids since no free atoms are available hence the Lattice specific heat is only considered
ie $C_V = C_{lattice}$ in crystalline solids

$$\text{or } C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V = \left(\frac{dU_{lattice}}{dT}\right)_V$$

The experimental ~~of~~ observation is as shown in figure



Q Give in detail the quantum theories put forth to explain the opserved C_v graph.

Sol Various theories have been put forth. to explain the (C_v, T) graph in case of crystalline solids.

Worth while to mention is the semi-classical theory called as Dulong and Petti's Law (optional only to read) Its salient features are.

1) atoms in crystaline solids are point particles with no structure & having THREE degrees of freedom.

2) As per semi-classical theory max energy per degree of freedom is $\frac{1}{2}kT$ here k = Boltzmann's Cont.

3) Particles interacting with harmonic forces the avg potential energy per degree of freedom $= \frac{1}{2}kT + \frac{1}{2}kT = kT$

4) As a given atom has three degrees of freedom hence. Total energy per degree of freedom $= 3kT$.

Thus if N is no of identical atoms in a crystal then Total Vibrational energy $= U = 3NkT$.

$$\therefore C_v = \left(\frac{dU}{dT}\right)_v = \left(\frac{d(3NkT)}{dT}\right)_v$$

$$C_v = 3Nk = 3R$$

$R \to$ Universal gas Cont
$N \to$ Avogadro No. (for 1 mole of solid)

$$C_v = 3R = 5.97 \text{ Kilo-cal/kilo-mole.}$$

as $K = 1.99$ kilo cal/kilomole K.

Thus $C_v = 5.97$ = constant called as Dulong & Petit's Law.

When this result is compared with the actual experimental opservation it is found that

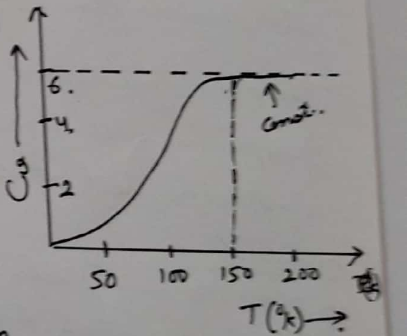
a) It is good aggrement at heigh temp.

b) It fails at low temperature because at low temperature it is observed. that the specific heat of all solids drops sharply and approach zero. at 0K. But as per above semi-classical theory it is independent of temperature.

This variation at low temperature was further explained by Einstein on basis of Quantum model (assumptions)

Imp

Q. Draw and explain the (C_v, T) graph for a typical solid



a) At high temp
$C_v = 3R = 5.97$ per mole. as explained by Dulong & Petit's law.
This is true for many compounds and heavy metals

b) For light elements (such as gases) the value at room temp is less than 3R.

c) At low temperatures C_v decreases exponentially st. $C_v \to 0$ as $T \to 0K$.

d) In temp range 0–20°K
For non metals $C_v = \alpha T^3$
For metals $C_v = \alpha T^3 + \gamma T$
($\alpha \to$ linear expansion coefficient)
($\gamma \to$ volume " ")
For layered compounds $C_v = \alpha T^2$
for linear Chain Compounds $C_v = \alpha T$

Q. Give Einsteins Theory of Specific Heat of solids with regards.

i) Why was it necessary

2) Its assumptions.

3) Derive lattice heat capacity based on this model. &

4) Explain / compare it with experimental observation at high & low temp.

Ans

1). Since the semiclassical theory or Dulong Petit's law could explain the experimental observation at high temperature but fails at lower temperatures Thus Einstein and Debye set up a model based on quantum mechanics

2) Assumptions of Einstein Model.

a) The atoms are identical & independent simple harmonic oscillators

b) Energy spectra of these oscillators are discrete in nature

c) Each atom has Three Degrees of freedom along X, Y & Z axis resp. Thus for a solid having N atoms Should have 3N no. of one-dimensional oscillators ie. (3N along X axis, 3N along Y axis & 3N along Z-axis)

d) As all these oscillators are distinguishable on basis of the positions occupied in the crystal hence they obey Maxwells-Boltzmann's distribution of Energy.

e) All atoms are in identical environment hence vibrate with same natural frequency.

3) Mathermatical Derivation

Now average energy of oscillators as per Maxwell-Boltzmans law of energy distribution is given as.

$$\overline{E} = \frac{\sum_{n=0}^{n=\infty} E_n e^{-E_n/kT}}{\sum_{n=0}^{n=\infty} e^{-E_n/kT}} = \frac{\sum_{n=0}^{n=\infty} nh\nu e^{nh\nu/kT}}{\sum_{n=0}^{n=\infty} e^{-nh\nu/kT}}$$

$$= \frac{h\nu\left[0 + e^{-h\nu/kT} + 2e^{-2h\nu/kT} + \dots \infty\right]}{\left[1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots \infty\right]}$$

let $x = -h\nu/kT$

$$\overline{E} = \frac{h\nu\left[0 + e^{x} + 2e^{2x} + \dots \infty\right]}{\left[1 + e^{x} + e^{2x} + \dots \infty\right]}$$

Since each term in numerator is differential coeff. of the corresponding term in the denominator

$$\overline{E} = h\nu \frac{d}{dx} \ln\left[1 + e^{x} + e^{2x} + \dots \infty\right]$$

Now $1 + e^{x} + e^{2x} + \dots \infty$ is an series with 1st term as 1 (unity) & common ratio e^{x} hence sum of the series upto $\infty = \frac{1}{1-e^{x}}$

$$\Rightarrow \ln\left(\frac{1}{1-e^{x}}\right) = -\ln(1-e^{x})$$

hence $\overline{E} = -h\nu \frac{d}{dx} \ln(1-e^{x})$

$$\overline{E} = \frac{h\nu e^{x}}{1-e^{x}}$$

$$\left[\because \frac{d}{dx} \ln(f x) = \frac{1}{f(x)} \frac{d}{dx} f(x)\right]$$

$$\overline{E} = h\nu \frac{1}{e^{-x}-1}$$

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

Now as per wave mechanics the ground state energy of harmonic oscillator is not zero but $\frac{1}{2}h\nu$

or $E_n = \left(n+\frac{1}{2}\right)h\nu$ [done in 5th sem]

Hence adding this first term.

$$\therefore \overline{E} = h\nu\left[\frac{1}{2} + \frac{1}{e^{h\nu/kT}-1}\right]$$

Now at 0k this first term is non zero. and gives the value of $\bar{E}$. But this term does not contribute to specific heat (lattice heat capacity)

Now for N_0 no. of ~~ato~~ atoms there are $3N_0$ oscillators (assumption c)

∴ Total energy

$$U = 3N_0\bar{E} = \frac{3N_0 h\nu}{e^{h\nu/kT}-1}$$

and molar lattice heat Capacity

$$C_v = \left(\frac{dU}{dT}\right)_v = 3N_0 k\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}$$

$$\left[\because \frac{d}{dx}\left(\frac{f(x)}{g(x)}\right) = \frac{\left[g(x)\frac{d}{dx}f(x)\right]-\left[f(x)\frac{d}{dx}g(x)\right]}{(g(x))^2}\right.$$

To simplify let $\Theta_E = \frac{h\nu}{k} =$ Einstein temperature

$$\boxed{C_v = 3N_0 k\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)}}$$

Einstein eqn for Molar specific heat.

or $$\boxed{C_v = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)}}$$

$N_0k = R$ → universal gas const.

N_0 → Avagdros no.

k → Botlzmann's constant.

4) Comparison of Einsteins result with observed results.

OR

Prediction and comparison of Einsteins Model with Experimental Results

Solution

Now as per Einstein Model.

$$C_v = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{e^{\Theta_E/T}-1}$$

Unit-II Section B #4

a) At very high temperature

ie $T >> \Theta_E$ s.t $\frac{\Theta_E}{T} << 1$

$$e^{\Theta_E/T} = 1 + \frac{\Theta_E}{T} + \frac{1}{2}\left(\frac{\Theta_E}{T}\right)^2 + \ldots\ldots$$

$$\simeq 1 + \frac{\Theta_E}{T} + \text{neglecting higher powers}$$

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

as $T \to \infty$ $\frac{\Theta_E}{T} \to 0$ or $C_v = 3R$

which is also Dulong Petit's law and it well explains the observed graph at high temperature

b) At low temperatures

$$T << \Theta_E \Rightarrow \frac{\Theta_E}{T} >> 1$$

here $e^{\Theta_E/T} + 1 \simeq e^{\Theta_E/T}$

$$\therefore C_v = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T})^2}$$

$$= 3R\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}$$

Thus as $T << \Theta_E$ $C_v \propto e^{-\Theta_E/T}$

Thus specific heat of solids decreases exponentially with decrease in temperature This variation is ~~in~~ not ~~good~~ in aggrement with observed result because

~~But~~ at very low temperatures it is observed that C_v varies as T^3 but as per Einstein theory $e^{\Theta_E/T}$ is a dominant factor which approaches zero as $T \to 0$.

Q. a) What are the basic drawbacks of Einstein model of specific heat.

b) Explaining the assumptions clearly derive expression for lattice specific heat on basis of "Debye model"

c) Discuss the high and low temp. limits and define Deby's T^3 law.

d) Give limitations (drawback) of Debye model. —(Do yourself from book)

e) Compare Einstein & Debye models. (Do yourself from Book)

Solution

a) Basic drawback of Einstein Model

i) In this model the atoms were supposed to vibrate as a single independent ~~used~~ entity and

(ii) the vibrational motion of an individual atom was equivalent to the vibrational motion of the whole crystal with same frequency. (ν) or ~~no~~ natural frequency of a single atom.

But in actual crystals have atoms which are in bound state forming a system of coupled oscillations. Each atom vibrates under the influence of a "Force Field" due to neighbouring atoms.

b) Assumptions of Debye Model.

1) Debye model takes into account the influence on a vibrating atom due to neighbouring atoms. and considered the Solid as a continuous Elastic body.

2) The internal energy does not reside with individual vibrating atoms but in "Elastic standing waves"

3) Energy of these Elastic Standing waves is quantized.

4) Quanta of vibration is a "PHONON" having energy $E = h\nu$ here
$\nu \rightarrow$ frequency of Elastic Standing waves

5) The PHONON travels with the speed of sound ~~waves~~ because sound waves are elastic in nature.

6) No of possible ~~vib~~ modes of vibration is

$$Z(\nu)\,d\nu = \left(\frac{4\pi V}{v^3}\right)\nu^2 . d\nu \quad —(1)$$

$Z(\nu) \rightarrow$ no of vib. modes in frequency range ν to $(\nu + d\nu)$

$V = L^3 \rightarrow$ volume of specimen (cubic)

$v \rightarrow$ velocity of PHONON
vel of propogation of waves.

Imp
Determination of Density of Modes $Z(\nu)d\nu$ should be studied seperately it may be asked as a seperate question.

7) **Derivation**

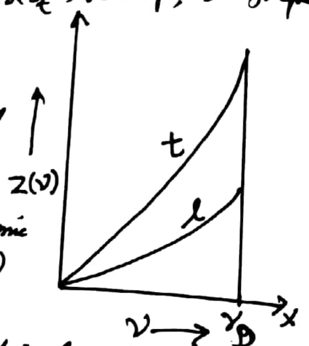
In solids there are two types of elastic waves.
i) longitudinal and ii) ~~the~~ Transverse having velocities v_l & v_t.
also transverse waves have two perpendicular directions of polarization while longitudinal waves have only one direction along the direction of propagation.

Taking these factors into consideration

$$\begin{pmatrix}\text{Density of}\\ \text{Modes}\end{pmatrix} = Z(\nu)d\nu = 4\pi V\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right]\nu^2 d\nu \quad \text{—(2)}$$

8) ~~Debye's~~ Debye's Approx v_l & v_t → velocity ; ν → frequency

Debye considered a continuum model (as λ of atoms is greater than interatomic distance b/w atoms)



Total no. of vibrational modes is 3N. this factor puts an upper limit to ~~no. of~~ frequency of elastic waves.

The value ν_D → ~~high~~ Highest value → Debye frequency

The value of ν_D can be determined as follows.

$$\int_0^{\nu_D} Z(\nu)d\nu = 3N$$

~~$\int_0^{\nu_D} 4\pi V\left[\frac{1}{v_l^3} + \frac{2}{v^3}\right]$~~

$$\int_0^{\nu_D} 4\pi V\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right]\nu^2 d\nu.$$

$$4\pi V\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right]\nu_D^3 = 3N$$

$$\nu_D = \frac{9N}{4\pi V}\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right]^{-1} \quad \text{—③}$$

9) Now avg energy (considering phonon gas as equalent in behavior to photon gas)

$\overline{E}$ = Energy per standing wave.

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

As per quantum mechanics a a quantum oscillator associated with each vibrational mode. of same ~~freq~~ frequency then the Vibrational energy of crystal will be given as.

Unit-II Section B #6.

$$U = \int_0^{\nu_D} \overline{E}\, Z(\nu)d\nu = \int_0^{\nu_D} Z(\nu)\frac{h\nu}{(e^{h\nu/kT}-1)}\cdot d\nu$$

Substituting value of $Z(\nu)d\nu$ from eqn 2

$$U = \int_0^{\nu_D} 4\pi V\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right]\frac{h\nu^3}{e^{h\nu/kT}-1}\cdot d\nu$$

$$= 4\pi V\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right]^2\int_0^{\nu_D}\frac{h\nu^3}{e^{h\nu/kT}-1}\cdot d\nu$$

Now $4\pi V\left[\frac{1}{v_l^3}+\frac{2}{v_t^3}\right] = \frac{9N}{\nu_D^3}$ (from 3)

$$U = \frac{9N}{\nu_D^3}\int_0^{\nu_D}\frac{h\nu^3}{e^{h\nu/kT}-1}\cdot d\nu \quad \text{—(4)}$$

let $\frac{h\nu}{kT} = x$ & $\frac{h\nu_D}{kT} = x_m$.

$\Rightarrow \nu = \frac{xkT}{h}$ $\therefore d\nu = \frac{kT}{h}\cdot dx$

hence eqn (4) becomes.

$$U = \frac{9N}{\nu_D^3}\left(\frac{kT}{h}\right)^4\int_0^{x_m}\frac{x^3}{e^x-1}\cdot dx.$$

$$= 9N\left(\frac{hT}{h\nu_D}\right)^3 kT\int_0^{x_m}\frac{x^3}{e^x-1}\cdot dx.$$

let Deby's Temp $= \theta_D = \frac{h\nu_D}{k}$

$\therefore x_m = \frac{\theta_D}{T}$. ; & $kT = R$

$$\boxed{U = 9R\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{e^x-1}\cdot dx} \quad \text{—(5)}$$

Specific Heat.

$$C_v = \left(\frac{dU}{dT}\right)_v = 9R\left(\frac{T}{\theta_D}\right)^3\int_0^{x_m}\frac{x^4e^x}{(e^x-1)^2}\cdot dx$$

$$= 3R\left(\frac{\theta_D}{T}\right)F_D$$

where $F_D = 3\left[\frac{T}{\theta_D}\right]^4\cdot\int_0^{\theta_D/T}\frac{e^x x^4}{(e^x-1)^2}\cdot dx.$

= Debye Function.

c) Discussion of Debyi Model at high & low temperature, Comparing with experimental observation and defintion of Debyi T^3 law.

Solution

Now as per Debyi model

$$C_v = 9NkT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x}{e^x-1}\,.dx. \qquad \boxed{=n5}.$$

A) At very heigh temperature

$$T >> \theta_D \Rightarrow x = \frac{h\nu}{kT} << 1$$

$$e^x - 1 = [(1+x+\dots)-1] \simeq x.$$

$$\therefore U = 9NkT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} x^2.dx.$$

$$U = 9NkT\left(\frac{T}{\theta_D}\right)^3 \cdot \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

$$U = 3NkT = 3RT$$

$$\therefore C_v = \left(\frac{dU}{dT}\right)_v = 3R$$

which is dulong Petits law well established by experimental observation

B) At low temperatures $T << \theta_D$

$$x_m = \frac{\theta_D}{T} \to \infty.$$

$$\therefore U = 9NkT\left(\frac{T}{\theta_D}\right)^3 \left(\int_0^\infty \frac{x^3}{e^x-1}\,.dx\right)$$

$$\text{Now} \int_0^\infty \frac{x^3}{e^x-1}\cdot dx = \frac{\pi^4}{15}$$

$$\therefore U = 9NkT\left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3}{5}\pi^4 R \frac{T^4}{\theta_D^3}$$

$$\therefore C_v = \left(\frac{dU}{dT}\right)_v = \frac{12}{5}\pi^4 R\left[\frac{T}{\theta_D}\right]^3 = 234R\left[\frac{T}{\theta_D}\right]^3$$

$$\text{or } \boxed{C_v \propto T^3}$$

This is called as Debye T^3 law. which is in good aggrement with the expenmental observation.

Now at very low Temp. the Vibrational energy is $\propto T^4$ which is analogue to the results of blak body radiations Stefans law. This shows that PHOTONS and PHONONS obey same statistics.