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B.Sc (PS)CHEMISTRY VI Sem

Lattice vibrations

from eq. (6) or (9), we find that  $\omega'_{ph} \neq \omega_{ph}$ . Such a process in which the frequency of the photon changes is called Umklapp or U-Process. In this process a photon is created or absorbed in addition to the Bragg's reflection and the momentum is transferred to the crystal as a whole.

### Specific heat:-

The specific heat of a substance is defined as the heat required to raise the temperature of one gram molecule of the substance through 1°C. i.e.

$$C = \frac{dQ}{dT} \quad (1)$$

where  $dQ$  is the amount of heat added to a system to raise its temperature from  $T$  to  $T+dT$ . The quantity of heat required to increase the temperature of a body is different under different conditions: accordingly, one can have various types of specific heats. For e.g.  $C_p$  or  $C_v$ .

Accordingly to the first law of thermodynamics, the heat added to a system is used up in two ways: firstly, to increase the internal energy of the system, thereby raising its temp. and secondly, to do some work on the system to increase its volume against an external pressure. It is the latter quantity which may have different values under different conditions. If the system expands against a constant pressure,

Then the first law can be written as

$$dQ = dE + p dV \quad \text{--- (2)}$$

The first term on the right hand side represents the change in internal energy of the system and the second one represents the work done to change the volume by an amount  $dV$  at a pressure  $p$ . If heat is added to the system at constant volume, the second term in eq. (2) vanishes and the specific heat at constant volume may be expressed as

$$C_v = \left( \frac{dQ}{dT} \right)_v = \left( \frac{dE}{dT} \right)_v \quad \text{--- (3)}$$

Similarly, one can express the specific heat at constant pressure as

$$C_p = \left( \frac{dQ}{dT} \right)_p$$

In gases, there is a large difference in  $C_p$  and  $C_v$ . However, in solids, due to a small change in volume,  $C_p$  is almost the same as  $C_v$  particularly at low temp. For this reason, the term 'specific heat' of solids is commonly used in case of solids. However, it strictly means the specific heat at constant volume and is given by eq. (3). Thus, in solids, most of the heat supplied is used up in increasing the internal energy. The increase in internal energy of a solid may occur in two ways:

- (i) the atoms, which ordinarily vibrate freely about their equilibrium positions, are set into vigorous vibrations. This is manifested by a rise in temperature.
- (ii) The free electrons in case of metals and semiconductors get thermally excited to a higher energy state.

The first contribution arises from the atomic vibrations and may be called the lattice specific heat. The second contribution arises from the electronic system and is a relatively small contribution. Thus, in general, the specific heat of a solid may be expressed as

$$C_{\text{solid}} = C_{\text{lat}} + C_{\text{elec}} \quad \text{--- (4)}$$

For further discussion ~~on this chapter~~, it is assumed that no free electrons are present and the specific heat of a crystal is only due to the excitation of thermal vibrations in the lattice, i.e., only the lattice specific heat is to be considered.

Heat capacity or specific heat is defined as the heat required to raise the temperature of the complete mass (or volume) of a solid through 1°C. Thus the specific heat is the heat capacity per gram (or per unit volume).

Some facts about the heat capacity:-

- (i) The heat capacity of most of the solids at room temperature is close to  $3Nk_B$ , where  $N$  is the number of atoms in the solid, and  $k_B$  is the Boltzmann's constant. For one mole of atoms, the heat capacity is given by  $3N_A k_B$  or  $25 \text{ J/mole-K}$  or  $6 \text{ cal/mole-K}$  resp.
- (ii) At lower temp. ( $T \rightarrow 0 \text{K}$ ), heat capacity decreases sharply and follows  $T^3$  law for insulators and  $T$ -law for metals. If metal becomes superconductor the decrease is even faster.
- (iii) In magnetic solids, the heat capacity increases near the Curie temp. when magnetic moments become ordered.

Classical theory of lattice heat capacity:-  
(~~concepts~~ Dulong and Petit's law).

In classical theory, it is assumed that each atom of the crystal acts as a three-dimensional harmonic oscillator (An atom vibrating about its equilibrium position and constitutes a 3-dim harmonic oscillator) and all the atoms vibrate independent of one another. Further, a system of  $N$  vibrating atoms or  $N$  independent 3-dim. harmonic oscillators is equivalent to a system of  $3N$  ~~is~~ identical and independent one-dim. harmonic oscillator, because each vibrating atom has three independent vibrational degrees of freedom, and, acc. to the principle of equipartition of energy, the vibrational energy is distributed equally among all the three degrees of freedom. Thus each vibrational degree of freedom can be regarded as a 1-dim. harmonic oscillator.

To find heat capacity, it is assumed that each harmonic oscillator vibrates with its natural freq.  $\omega_0$ , energies of these oscillators may be diff. (because they may vibrate with diff. amplitude) varying continuously from 0 to  $\infty$ . In order to determine heat capacity of the solid, we find out the average thermal energy of a single 1-dim. harmonic osc. and multiply it by  $3N$ .

Energy  $E$  of a 1-dim. H.O of mass  $m$  and angular freq.  $\omega_0$  is given by

$$E = \frac{p^2}{2m} + V(x)$$

$$= \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 x^2$$

— (1)

from eq. (6) or eq. (9), we find that  $\psi_{ph} \neq \psi_{pr}$  such a process is whi

where  $\frac{p^2}{2m}$  rep. K.E,  $p$  being the momentum and  $V(x)$  is  $\frac{1}{2}m\omega_0^2 x^2$  the P.E at a displacement  $x$  from the mean position. Assuming the distribution of oscillators in energy obeys the Maxwell-Boltzmann distribution law, the avg. energy of each H.O is given by

$$\bar{E} = \frac{\int E \exp\left(-\frac{E}{k_B T}\right) dE}{\int \exp\left(-\frac{E}{k_B T}\right) dE} \quad \text{--- (2)}$$

using eq. (1) in (2) we get

$$\bar{E} = \frac{\iint_{p, x} \left(\frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{p, x} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}$$

$$= \frac{\iint_{p, x} \left(\frac{p^2}{2m}\right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{p, x} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx} +$$

$$\frac{\iint_{p, x} \left(\frac{m\omega_0^2 x^2}{2}\right) \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}{\iint_{p, x} \exp\left(-\frac{p^2}{2mk_B T}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dp dx}$$

$$= \frac{\int_p \left(\frac{p^2}{2m}\right) \exp\left(-\frac{p^2}{2mk_B T}\right) dp}{\int_p \exp\left(-\frac{p^2}{2mk_B T}\right) dp} + \frac{\int_x \left(\frac{m\omega_0^2 x^2}{2}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dx}{\int_x \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dx}$$

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$$= \frac{\int_p \left(\frac{p^2}{2m}\right) \exp\left(-\frac{p^2}{2mk_B T}\right) dp}{\int_p \exp\left(-\frac{p^2}{2mk_B T}\right) dp} + \frac{\int_x \left(\frac{m\omega_0^2 x^2}{2}\right) \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dx}{\int_x \exp\left(-\frac{m\omega_0^2 x^2}{2k_B T}\right) dx}$$

$$N \omega \int_{-\infty}^{\infty} u^2 \exp(-au^2) du = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$$

$$\text{and } \int_{-\infty}^{\infty} \exp(-au^2) du = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$\therefore \bar{E} = \frac{1}{2m} \cdot \frac{\frac{1}{4} [\pi (2mk_B T)^3]^{1/2}}{\frac{1}{2} [\pi (2mk_B T)]^{1/2}} + \frac{1}{2} m \omega_0^2 \frac{\frac{1}{4} [\pi (\frac{2k_B T}{m\omega_0^2})]^{3/2}}{\frac{1}{2} [\pi (\frac{2k_B T}{m\omega_0^2})]^{1/2}}$$

$$= \frac{1}{2} k_B T + \frac{1}{2} k_B T = k_B T \quad \text{--- (3)}$$

Thus total vibrational energy of a crystal containing  $3N$  one-dim. H.O becomes

$$E = 3N\bar{E} = 3Nk_B T \quad \text{--- (4)}$$

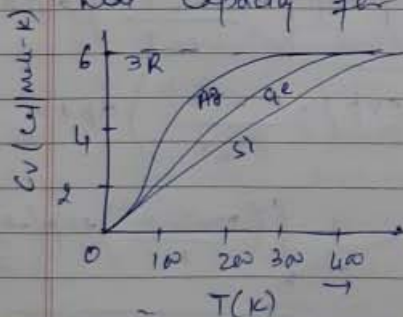
Thus heat capacity

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3Nk_B \quad \text{--- (5)}$$

Thus molar heat capacity is given by

$$C_{m, V} = 3N_A k_B = 3R = 5.96 \text{ cal/mole-K} \quad \text{--- (6)}$$

Thus according to classical theory, the molar heat capacity of all the solids is constant and is indep. of temp. & freq. This is called Dulong and Petit's law. The above result is in good agreement with the observed heat capacity for a number of solids, including



heat capacity as a func. of Temp.

metals at high temp & room temp. too. The theory however failed to account for heat capacity at low temp.

The discrepancy was resolved first by Einstein & then Debye by using quantum theory.

## Einstein theory of lattice heat capacity:-

Einstein attempted to resolve the discrepancies of the classical theory of specific heat by applying the Planck's quantum theory. He retained all the assumptions of the classical theory as such except replacing the classical harmonic oscillators by quantum harmonic oscillators which can have only discrete energy ~~levels~~ values. The salient features of the Einstein's theory are listed below:

- (i) A crystal consists of atoms which may be regarded as identical and independent harmonic oscillators.
- (ii) A solid consisting of  $N$  atoms is equivalent to  $3N$  one-dimensional harmonic oscillators.
- (iii) All the oscillators vibrate with the same natural frequency due to the identical environment of each.
- (iv) The oscillators are quantum oscillators and have discrete energy spectrum rather than the continuous one as for classical oscillators.
- (v) Any number of oscillators may be present in the same quantum state.
- (vi) The atomic oscillators form an assembly of systems which are distinguishable or identifiable due to their location at separate and distinct lattice sites and hence obey the Maxwell-Boltzmann distribution of energies.

Considering the Planck's quantum theory, the discrete energy values of an oscillator with freq.  $\nu$  are given by

$$E_n = nh\nu = n h \omega_0 \quad \text{--- (1)}$$

where  $n = 0, 1, 2, 3, \dots$  is called the quantum no. Einstein later used the wave mechanical result

which gives the energy levels of the harmonic oscillator as

$$E_n = \left(n + \frac{1}{2}\right) h\nu = \left(n + \frac{1}{2}\right) h\omega_0 \quad \text{--- (2)}$$

where  $\frac{1}{2} h\nu_0$  is the temperature independent zero point energy contribution to the internal energy of the oscillator. To calculate the average energy of an oscillator, we replace integration by summation in the expression for the Maxwell-Boltzmann distribution of energy and obtain

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n \exp\left(-\frac{E_n}{k_B T}\right)}{\sum_{n=0}^{\infty} \exp\left(-\frac{E_n}{k_B T}\right)} \quad \text{--- (3)}$$

Using eq. (2), we get

$$\begin{aligned} \bar{E} &= \frac{\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) h\nu_0 \exp\left[-\left(n + \frac{1}{2}\right) \frac{h\nu_0}{k_B T}\right]}{\sum_{n=0}^{\infty} \exp\left[-\left(n + \frac{1}{2}\right) \frac{h\nu_0}{k_B T}\right]} \\ &= h\nu_0 \frac{\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \exp\left[\left(n + \frac{1}{2}\right) \alpha\right]}{\sum_{n=0}^{\infty} \exp\left[\left(n + \frac{1}{2}\right) \alpha\right]} \quad \text{--- (4)} \end{aligned}$$

$$\text{where } \alpha = -\frac{h\nu_0}{k_B T}$$

$$\therefore \bar{E} = \frac{h\nu_0}{2} \left( \frac{e^{x/2}}{2} + \frac{3e^{3x/2}}{2} + \frac{5e^{5x/2}}{2} + \dots \right)$$

$$\left( e^{x/2} + e^{3x/2} + e^{5x/2} + \dots \right)$$

$$= \frac{h\nu_0}{2} \frac{d}{dx} \ln \left[ e^{x/2} + e^{3x/2} + e^{5x/2} + \dots \right]$$

$$= \frac{h\nu_0}{2} \frac{d}{dx} \ln \left[ e^{x/2} \left( 1 + e^x + e^{2x} + \dots \right) \right]$$

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

$$\therefore \bar{E} = \frac{h\nu_0}{2} \frac{d}{dx} \left[ \frac{x}{2} - \ln(1 - e^x) \right]$$

$$= \frac{h\nu_0}{2} \left[ \frac{1}{2} + \frac{e^x}{1 - e^x} \right] = \frac{h\nu_0}{2} \left[ \frac{1}{2} + \frac{1}{e^{-x} - 1} \right]$$

$$= \frac{h\nu_0}{2} \left[ \frac{1}{2} + \frac{1}{e^{h\nu_0/k_B T} - 1} \right]$$

$$= \frac{1}{2} h\nu_0 + \frac{h\nu_0}{\exp\left(\frac{h\nu_0}{k_B T}\right) - 1} \quad (5)$$

However if eq.(1) is used in eq.(3) then

$$\bar{E} = \frac{h\nu_0}{\exp\left(\frac{h\nu_0}{k_B T}\right) - 1} \quad (6)$$

Expressions eq.(5) & (6) are identical except with the difference of energy  $\frac{1}{2} h\nu_0$  which is the temperature independent zero point energy as, for  $T=0$ ,  $\bar{E} = \frac{1}{2} h\nu_0$ .

Thus according to quantum mechanics, the atoms are not at rest even at 0°K and each atom possesses the vibrational energy of  $\frac{1}{2} h\nu_0$ . This energy, however, does not contribute to  $C_v$ .

More Expression for the internal energy of the crystal becomes

$$E = 3N\bar{E} = \frac{3N\hbar\omega_0}{2} + \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1} \quad (7)$$

$$\therefore C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right) \frac{e^{\hbar\omega_0/k_B T}}{(e^{\hbar\omega_0/k_B T} - 1)^2} \quad (8)$$

let  $\theta_E = \frac{\hbar\omega_0}{k_B}$  (9)

where  $\theta_E$  is the characteristic temperature known as the Einstein temperature.

$$\therefore C_V = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (10)$$

Now consider the following case:

(i) High temperature behaviour:

for temp.  $k_B T \gg \hbar\omega_0$  or  $T \gg \theta_E$

We can write

$$e^{\hbar\omega_0/k_B T} - 1 \approx 1 + \frac{\hbar\omega_0}{k_B T} + \dots - 1 = \frac{\hbar\omega_0}{k_B T} \quad (11)$$

using eq (11), hence eq. (10) or eq. (8) becomes.

$$C_V = 3Nk_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 \frac{\left(1 + \frac{\hbar\omega_0}{k_B T}\right)}{\left(\frac{\hbar\omega_0}{k_B T}\right)^2}$$

$$= 3Nk_B \left(1 + \frac{\hbar\omega_0}{k_B T}\right)$$

for large  $T$ ,  $\frac{\hbar\omega_0}{k_B T} \rightarrow 0$  and we get

$$C_V = 3Nk_B = 3R$$

which is the Dulong and Petit's law as obtained from classical theory.

(ii) low temp. behaviour:-

low temp. such that  
 $k_B T \ll h \omega_0$  or  $T \ll \theta_E$

we can write

$$e^{h\omega_0/k_B T} - 1 \approx A \exp(h\omega_0/k_B T)$$

hence eq. (5) becomes

$$\bar{E} = \frac{1}{2} h \omega_0 + h \omega_0 e^{-h\omega_0/k_B T} \quad (12)$$

It shows that, at low temp., the average vibrational energy decreases exponentially with decrease in temp. The expression eq. (8) becomes

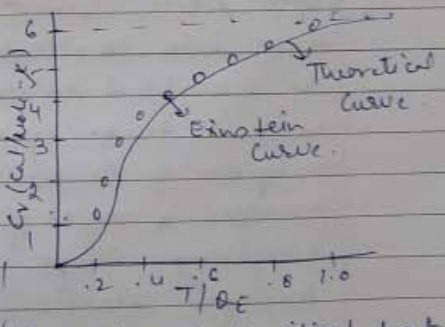
$$C_V = 3Nk_B \left( \frac{h\omega_0}{k_B T} \right)^2 e^{-h\omega_0/k_B T} \quad (13)$$

or in terms of  $\theta_E$ , above expression becomes

$$C_V = 3Nk_B \left( \frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \quad (14)$$

Thus for low temp., the heat capacity is proportional to  $e^{-\theta_E/T}$  which is the dominating factor. However, experimentally it is found to vary as  $T^3$  for most of the solids.

Although Einstein model provides a much better explanation for the variation of heat capacity with temp than classical theory, it fails to account for the values of specific heat at very low temp.



The discrepancy arises due to the oversimplified assumption of the Einstein's model in which atomic oscillates. Comparison of theoretical heat capacity of diamond calculated from Einstein's model with the experimentally observed values.

are considered to vibrate independently at the same frequency. These oscillators, in fact, are coupled together and there may be a number of possible vibrational frequencies rather than a single frequency  $\omega_0$ . This fact is accounted for in the Debye's Model.

### Debye's Model:-

The Einstein's theory assumed that the atoms of a crystal vibrate totally independent of one another. The vibrational motion of the crystal as a whole was considered to be the same as the vibrational motion of a single atom and therefore, all the atomic vibrations of the crystal were assigned a common freq.  $\omega_0$  which is the natural freq. of vibration of a single atom. This assumption is oversimplified since the atoms are bound together in a crystal and form a system of coupled harmonic oscillators which cannot vibrate independently. The fact was taken into consideration by Debye. In Debye's model, the vibrational motion of the crystal as a whole was considered to be equivalent to the vibrational motion of a system of coupled harmonic oscillators which can propagate a range of frequencies rather than a single frequency. Debye proposed that crystals can propagate elastic waves of wavelengths ranging from low frequencies to high frequencies corresponding to infrared absorption, which means that crystal can have a number of modes of vibration. The number of vibrational modes per unit frequency range is called density of modes  $\rho(\omega)$ .

