Ques : Describe Einstein's theory of specific heat of solids. Discuss its success and failure. (2011, 2013, 2015)

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Ans : Dulong and Petit's law has been explained by Einstein for the first time in 1907on the basis of quantum theory of heat radiation. According to quantum theory of heat radiation, heat is radiated in the form of discrete particles known as photon. Each particle (photon) has energy equal to $h\nu$ where h = Planck's constant and ν = frequency of heat radiation.

Einstein proposed his theory under following assumptions.

(i) A solid is made up of atoms. at absolute zero temperature (0K) , these atoms are at rest under the action of mutual attraction or repulsion. The energy of solid in this state is zero. But when the temperature of the solid is raised i.e, heated then these atoms begin to vibrate about their mean position of equilibrium under the action of restoring force , hence these atoms begin to excute SHM. The frequency of these vibration is one and the same i.e, natural and characteristic frequency of the particular solid under consideration.

(ii) Each atom of solid has three degree of freedom like monoatomic gas molecule.

(iii) The mean energy per degree of freedom is not KT but $\frac{h\nu}{e^{h\nu/KT}-1}$ as calculated by Planck by using quantum theory.

Theory : Every atom has three degree of freedom. So energy of each atom of solid $=\frac{3h\nu}{e^{h\nu/KT}-1}$

Total energy of one gram atom of the solid consisting of N atoms is given by $E=\frac{3Nh\nu}{e^{h\nu/KT}-1}$

Atomic heat of the solid at constant volume is $C_V=\frac{dE}{dT}=3Nh\nu\frac{d\left(e^{h\nu/KT}-1\right)^{-1}}{d\left(e^{h\nu/KT}-1\right)}\times\frac{d\left(e^{h\nu/KT}-1\right)}{dT}$

$$\Rightarrow C_V=3Nh\nu\times(-1)\left(e^{h\nu/KT}-1\right)^{-2}\times e^{h\nu/KT}\times\frac{h\nu}{K}\times(-1)T^{-2}=\frac{3Nh^2\nu^2}{KT^2}\times\frac{e^{h\nu/KT}}{\left(e^{h\nu/KT}-1\right)^2}$$

$$\Rightarrow C_V=3NK\times\frac{e^{h\nu/KT}}{\left(e^{h\nu/KT}-1\right)^2}\times\left(\frac{h\nu}{KT}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

This equation can be conveniently written as $C_V=3R\left(\frac{e^{\theta/T}}{\left(e^{\theta/T}-1\right)^2}\left(\frac{\theta}{T}\right)^2\right)$ .... (2)

where NK = R = gas constant per gramatom and $\theta=h\nu/K$

The value of ν giving fit for a particular solid is represented by ν_E known as Einstein's frequency for that solid and θ corresponding to ν_E is represented by θ_E known as Einstein's temperature.

Equation (1) is known as Einstein's equation for the atomic heat (or specific heat) of the solid at constant volume. From equation (2), it is clear that atomic heat (or specific heat) is a function of temperature. The experimentally observed variation of atomic heat of solid are as follows.

(i) At high temperature, the atomic heat approaches the constant value 3R as given by Dulong and Petit's law.

Explanation :

$$C_V=3R\frac{e^{h\nu/KT}}{\left(e^{h\nu/KT}-1\right)^2}\left(\frac{h\nu}{KT}\right)^2=3R\cdot\frac{1+\frac{h\nu}{KT}+\frac{1}{\lfloor\underline{2}}\left(\frac{h\nu}{KT}\right)^2+\frac{1}{\lfloor\underline{3}}\left(\frac{h\nu}{KT}\right)^3+\cdot\cdot\cdot}{\left(1+\frac{h\nu}{KT}+\frac{1}{\lfloor\underline{2}}\left(\frac{h\nu}{KT}\right)^2+\frac{1}{\lfloor\underline{3}}\left(\frac{h\nu}{KT}\right)^3+\cdot\cdot\cdot-1\right)^2}\left(\frac{h\nu}{KT}\right)^2$$

Dr. Md. NAIYAR PERWEZ

$$C_V = 3R\cdot\frac{1+\frac{h\nu}{KT}+\frac{1}{2!}\left(\frac{h\nu}{KT}\right)^2+\frac{1}{3!}\left(\frac{h\nu}{KT}\right)^3+\cdots}{\left(\frac{h\nu}{KT}\right)^2\left(1+\frac{1}{2!}\left(\frac{h\nu}{KT}\right)+\frac{1}{3!}\left(\frac{h\nu}{KT}\right)^2+\cdots\right)^2}\left(\frac{h\nu}{KT}\right)^2 = 3R\cdot\frac{1+\frac{h\nu}{KT}+\frac{1}{2!}\left(\frac{h\nu}{KT}\right)^2+\frac{1}{3!}\left(\frac{h\nu}{KT}\right)^3+\cdots}{\left(1+\frac{1}{2!}\left(\frac{h\nu}{KT}\right)+\frac{1}{3!}\left(\frac{h\nu}{KT}\right)^2+\cdots\right)^2}$$

AS T is high i.e. $T\to\infty$ so $\frac{h\nu}{KT}\to 0$ Using this in the above equation we get

$$C_V = 3R\cdot\frac{(1+0+0+0+\cdots)}{(1+0+0+0+\cdots)^2} \Rightarrow C_V = 3R$$

This result agrees well with the experiment and Dulong and Petit's law.

(ii) The atomic heat of solid decreases with decrease in temperature and C_V tends to zero at absolute zero temperature.

Explanation : If $T\to 0$ then $\frac{h\nu}{KT}\to\infty \Rightarrow e^{\frac{h\nu}{KT}}\to\infty$ and $e^{\frac{h\nu}{KT}}-1\approx e^{\frac{h\nu}{KT}}$

Using these in equation (1),

$$C_V = 3R\frac{e^{h\nu/KT}}{\left(e^{h\nu/KT}-1\right)^2}\left(\frac{h\nu}{KT}\right)^2 = 3R\cdot\frac{e^{h\nu/KT}}{\left(e^{h\nu/KT}\right)^2}\left(\frac{h\nu}{KT}\right)^2 = 3R\cdot\frac{(h\nu/KT)^2}{e^{h\nu/KT}}$$

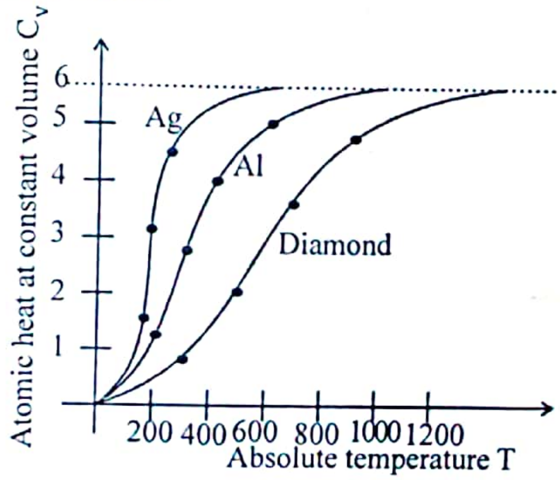
$$\Rightarrow C_V = 3R\cdot\frac{(h\nu/KT)^2}{1+h\nu/KT+\frac{1}{2!}(h\nu/KT)^2+\frac{1}{3!}(h\nu/KT)^3+\cdots}$$

$$\Rightarrow C_V = \frac{3R}{\frac{1}{(h\nu/KT)^2}+\frac{1}{(h\nu/KT)}+\frac{1}{2!}+\frac{(h\nu/KT)}{3!}+\cdots} = \frac{3R}{0+0+\frac{1}{2!}+\infty+\infty+\cdots} = \frac{3R}{\infty} \Rightarrow C_V = 0$$

This is again in good agreement with experimenatl result and Dulong and Petit's law.

(iii) The experimental curves drawn for atomic heat of solid against temperature show that the curves has same form for all substances as shown in figure.

According to Einstein's equation (1) atomic heats of different elements differ only because of different ν_E, the characteristic frequency. At corresponding temperature such that the ratio ν/T is same for all solids then from equation (1), the atomic heats will also be same for all solids. Thus the experimental curves have the same from for all substances. This agreement also fits with experimental fact and Dulong and Petit's law.



Dr. Md. NAIYAR PERWEZ

Hence Einstein's theory predicts the correct value of atomic heat for various elements as observed experimenatlly. In other words Einstein's theory is in good agreement with the experimental facts.

Limitations (Failure) of Einstein's theory :

(i) The value of atomic heats of solid substances agrees well at very high temperature and at very low temperature with the experimental curves but variation in between them does not exactly follows. Some elements like aluminium, copper, iron etc, atomic heats at low temperature decreases more rapidly than that expected by Einstein's theory.

(ii) The assumptions that the vibrations of all atoms are simple harmonic and they all have one and same frequency, is not valid. In fact the vibrations of an atom are complex in nature because it is under the feild of force due to large number of neighbouring vibrating atoms.

(iii) In Einstein's theory, frequency ν and $h\nu / KT$ have been obtained empirically and can not be verified from any other independent physical data.