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HEAT CAPACITY OF SOLIDS. DULONG - PTI LAW. EINSTEIN-DEBAY THEORY

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Annotation

This article discusses the heat capacity of solids. Data on the Dulong-Pti and Einstein-Debay theories in the calculation of the heat capacity of solids in the field of high and low temperatures are given.

Keywords : Harmonic oscillator, Dulong-Pti's law, Planck's hypothesis, Bolsman's law, characteristic temperature.

At the nodes of the crystal lattice, the particles oscillating around the equilibrium state consist of harmonic oscillators, which can be considered to oscillate along the x, y, z axes perpendicular to each other. In other words, these oscillators have three degrees of freedom. Each level of freedom is equal $E = kT$ to the total energy. This is becouse the kinetic and potential energies of the oscillator are equal to each other and equal to each other and equal $E_k = \frac{1}{2}kT$ to the average energy corresponding to each degree of freedom. Thus, since a particle consists N of an energy corresponding kT to each degree of freedom in a crystall, its total energy is equal to $U = 3NkT$ (1). Becouse one commodity $N = N_A$ is for a substance $U = 3N_AkT = 3RT$ (2). The amount of heat used to heat the body is used to increase the vibrational energy of the oscillator. Therefore, the constant heat capacity is equal to $C_V = \frac{dU}{dT} = 3R = 6\frac{cal}{mol \cdot K} = 25{,}12\frac{J}{mol \cdot K}$.(3) shows that the molar heat capacity of solids does not depend on their type and temperature. This law is called Dulong - Pti's law.

For most solids, this law holds. However, the study of the temperature-dependent changes in the heat capacity of solids shows that three are deviations from Dulong -

Pti's law at low temperatures. This connection is especially noticeable in beryllium, boron, silicon and diamonds. Subsequent studies have shown that even in crystals in which the Dulong - Pti law holds, the heat capacity decreases significantly when the temperature approaches zero. Thus, for some substances, at low temperatures, the Dulong - Pti law is not followed and deviations are observed.

For many crystals, the above classical theory does not apply. To overcome such imbalances and to derive the law of temperature change of the heat capacity of solids, Einstein used Planck's hypothesis to reveal the law of radiation of an absolutely black body.

According to this hypothesis, any harmonic oscillating around the equilibrium state receives discrete values proportional to the oscillator frequency without receiving continuous values. This energy is the energy of the quantum emitted by the harmonic oscillator and is equal to $\varepsilon = h\nu$ (4). Where $h = 6{,}62 \cdot 10^{-34}\, J \cdot s$ is the Planck constant. If the crystal consist of a N harmonic oscillator, the total energy is equal to $\varepsilon = Nh\nu$ (5). Particulate matter can oscillate at different frequencies, and their vibrational energies vary accordingly. For simplicity, Einstein believed that all particles oscillate at the same frequency. Let's take a brief look at Einstein's theory. Assuming that the probability of vibration of a vibration particle in a crystal, such as a harmonic oscillator, obeys Bolsman's law $n = n_0 e^{-\frac{Nh\nu}{kT}}$ (6), it is possible to determine the average vibrational energy corresponding to each particle:

$$\bar{\varepsilon} = \frac{\sum \varepsilon n_0 e^{-\frac{Nh\nu}{kT}}}{\sum n_0 e^{-\frac{Nh\nu}{kT}}} = \frac{h\nu \sum N e^{-\frac{Nh\nu}{kT}}}{\sum e^{-\frac{Nh\nu}{kT}}} \qquad (7) \qquad \text{when } N >> 1$$

$$\frac{\sum N e^{-\frac{Nh\nu}{kT}}}{\sum e^{-\frac{Nh\nu}{kT}}} = -\frac{d}{d(\frac{h\nu}{kT})} \ln \sum e^{-\frac{Nh\nu}{kT}} = -\frac{d}{d(\frac{h\nu}{kT})} \ln \frac{1}{1 - e^{-\frac{h\nu}{kT}}} = \frac{1}{e^{\frac{h\nu}{kT}} - 1} \qquad (8)$$

Given (8), (7) is

$$\bar{\varepsilon} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \qquad (9)$$

Its total energy for 1 mole of crystall

$$U = 3N_A \bar{\varepsilon} = 3N_A \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \qquad (10)$$

That heat capacity is $C_V = \frac{dU}{dT} = \frac{3N_A k(\frac{hv}{kT})^2 e^{\frac{hv}{kT}}}{(e^{\frac{hv}{kT}} - 1)}$ (11). This formule shows that when $hv << kT$, that is, at high temperatures $C_V = 3N_A k = 3R$ (12). This is $e^{\frac{hv}{kT}}$ becouse if $hv << kT$ we spread $e^{\frac{hv}{kT}} = 1 + \frac{hv}{kT} + \frac{1}{2!}(\frac{hv}{kT})^2 + \ldots$ (13) on a line and put it on (11), we get the above conclusion (12). (11) shows that the value of C_V decreases exponentially with decreasing temperature. However, the study of the heat capacity of solids in relation to temperature showed that there are deviations from Einstein's formula at low temperatures, and that the heat capacity at such temperatures is proportional to the third degree of temperature. Furthermore, in Einstein's theory, it is assumed that the vibrational energy of each oscillating harmonic oscillator is independent of each other.However, such an approach does not fully take into account the value of potential energy, which depends on the interaction between the particles. In fact, collective action occurs due to the interaction of particles in crystals. Later, considering such interactions between particles, Debay further developed Einstein's theory. According to Debay's theory, the oscillation of a particle affects a neighboring particle , and so on. affects. During this time, collective motion occurs, just as sound waves propagate through a solid body. Thus, (the stimuls of oscillating motions is sound quantum-phonons) it can be assumed that thermal oscillations in solids consist of elastic stable waves. The number-frequency of oscillating movements is determined by the quantity-degree of freedom. The total energy of such motions is equal to $U = \sum_{i=1}^{3N} \frac{hv_i}{e^{-\frac{hv}{kT}} - 1}$ (14) and the heat capacity of solids decreases from a certain temperature T_D(Debye's characteristic temperature). This temperature is the temperature at which the energy of the thermal motion is equal to kT_D the maximum energy of the oscillator. $kT_D = hv_m$ or at values below $T_D = \frac{hv_m}{k}$ (15) -T_D temperature, the heat capacity decreases in proportion to the third degree of temperature. This is consistent with the experimental results.

In metals, the heat capacity of the free electrons in the space must be taken into account, along with the positive ions in the crystals lattice node.

However, at high temperatures, the contribution of electrons to the the total heat capacity is very small. Since the heat capacity of the particles in the lattice decreases T^3 proportionally to the heat capacity of the electrons with decreasing T of temperature, the contributions of electrons to the heat capacity at low temperatures must be taken into account, and its contribution increases with decreasing temperature.

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