HEAT CAPACITY OF A SOLID

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Annotation.

The article describes the basic properties of the heat capacity of crystalline bodies. From the standpoint of classical theory, it is impossible to explain the dependence of heat capacity on temperature. Between the regions of low and high temperatures lies a fairly wide range of so-called average temperatures, in which there is a gradual transition from Debye's law to the law of Dulong and Petit.

Keywords: Molar heat capacity,internalenergy, solid, temperature, vibrational, lattices, kinetic and potential energy, frequency.

According to classical concepts, a crystal consisting of N atoms is a system with 3NN vibrational degrees of freedom, each of which hasthe same energy equal to kT in the medium (1/2 kKt in the form of kinetic and 1/2 KT in the form of potential energy). The internal energy of one mole of a solid is therefore U = 3kT*NaN_A =3R. (k is the Boltzmann constant,$_A$ - Na is the Avogadro number, and R is the universal gas constant). Hence, for the molar heat capacity of a solid, we have:

$$C = \frac{dU}{dT} = 3R = 25\ J/(mol * K).$$

Note that for solids, we are talking about the molar heatcapacity at a constant volume with$_v$.

Indeed, the French physicists Dulong and Petit (1819) experimentally established that the heat capacity of all solids does not depend on температуtemperature and is approximately equal to 25 J/(mol*K). This statement is called the law of Dulong and Petit. Further investigations showed that the heat capacity of solids does not depend on temperature only in the high temperature range (T/θ>1) and decreases with decreasing temperature T (Fig.1From the standpoint of classical theory, it is impossible to explain the dependence of heat capacity on temperature.

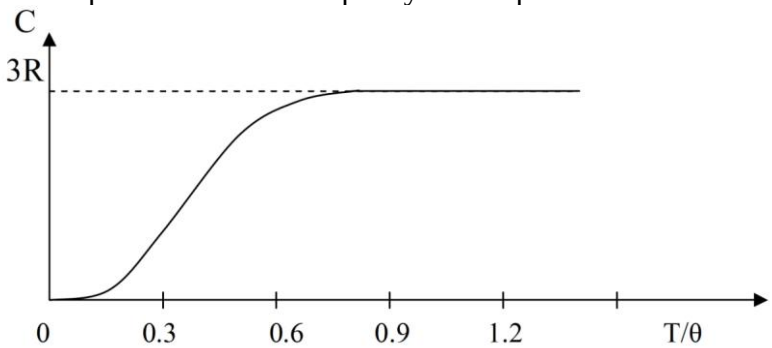

figure1

The theory of heat capacity of crystalline bodies was created by Einstein and Debye. The main provisions of the theory were based on the solid state model, according to which a lattice of N atoms

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 12 Issue: 09 in September-2023
https://www.gejournal.net/index.php/IJSSIR

was identified with a system of N independent harmonic quantum oscillators oscillating with the same frequency, according to Einstein, and dependent quantum oscillators oscillating with different frequencies, according to Debye. At a certain temperature, a 3N oscillation system is established in the crystal. These vibrations, when they reach the crystal surface, are reflected from it and form standing waves associated with the crystal size and its elastic properties. The number of independent standing waves in a solid is 3N. Let us consider the derivation of the Debye heat capacity.

The internal energy of a solid U consists of the energy of normal lattice vibrations. The number of normal vibrations perspectral region dw is g(ω)w)dw ($dZ = g(\omega)w\,dw = \frac{3V}{2\pi^2 v^3}\omega^2 w\,2\,dw$). Multiplying this number by the average energy of the normal oscillation ($\langle E_{n.k}\rangle = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$), we obtain the total energy of normal vibrationsenclosedin the interval dω

$$dU = < e_{n..k.} > g(\omega)d\omega$$

Integrating this expression over the entire spectrumof normal vibrations, i.e., in the range from 0 to $\omega d_д$, we obtain the total energy of thermal vibrations of the solid lattice.

$$U = \int_0^{\omega_d} < e_{n..k.} > g(\omega)dw.$$

Substituting in this expression g(ω) from ($\left(g(\omega) = 9N\frac{\omega^2}{\omega_d^3}\right)$) and $e_{n.\,k.}$. from ($\langle e_{n.k}\rangle = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$), we obtain

$$U = \frac{9N}{\omega_d^3}\int_0^{\omega_d}\frac{\hbar\omega^3 d\omega}{e^{\frac{\hbar\omega}{kT}}-1} \quad (1)$$

Let us pass to the dimensionless quantity $x = \omega\omega/kT$ and to the number of atoms in 1 mol. Then (3.11) is rewritten as follows:

$$U = U_0 + 9r\theta_d\left(\frac{T}{\theta_d}\right)\int_0^{4\frac{\theta_d}{T}}\frac{x^3 dx}{e^x - 1} \quad (2)$$

where $U_◦ = 9r\theta/8$ is the zero energy of one mole of the crystal.

Heat capacity of one mole of a crystal according to Debye

$$C_{Cv} = 3R\left[12\left(\frac{T}{\theta_d}\right)^3\int_0^{\frac{\theta_D}{T}}\frac{x^3}{e^x-1} - \frac{3\left(\frac{\theta_d}{T}\right)}{e^{\frac{\theta_d}{T}}-1}\right]. \quad (3)$$

The main problem of the theory of heatcapacity is the dependence with$_v$(T). Consider this question for two temperature ranges.

Low temperature range (T< <$\boldsymbol{\Theta}$Od)

For such temperatures, the upper limit of integration in (2) can be replaced by infinity. Then $\int_0^\infty \frac{x^3}{e^x-1} = \frac{\pi^4}{15}$ and we get

$$U = U_{=}U0 + \frac{3\pi^4}{5}R_д\left(\frac{d\,T}{\theta_d}\right)^4$$

ДиффференциDierentiating in T, we find with$_v$:

$$C_{Cv} = \frac{12\pi^4}{5}R\left(\frac{T}{\theta_D}\right)^3 \sim T^3 \quad (4)$$

ISSN 2277-3630 (online), Published by International journal of Social Sciences & Interdisciplinary Research., under Volume: 12 Issue: 09 in September-2023
https://www.gejournal.net/index.php/IJSSIR

We have obtained the so-called Debye's law, according to which, in the region of low temperatures, the heat capacity of the lattice changes in proportion to the cube of temperature.

High temperature range (T> > $\boldsymbol{\Theta}_{Od}$)

For such temperatures, the value of x in (2) is small, so that in the expansion of the exponent $e^x = 1+x+...$ you can limit yourself to the first two terms. Then

$$U = U_0 + 9R\theta_d\left(\frac{T}{\theta_d}\right)^3 \int_0^{4\frac{\theta_d}{T}} x^2 dx = 3RT \sim T$$

The heat capacity of the crystal is $C_v = \frac{dU}{dT} = 3R = 25\ J/(mol * K)$.

The latter relation expresses the law of Dulong and Petit.

Between the regions of low and high temperatures lies a fairly wide range of so-called average temperatures, in which there is a gradual transition from Debye's law to the law of Dulong and Petit. This is the most difficult temperature range to analyze, where the heat capacity is calculated using formula (3).

Thus, the general picture of the temperature dependence of the heat capacity of crystalline bodies can be qualitatively explained as follows:

In the region of low temperatures ($T<<_{Od}$), the internal energy of the body increases with increasing temperature, firstly, due to an increase in the degree of excitation of the kd-normal oscillation, i.e., an increase in their average energy En. k., proportional to T; secondly, due to the inclusion of more and more new normal vibrations in the oscillatory process, causing an increase in energy proportional to T3. The energy of the lattice as a whole increases in proportion$^{to\ T4}$, and the heat capacity increases in proportion to T3 (Debye's law).

As we approach the Debye temperature, the second mechanism gradually reduces its contribution to the internal energy of the body and the dependence of I on T is weakened. At the Debye temperature, the entire spectrum of normal lattice vibrations is already excited, so the second mechanism of energy growth is completely turned off in this case, only the first mechanism works, causing an energy increase proportionalto T and the independence of$_{Cv}$ from T (the law of Dulong and Petit).

In general, the agreement of Debye's theory with the experiment is quite satisfactory not only from the qualitative, but also from the quantitative side. However, this theory is also approximate and is well suited only for describing bodies with simple crystal lattices. For a precise description of bodies with a more complex structure, it is not applicable.

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