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HEAT CAPACITY OF CRYSTALS. EXPLANATION OF THE TEMPERATURE DEPENDENCE OF HEAT CAPACITY

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ABSTRACT

The article outlines the main applications 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 region of so-called average temperatures, in which there is a gradual transition from Debye's law to Dulong and Petit's law .

Keywords: molar heat capacity , Dulog and Petit's law , Debye's law, Internal energy of a solid, high temperatures, low temperatures, vibrations, Einstein and Debye theory, lattices.

INTRODUCTION

When a solid body is heated, the heat goes to increase the vibrational energy of the atoms. The energy of oscillatory motion consists of kinetic and potential energy. Each vibration can be decomposed into three components along the coordinate axes. Therefore, each particle has three vibrational degrees of freedom $i_{to} = 3$.

With harmonic vibrations, the kinetic energy of the oscillatory motion is equal to the potential . According to the law of uniform distribution of energy across degrees of freedom, for each vibrational degree of freedom there is 1/2 kT in the form of kinetic energy and 1/2 kT in the form of potential energy. Therefore, the total energy of the oscillating particle will be equal to:

$$U_0 = i_к \cdot 2 \cdot \frac{1}{2} kT = i_к kT = 3kT \quad (1)$$

Internal energy of 1 mole of a solid:

$$U = U_0 N \quad (2)$$

where N is the number of particles in one mole of a solid.

For chemically simple substances, the number of particles in 1 mole is equal to Avogadro's number $N = N_a$. Then from (1) and (2):

$$U = U_0 N_a = 3kTN_a = 3RT \quad (3)$$

The coefficient of volumetric expansion of solids is very small, therefore $C_p \approx C_V = C$. Consequently, all the heat supplied to a solid body goes to increase its internal energy. Then the molar heat capacity of the solid is:

$$C = \frac{dU}{dT} = \frac{d(3RT)}{dT} = 3R = 25{,}1\frac{Дж}{моль \cdot К} \quad (4)$$

According to (4), the molar heat capacity of chemically simple solids is equal to 3 R and does not depend on temperature. This is the law of Dulong and Petit (1818). Dulong and Petit's law holds true for many substances at room temperatures.

When determining the molar heat capacity of chemically complex substances, it is necessary to take into account the total number of particles in 1 mole of a given substance. For chemically complex substances, the total number of particles in 1 mole is equal to Avogadro's number multiplied by the number of atoms that make up the molecule of this substance. For example, KCl - in one mole of N_a potassium atoms and N_a chlorine atoms - a total of $2N_a$ particles. The molar heat capacity of such a crystal is 2*3 R = 6 R. In the case of triatomic molecules, the molar heat capacity is 9 R , for tetraatomic molecules - 12 R.

These arguments coincide with the empirically established Neumann- Kopp law :

The molar heat capacity of solid compounds is equal to the sum of the atomic heat capacities of the elements that are included in this compound:

$$C = 3Rn \quad (5)$$

where n is the number of atoms included in the molecule of a given compound.

This law, as well as the law of Dulong and Petit, is satisfied at fairly high temperatures, at which the vibrations of particles can be considered independent.

Some substances do not obey Dulong and Petit's law. The molar heat capacity of diamond at room temperatures is much less than 3R , and only at temperatures higher than 1000 °C does it approach the value of 3R.

This is not the only deviation from Dulong and Petit's law . At low temperatures, the heat capacity of crystalline substances quickly decreases and tends to zero at absolute zero temperature (Fig. 1).

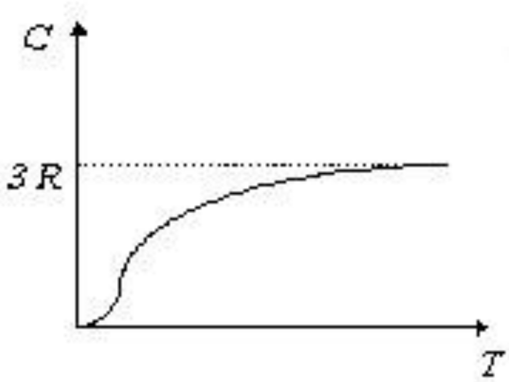

Fig.1. Dependence of heat capacity on temperature

Near absolute zero, the heat capacity of all crystals is proportional to T^3, and only at a sufficiently high temperature, characteristic of each substance, do the laws of Dulong and Petit (4) and Neumann- Kopp (5) begin to be fulfilled.

These laws are a consequence of the law on the uniform distribution of energy across degrees of freedom. The fact that solids do not obey these laws indicates that the law on the uniform distribution of energy across degrees of freedom is approximate and is not applicable at low temperatures.

An accurate, quantum theory of the heat capacity of crystals was created by Einstein and Debye. Quantum heat capacity theory takes into account:

1. Quantization of the energy of oscillatory motion - the energy of oscillatory motion can only take on some discrete values;
2. Vibrations of particles in a crystal lattice are not independent.

From Debye's theory it follows that at temperatures close to absolute zero, the internal energy of a solid is proportional to the fourth power of temperature:

$$U = aT^4 \quad (6)$$

where a is a constant depending on the vibration frequency of the particles.

Therefore, the heat capacity of crystals is:

$$C = \frac{dU}{dT} = 4aT^3 \quad (7)$$

(7) – Debye's law of cubes. From Debye's theory it follows that, starting from a certain temperature that differs for different substances (Debye characteristic temperature), the heat capacity begins to rapidly decrease with decreasing temperature.

The Debye temperature is considered the boundary between low and high temperatures (and not only for heat capacity). Debye temperature for silver – 210 °C , aluminum – 400 °C , diamond – 2000 °C.

For crystals that do not obey the Dulong and Petit law at room temperatures (diamond, boron, silicon), the characteristic temperatures are greater than 1000 °C , and therefore room temperatures are low for them.

As experiments have shown, for some substances the heat capacity is proportional to T^2, and for some ~ T. This is due to the structural features of the crystal lattice. If particles are connected to neighboring particles equally strongly in all three directions, Debye's law of cubes is satisfied. If a substance has a layered structure (graphite, mica), then the connection of particles in two directions (in one plane) is stronger than in the third direction (between layers). For these substances, the heat capacity is ~ T^2. If the substance is made up of particles with a chain bond and the chains are weakly connected to each other, then the heat capacity is ~ T (HF , BiO_3, fused quartz).

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