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LAWS FOR THE HEAT CAPACITY OF ELEMENTS OF THE PERIODIC SYSTEM

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UDC 536.63:546

We show a correlation between the derivative of the heat capacity with respect to the reduced temperature of elements and their group number at temperatures above the Debye temperature. We derive a relation which reflects the character of the variation of the heat capacity of the elements as a function of the characteristics of their electron structure.

For a long time the fundamental rule for the heat capacity of elements at high temperatures ($T > \theta_D$) was the empirical Dulong and Petit law. According to this law the molar heat capacities of monatomic solids at temperatures of the order of 300°K are approximately 25 J/mole·°K. However, experimental data at higher temperatures showed that deviations from the Dulong and Petit law in a number of cases increase to tens of percent [1]. It has been noted by many authors [2, 3, etc.] that the heat capacity of elements varies periodically with their atomic number. All this urgently required explanation. Since there is no single reliably theory, it is evident that answers to the questions posed can most likely be obtained by seeking new more general empirical relations.

Actually, by correlating accumulated experimental data Ivanova [4] showed that the Dulong and Petit law is a special case of a more general law: the molar heat capacities of

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 45, No. 6, pp. 969-974, December, 1983. Original article submitted June 29, 1982.

TABLE 1. Experimental Values of Coefficients a_0 and a_1

z	1	2	3	4	5	6	7	8
a_0, J/mole · K	23,80	22,91	24,75	23,82	23,86	24,74	24,13	23,65
a_1, J/mole · K^2	6,286	9,525	8,214	8,660	10,90	11,82	17,57	16,14

various solids at equal values of T/T_{tr} are nearly the same. This law applies only to elements at temperatures $T = (0.4\text{–}0.6)T_{tr}$. Taking this into account, Ivanova [4] recommended that a relation of the form

$$C_p = a_0 + a_1 \frac{T}{T_{tr}} \tag{1}$$

with $a_0 = 22.12$ and $a_1 = 8.319$ be used to calculate high-temperature heat capacities of low-melting elements, mainly metals with $T_m \leqslant 2100°K$.

Later Filippov [1, 5, 6] proposed relations similar to (1) with $a_0 = 23.82$ and $a_1 = 13.1$, $a_0 = 24.94\text{–}25.12$ and $a_1 = 12.56$ for metals of groups IV–VIII of the periodic table with higher melting points.

In equations of form (1) the individuality of the substances is taken into account not only by the phase transition temperatures, but also by the values of a_0 and a_1 in the transition from low-melting to higher-melting elements. Using this last fact, we can hope to obtain a single equation for all the substances considered which reflects a more fundamental law of variation of the molar heat capacity of elements based on the characteristics of their electron structure.

Equation (1) is essentially an equation relating the linear regression of the dependent variable, the molar heat capacity C_p of the elements, on the single independent variable T/T_{tr}. As a second variable it is of interest to consider the number of the group to which the element belongs, especially as the relation between the electron component of the molar heat capacity of metals ΔC^e and the number of valence electrons per atom [7]

$$\Delta C^e = \frac{\pi^2 Rk}{2\varepsilon_F} zT \tag{2}$$

was derived on the basis of the free electron model.

According to [8–11], high-temperature experimental data of the heat capacities of the following 56 elements of the periodic system have been analyzed: Li (2), Na (2), K (2), Cu (3), Rb (1), Ag (2), Cs (2), Au (3), Be (2), Mg (2), Ca (2), Zn (2), Cd (2), Ba (2), B (2), Al (2), Ge (2), Sc (1), Ga (2), Y (1), In (2), La (1), Tl (3), Ac (1), C (2), Si (2), Ti (2), Zr (2), Sn (2), Hf (2), Pb (4), P (2), V (3), As (1), Nb (4), Sb (2), Ta (5), Bi (3), S (1), Cr (2), Se (1), Mo (4), Te (2), W (4), Mn (2), Tc (1), Re (3), Fe (2), Co (2), Ni (2), Ru (3), Rh (2), Pd (3), Os (1), Ir (3), and Pt (2). (The number in parentheses following a chemical symbol is the number of the reference from which the data on the heat capacity of that element were taken.)

On the basis of the experimental data in [8–11], and using the method of least squares for the elements within the limits of each group, we derived empirical laws of the form (1) for the temperature dependence of the molar heat capacity. The values of the coefficients a_0 and a_1 appearing in these equations are listed in Table 1. The value of a_0 is approximately constant, while a_1 tends to increase with increasing group number z of the elements of the periodic system. This enables us to write Eq. (1) in the form

$$C_p = 23.96 + (4.581 + 1.457z) \frac{T}{T_m}. \tag{3}$$

Figure 1 shows average (within the limits of groups of the system) molar heat capacities of elements for various values of the reduced temperature T/T_m, calculated with Eq. (3), data from [1, 4–6], and the average experimental results from [8–11]. It can be seen from the figure that the experimental values are best described by Eq. (3) which, in contrast with [1, 4–6], follows the actual increase of the molar heat capacities of elements with increasing group number of the elements in the periodic system.

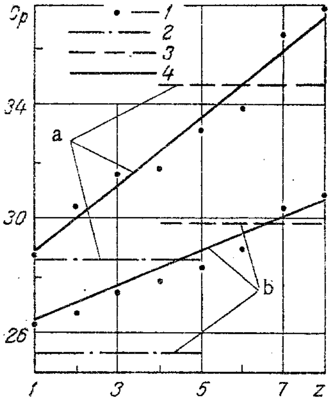

Fig. 1

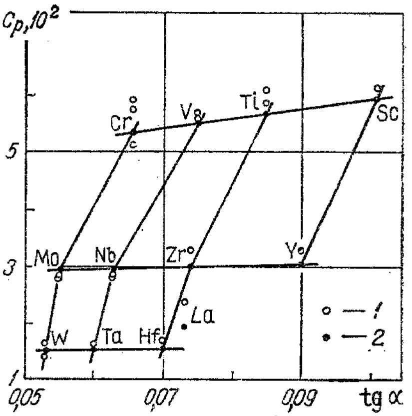

Fig. 2

Fig. 1. Comparison of calculated and experimental values of molar heat capacities C_p (J/mole·°K) of elements as a function of z: 1) experimental values; 2) [4]; 3) [6]; 4) according to our data; a) $T/T_m = 0.8$; b) $T/T_m = 0.4$.

Fig. 2. Heat capacities C_p (J/kg·°K) of metals as a function of the universal parameter tanα at $T/T_m = 0.3$. 1) from experiment; 2) our data.

The question of the degree of reliability of the experimental values of the heat capacities of various materials is one of the most pressing in contemporary thermophysical research. Here two facts should be taken into account.

First, it is very difficult to choose the most reliable values of the heat capacities of materials from the large number of published results presently available. In each specific case in deciding among values in various references and taking account of the individual author's estimates of errors, it is intuitively assumed that the distribution of errors is unbiased. Such a hypothesis is unjustifiably strong if account is taken of the practically complete lack of objective criteria of the truth of the results of experimentally determined thermophysical properties of materials.

Secondly, as a rule only random errors of an experimental determination of desired parameters are subject to a quantitative estimate. However, in a broad sense, many systematic errors which remain unchanged in series of experiments performed by one group, but change when the research is performed in neighboring laboratories using other methods or other equipment may also be considered random.

The coefficients in Eqs. (1) and (3) clearly include both systematic and random components. This requires the use of statistical processing methods to estimate the confidence intervals of the coefficients a_0 and a_1 in Eqs. (1) and (3), the regression equations, and the predicted values of the molar heat capacity.

A comparative analysis of experimental and calculated data favors a normal distribution law for the deviations from the linear relations (1) and (3). Consequently, suitable methods (e.g., [12]) developed on the assumption of normal distribution of random values can be used for the desired statistical characteristics. It can be shown that the coefficients a_0 and a_1 in the regression equations (1) and (3) are significant.

The confidence intervals for the significant parameters were determined by the usual scheme from the condition

$$P[-t_{\alpha,r} < (a_i^* - a_i)/S_{a_i} < t_{\alpha,r}] = 1 - \alpha. \qquad (4)$$

The calculated confidence intervals of the coefficients a_0 and $a_1(z)$ of Eq. (3) and the predicted values of the molar heat capacity C_p of the elements are shown in Table 2. For comparison similar estimates were made for the regression equation (1) with values of the coefficients a_0 and a_1 proposed by Ivanova [4] and Filippov [6]. Here we followed the recommendations of [1, 4-6] with respect to the ranges of possible application of the known relations. In determining the confidence intervals of the predicted values of the molar heat capacities C_p of elements we also took account of an additional source of variation — the scatter of points around the regression line.

TABLE 2. Confidence Intervals of a_0, a_1, and C_p

Ref.	$\pm \mathrm{tg}\alpha S_{ai}$		
	a_0	a_1	C_p
[4]	4,78	4,78—5,41	7,28
[6]	3,93	3,92—4,44	5.96
Our data	2,02	2,00—2,28	3,08

Table 2 shows that the confidence intervals examined (regions where the mathematical expectations of the values of a_0, a_1, and C_p can be found with a probability $P = 0.95$) are narrowest for Eq. (3), which covers a larger collection of materials than considered in [1, 4-6]. Consequently, it can be concluded that heat capacities of the elements can be predicted with greater certainty by Eq. (3) than by Eq. (1) with the values of a_0 and a_1 proposed earlier [1, 4-6].

The high degree of reliability of the values of the heat capacities of elements calculated with Eq. (3) can be confirmed by using the system of unpolarized ion radii [13]. Here the linear character of the dependence of properties on a universal parameter $\tan\alpha$ reflecting the characteristics of the structure of the outer electron shells of atoms corresponds to the reliable experimental data on the physicochemical properties of element-analogs. The known experimental values [8-11] of the heat capacities of elements of a fragment of the periodic system at the temperature $T/T_m = 0.3$ are plotted against $\tan\alpha$ in Fig. 2 together with the values calculated with Eq. (3). The calculated values of the heat capacities of the elements agree with the experimental values within ±5%, and are practically a linear function of $\tan\alpha$ in the series of the periodic system.

Figure 2 shows that the heat capacity of La is an exception to the above, but its calculated value is in satisfactory agreement with the known experimental data. The laws of behavior of the heat capacities of elements with incomplete inner electron shells deserve separate consideration.

The broad possibilities of using Eq. (3) to predict the heat capacities of little-studied elements can be illustrated by the example of $^{223}_{87}\mathrm{Fr}$. The estimated [14] melting point of this element is 282°K, and its heat capacity at 273°K is 29.80 J/mole·°K. From Eq. (3) the heat capacity of this francium isotope is 30.98 J/mole·°K, which agrees with the experimental value within 4%.

Equation (3) can be recommended for practical calculations of heat capacities of a wide variety of elements at temperatures $T > \theta_D$ and $0.3T_m < T < T_m$ when there are no structural transformations.

Taking account of the scheme shown in Fig. 2 and the known relation for the melting point [3]

$$T_m^{1/2} = 3.1 \cdot 10^{-3} (2n^2 + 1)\, \theta_D, \tag{5}$$

derived by Oshcherina, it can be concluded that Eq. (3) establishes a sufficiently unambiguous relation between the heat capacity of elements and their position in the periodic system.

NOTATION

T, absolute temperature; θ_D, Debye temperature; T_{tr}, temperature of first phase transition; T_m, melting point; a_0 and a_1, coefficients in Eq. (1); C_p, heat capacity of an element; ΔC^e, electron component of molar heat capacity; z, number of valence electrons per atom (number of group of elements); ε_F, Fermi energy; P, probability; α, confidence level; r, number of degrees of freedom; a_i^* and a_i, theoretical and calculated values of parameter; S^2, residual variance; $\tan\alpha$, universal parameter; n, principal quantum number (number of period); R, universal gas constant; k, Boltzmann constant.

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METHOD FOR CALCULATING THE STABILITY BOUNDARY (SPINODAL) OF A HOMOGENEOUS STATE OF A MATERIAL

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UDC 536.71

A method is developed for calculating the stability limit of a homogeneous state of a material based on isochoric heat-capacity measurements.

It was shown in [1] that the behavior of isochoric heat capacity can be described over a wide range of state parameters including the critical region by an equation of the form

$$C_V^*(\varphi,\ \tau) = A_s|1 - A_2(\varphi)\tau|^{-\alpha} + \text{regulation terms}. \tag{1}$$

Equation (1) generalizes the power law of scale theory for noncritical isochores, and compared to traditional methods of C_V calculation has the advantage that it correctly describes C_V behavior in the metastable region and near the stability boundary of the homogeneous state (spinodal). In fact, it follows from Eq. (1) that for $\tau_s(\varphi)$ satisfying the condition

$$A_2(\varphi)\tau_s - 1 = 0, \tag{2}$$

the isochoric heat capacity increases without limit. This has been well confirmed by experimental [2-5], numerical [6, 7], and theoretical [8-12] studies. From Eq. (2) we have

$$\tau_s(\varphi) = A_2^{-1}(\varphi), \tag{3}$$

from which follows the physical meaning of the regulation terms of Eq. (1). Consequently, $A_2(\varphi)$ defines the geometric location of singular points on the thermodynamic surface. For each isochor there exists a temperature $\tau_s(\varphi)$ satisfying the condition $\tau_s(\varphi) \leqslant \tau_c(\varphi)$ (this condition follows from the properties of the function $A_2(\varphi)$ studied in [1]), at which C_V increases without limit. Knowing the value of the regulated parameter of $A_2(\varphi)$ for each isochor, Eq. (3) may be used to calculate the temperature at which C_V diverges. Thus these values of τ_s and φ define the position of the spinodal curve.

Table 1 presents values of temperature and density on the saturation line and spinodal curve, calculated from C_V data for a number of n-alkanes [13, 14]. Table 2 compares spinodal

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 45, No. 6, pp. 974-977, December, 1983. Original article submitted July 13, 1982.

0022-0841/83/4506-1421$07.50