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HEAT CAPACITY OF METALS NEAR THE MELTING POINT AND THE VACANCY MECHANISM OF MELTING*

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The vacancy mechanism of the melting process is utilized as a starting point for deriving the formula for the difference of the heat capacity of the liquid and solid metal in the neighbourhood of the melting point. From these calculations it follows that the difference $C_{pl}-C_{ps}$ is the same for all the metals and equals 3.50 J/g. atom K. This result is compared with the existing in the literature experimental data for 39 metals and the agreement is found to be good.

In a series of papers [1–4] the existence of correlations between the changes of various physical properties of metals at the melting point and changes of the same properties of metals due to the creation of vacancies has been demonstrated. On the basis of these correlations a vacancy mechanism of the melting process of metals has been proposed, according to which:

— Melting starts when the vacancy concentration in solid metal reaches a critical value of the order of 10^{-3}, and

— The melting process is a process of creation of additional vacancies at the cost of the heat of melting. The vacancy concentration increase *during* the melting of metals is approximately equal to $\Delta c \simeq 0.1$.

The present paper is an attempt to derive a formula for the difference of the atomic heat capacity of solid and liquid metals at the melting point. The basis for these calculations is the proposed vacancy mechanism of the melting process. The comparison of the results obtained in this way with the existing experimental data may serve as an important test for the correctness of the proposed vacancy mechanism of melting of metals.

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It is well known [5] that vacancies contribute significantly to the specific heat. The increase in atomic specific heat caused by vacancy formation is especially pronounced near the melting point and can be represented by the formula

$$C_{vac} = AN_A \exp(-E_f/kT)E_f^2/kT^2, \tag{1}$$

where N_A is Avogadro's number, E_f — vacancy formation energy, k — Boltzmann constant and A — constant (entropy factor).

According to the second postulate of the proposed vacancy mechanism of the melting process, the changes of all the physical properties of metals in the neighbourhood of the melting point are governed by the change of the vacancy concentration taking place during melting [1–4,6]. Assuming that the vacancy formation entropy does not changes significantly during the melting one obtains the following expression for the change of the atomic heat capacity of metals at the melting point

$$C_{pl} - C_{ps} = A\frac{N_A}{k}\left[\frac{E_{fl}^2}{T_m^2}\exp(-E_{fl}/kT_m) - \frac{E_{fs}^2}{T_m^2}\exp(-E_{fs}/kT_m)\right], \tag{2}$$

where T_m is the melting temperature. Subscripts 1 and s denote the liquid and solid state of metal, respectively.

TABLE I

Experimental values of the heat capacity of liquid, C_{pl}, and solid, C_{ps}, metals at the melting point. All the values are given in J/g. atom K

Metal	C_{pl}	C_{ps}	$C_{pl}-C_{ps}$	Metal	C_{pl}	C_{ps}	$C_{pl}-C_{ps}$
Li	30.50 [7]	29.29 [8]	1.21	Rh	41.84 [13]	39.50 [13]	2.34
Na	31.88 [9]	31.21 [10]	0.67	Pd	41.17 [26]	36.61 [27]	4.56
K	32.80 [11]	32.01 [10]	0.79	Ir	41.84 [13]	39.08 [10]	2.76
Rb	34.41 [12]	32.38 [13]	1.03	Pt	36.48 [28]	35.02 [13]	1.46
Cs	26.40 [35]	24.40 [35]	2.00	Ag	28.03 [35]	25.31 [35]	2.72
Ca	44.77 [8]	43.51 [8]	1.26	Cu	34.64 [29]	31.17 [10]	3.47
Ba	43.10 [14]	39.25 [14]	3.85	Zn	45.44 [35]	41.68 [35]	3.76
Ti	45.48 [15]	38.07 [16]	7.41	In	68.62 [35]	64.44 [35]	4.18
Zr	41.84 [17]	37.40 [18]	4.44	Pb	52.30 [35]	48.53 [35]	3.77
V	50.21 [17]	47.99 [19]	3.22	Y	39.79 [13]	35.02 [13]	4.77
Nb	39.33 [17]	35.31 [13]	4.02	La	44.35 [30]	40.38 [30]	3.97
Ta	35.36 [13]	33.14 [10]	2.22	Ce	40.38 [31]	37.87 [31]	2.51
Mo	58.58 [20]	54.14 [21]	4.44	Pr	41.71 [32]	38.45 [33]	3.26
W	74.85 [22]	67.15 [23]	7.70	Nd	47.32 [34]	44.56 [34]	2.76
Re	45.19 [10]	42.50 [13]	2.69	Sm	50.21 [31]	46.94 [13]	3.27
Fe	46.02 [13]	42.55 [13]	3.47	Gd	37.15 [12]	28.28 [12]	8.87
Co	40.50 [13]	37.74 [13]	2.76	Dy	46.02 [31]	42.55 [31]	3.47
Ni	38.99 [24]	36.19 [13]	2.80	Tm	41.38 [13]	37.49 [13]	3.89
Ru	51.88 [25]	47.28 [25]	4.60	Mg	36.82 [35]	34.31 [35]	2.51
				U	47.48 [36]	42.77 [36]	4.71

As it has previously been shown [1], the ratio E_{fs}/T_m is for all the metals the same and equals 1 eV/1200 K. It is also known that the value of the vacancy formation energy in the liquid state, E_{fl}, is equal to 0.9 E_{fs} [6]. Therefore, taking into consideration the fact that the entropy factor A has for all the metals the same value of 60.34 [1], one finally obtains

$$C_{pl} - C_{ps} = 3.50 \text{ J(g. atom)}^{-1}\text{K}^{-1}. \tag{3}$$

It can also be stated that for all the metals the change of the atomic specific heat at the melting point has the same value. In Table I the data available in the literature on the atomic specific heat for both the solid and liquid states of 39 metals for the temperature range close to the melting point are collected and the values of the difference $C_{pl} - C_{ps}$ are calculated. It has been found, that the mean value of the difference $C_{pl} - C_{ps}$ equals 3.42 J (g. atom)$^{-1}$K^{-1} and the standard deviation does not exceed 1.75 J (g. atom)$^{-1}$K^{-1} (50%). Taking into account the difficulties encountered in the measurements of the heat capacity of metals in the high-temperature range, it is fair to say that the agreement between the theory and experiment is very good. This agreement corroborates the correctness of the proposed vacancy mechanism of melting of metals.

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