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HEAT CAPACITY OF URANIUM METAL AT LOW TEMPERATURES. A REMINISCENCE.

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SUMMARY

The heat capacity C_p of uranium at constant pressure was determined between 17.2 and 263.8 K in 100 steps and corrected to the heat capacity at constant volume C_v. Taking into account the contribution C_{el} by free electrons C'_v values could be calculated rendering a mean Debye temperature of 216. The standard entropy at 0 °C was determined to 45.4 J K^{-1} mol^{-1}; the c_p value to 27.8 J K^{-1} mol^{-1}. The obtained figures are compared with those cited in the literature.

INTRODUCTION

Measurements of specific heats date back to the beginning of this century when Gaede (ref. 1) developed the first low temperature calorimeter, followed by Nernst (ref. 2) and Eucken (ref. 3) and their collaborators. The data obtained were not only important for Nernst in verifying his Third Law of Thermodynamics but also for tabulating fundamental values such as entropy and free energy. Thus low temperature calorimetry was the standard method in chemical thermodynamics. The early instruments which were tedious to operate became more and more sensitive and flexible with the time and are nowadays often computer controlled with automatic data acquisition. Moreover, the earlier sample sizes of some hundred grams (or even a few kilograms) decreased to some grams or less in more recent experiments (see e.g. ref. 4). Reviews about this development are given by Eucken (ref. 5), Stout (ref. 6), Westrum et al. (ref. 7) and Gmelin (refs. 8,9). When Westrum (ref. 10) looking for future techniques and applications of low temperature thermodynamics asked "Low-temperature calorimetry - quo vadis?", the present paper could be entitled "Unde venis - low temperature calorimetry?". It presents data which were evaluated during 1943 and 1944 in the "Physikalisch-Chemisches Institut München" under the direction of Professor

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K.Clusius but never published thereafter. As only few values are known about metallic uranium we thought it worthwile to publish these old results and compare them with those of other groups. At the same time this article is an hommage to the late Professor Klaus Clusius of Würzburg, München and Zürich who made so many important contributions to low temperature calorimetry.

The investigations were carried out by means of a modified Nernst/Eucken calorimeter. Following Hemminger and Höhne (ref. 11) this calorimeter can be listed in the group of instruments "... measuring a time-dependent temperature difference". Translating Nernst's own words: "The principle of this method consists just in the fact that the substance under investigation serves itself as calorimeter and is warmed up by a few degrees (or even less) by means of a platinum wire whom a measured quantity of electric energy is added; this warming is determined by the same platinum wire serving at the same time as resistance thermometer" (ref. 12). The Nernst calorimeter is often counted as an adiabatic one, although it is more correct to call it quasi-adiabatic. This type of instrument is still the most prominent one for the evaluation of specific heat capacities, especially at very low temperatures.

The experiments presented here belong to a series of investigations of various metals at low temperature: e.g. palladium (ref. 13), indium (ref. 14) and cobalt (ref. 15). The experiments on uranium were performed one year later than those of Jones et al. (ref. 16) who worked in the context of the American "Manhattan Project". In both cases the experiments were performed during the war and could not be published immediately.

At the time of these measurements only three single values for the heat capacity of uranium were known: 13.8 J/(K mol) at 50 K (ref. 17) presenting a mean value for the temperature range 18 to 80 K; 27.90 J/(K mol) between 0 ^{o}C and 98 ^{o}C (refs. 18,19; see also refs. 20,21) and 61.7 J/(K mol) between 11 and 98 ^{o}C (refs. 22,23). Thus it seemed necessary to establish accurate figures in a step-by-step manner up from very low temperatures. Meanwhile, further original data are known for C_p at low temperatures (ref.16; refs. 24-27) and figures cited in monographs (e.g. refs. 28,29) and Table Works (refs. 30,31).

MATERIALS AND METHODS

The modified Nernst vacuum calorimeter (ref. 12) was described in detail in (refs. 32,33). Briefly, the cylindrical sample hung in a copper shield which was essential for the temperature homogeneity inside the calorimeter (Fig. 1). The shield itself was surrounded by two thin metal boxes. These could be either filled with liquid helium for thermal equilibration or evacuated for thermal insulation. The whole setup was placed in a Dewar vessel, surrounded by the cooling medium. Because of the massive shield, this calorimeter is sometimes called an "isothermal" one. It corresponds to that developed by Giauque (see ref. 6).

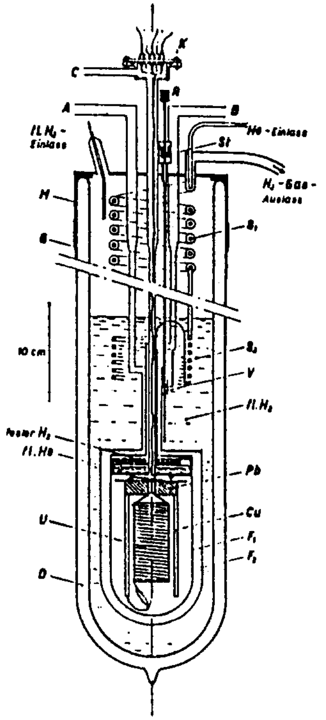

Fig. 1 Sketch of the vacuum calorimeter, with U: as calorimeter used sample; Cu/Pb: protective shield; F_1, F_2: two metallic boxes; D: Dewar vessel (from ref. 27).

The uranium specimen was turned from an original block of approximately 800 g. As the surface temperature during this procedure increased considerably the specimen was continuously kept under a film of thick oil. The surface showed several shrink-holes which had to be taken into consideration for the weight/volume relationship. The final size of the cylindrical specimen came to an external diameter of 17.1 mm and a length of 35.4 mm (Fig. 2). The mass of 121.908 g corresponded to 0.51215 mol uranium. The expected mass for an uranium cylinder of 8.13 cm^3 would be 155.3 g at a mass density of 19.1 g/cm^3 given in the literature. Here the calculated density amounted to 15.0 g/cm^3 in good agreement with a determination of 15.1 g/cm^3 in benzene. Another part of the original block rendered a value of 16.95 g/cm^3. The size of the specimen (roughly 0.5 g-atom) is in accordance with experiments on other metals and with the experience that smaller sample sizes facilitate the temperature equilibration during the measurements.

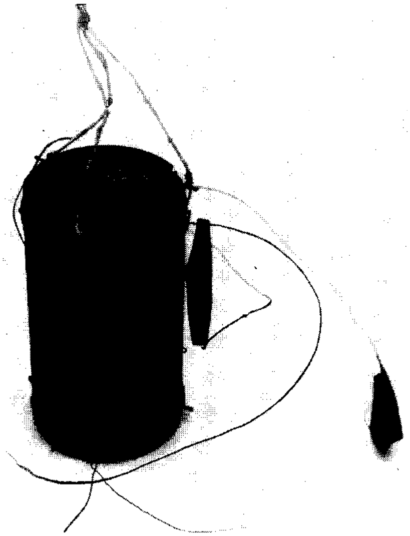

Fig. 2 Specimen (U in Fig. 1) with the different wires for heating and temperature measurement.

To check if the density differences were due to contaminations by other material or to a larger number of shrink-holes the uranium was chemically investigated. In two independent examinations the recovery of uranium was 100.1 % and 99.1 %, resp. Moreover, an analysis for calcium traces yielded a negative result. Thus it had to be concluded that shrink-holes were responsible for the low specific density of the material. The chemical impurities were so small that they could be neglected in the c_p determination at these low temperatures (ref. 7).

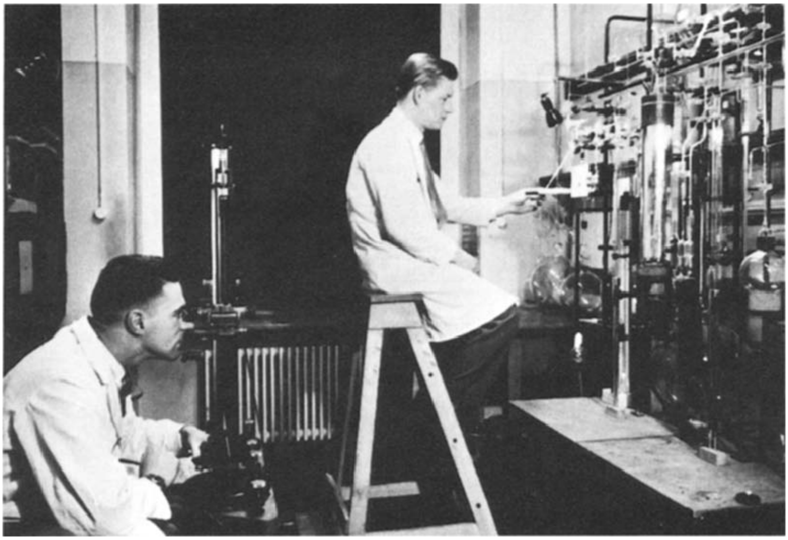

Fig. 3 Instrumental setup and reading of the galvanometric deflection.

A groove with an incline of 1.4 mm was turned into the surface of the cylinder to house the heating wire together with the resistance wire for temperature measurements. Both wires were carefully separated by a layer of tissue paper impregnated by japanning. The heating wire was made from constantan with an outer diameter of 0.05 mm and a total resistance of 360 Ohm. The heating current was calibrated against a standard cell. The lead wire used by Clusius and Goldmann (ref. 32) for temperature determinations was exchanged for a platinum wire with a diameter of 0.05 mm and a zero resistance of 177.2 Ohm. This value changed only by less than 0.05 % for consecutive runs. The platinum thermometer was calibrated at the ice point, at the boiling point of hydrogen and that of nitrogen. The latter temperature was controlled by means of an oxygen vapour pressure thermometer, for the former ones the exact atmospheric pressure was used for the calculation of T. For the region from 14 to 85 K the table of Onnes and Tuyn (after ref. 34) was applied, for the region from 73 to 273 K that of Henning (ref. 35), each time adapted to the calibration points. Fig. 3 gives an impression of the complete instrumental setup with calorimeter and glass connections for cooling media and vacuum (right side) and with the tedious temperature observation system at the left.

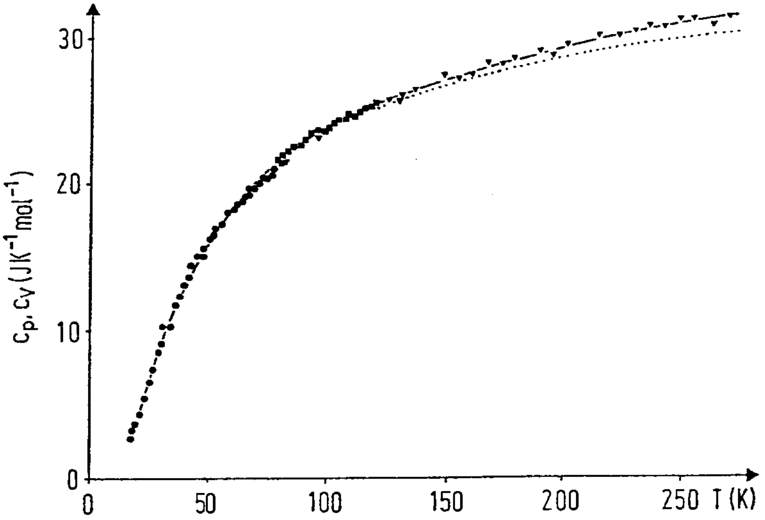

Fig. 4 Slope of the calorimetrically determined specific heat capacity c_p for uranium between 17.2 and 268.7 K. The isolated point results from Dewar (ref. 17) representing a mean value for the range from 18 to 80 K. (Upper line: c_p, lower line: c_V)

RESULTS AND DISCUSSION

Three independent runs were performed which were slightly overlapping as shown by the three different symbols in Fig. 4. The small contributions to the heat capacity by the platinum and the copper wires were calculated from curves in the literature, those by the insulating material determined in an additional set of experiments. These corrections were subtracted from each single point and the curve smoothed by a polynomial of higher order giving mean standard deviations of less than 1% . The values presented in Table 1 for equally spaced temperatures are taken from this smoothed curve.

For the further evaluation of C_V values from the calorimetrically obtained C_p data the equation

$$C_p - C_V = \alpha^2 V T / \chi \qquad (1)$$

can be used where α is the cubic expansion coefficient, χ the compressibility , T the absolute temperature and V the molar volume. V equals M/ϱ , where M is mass and ϱ the density. These characteristic values of metallic uranium can be found in standard table works. To facilitate the comparison with results of other authors these values, mainly taken from (ref. 30), are compiled in Table 2. Older values are transformed to SI-units by the relation 1 cal = 4.187 J. The freezing point is chosen as 273.16 K.

TABLE 1

Specific heat capacity c_p in J $(K\ mol)^{-1}$ and Debye temperature Θ in K for uranium between 20 and 273 K taken from the smoothed curve

T	c_p	Θ	T	c_p	Θ
20	3.448	156	120	22.593	188
25	6.084	158	130	23.175	181
30	8.293	162	140	23.673	168
35	10.153	169	150	24.113	150
40	11.736	172	160	24.519	127
45	13.093	176	170	24.913	99
50	14.269	180	180	25.302	
55	15.295	182	190	25.700	
60	16.208	184	200	26.102	
65	17.024	188	210	26.483	
70	17.765	190	220	26.822	
75	18.440	192	230	27.094	
80	19.059	193	240	27.282	
85	19.629	194	250	27.404	
90	20.156	194	260	27.525	
100	21.098	194	270	27.793	
110	21.906	193			

C_v is assessed more easily by theoretical considerations: Since α is proportional to C_p over a wide temperature range and is independent of temperature, equation (1) was transformed by Nernst and Lindemann (ref. 36) to

$$C_p - C_v = A\ T\ C_p^2 \qquad (2)$$

where A is constant. With the data of Table 2 for uranium it amounts to

$A = 1.78 \times 10^{-5}$ mol cal^{-1} or

$A = 4.25 \times 10^{-6}$ mol J^{-1}.

Again, other values are used in the literature (Table 3). But these differences are less important as they give rise to a maximum deviation of not more than 0.4 % at higher temperatures. A further half empirical transformation done by Nernst and Lindemann leads to the equation:

$$C_p - C_v = 0.0214\ C_p^2\ T\ /\ T_m\ , \qquad (3)$$

where T_m is the melting point of the specimen.

TABLE 2

Selected physical data for uranium at room temperature

(The figures in brackets are given by Jones et al. 1952)

Relative atomic mass	238.03	(238.07)
Molal volume (cm^3/mol)	12.44	(12.56)
Density (g/cm^3)	19.1	(18.95)
Thermal cubic expansion coefficient (K^{-1})	45.9	(50.0)
Isothermal compressibility (10^{-8} cm^2/N)	8.17	(8.4)
Melting temperature (K)	1403	

All solids approach the ideal state near the absolute zero point. The specific heat capacity decreases in this region with the third power of T ("Debey's T^3-law"). Multiplying the temperature scale with an individual factor $1/\Theta_D$, the C_p versus T curves of most solids become congruous. This factor $1/\Theta_D$ was first postulated by Debye and is therefore called the Debye temperature. Θ_D is related to the maximum oscillation frequency of the atoms, v_{max}, and the melting temperature T_m and can be calculated according to (ref. 36) by

$$v_{max} = 2.80 \times 10^{12}\ [\ T_m\ /\ (V^{2/3}\ M)\ ]^{1/2} \qquad (4)$$

with the molar volume V (cm^3/mol) and the relative atomic mass M. Combination with the definition of the Debye temperature

$$h\ v_{max} = k\ \Theta_D \qquad (5)$$

through the Planck constant h and the Boltzmann constant k leads to the numeric relation

$$\Theta_D = 134\ [\ T_m\ /\ (V^{2/3}\ M)\ ]^{1/2} \qquad (6)$$

(ref. 31). Inserting the characteristic figures for uranium gives a Debye temperature Θ_D = 140.3 K, while the Madelung-Einstein equation

$$\Theta_D = 1.45 \times 10^{-3}\ /\ (\chi^{1/2}\ \varrho^{1/6}\ M^{1/3}) \qquad (7)$$

with the isothermal compressibility χ and the density ϱ (see e.g. ref. 31) gives 159 K. The latter value corrresponds better to the characteristic figures obtained by other authors: 162 K (ref.16), 165 K (ref. 24) and 170 K (ref. 25). These values are presented in the literature without reasoning so that it is difficult to explain the differences.

The Debye temperature Θ can also be calculated from the experimental values determined for C_v at a temperature T and with the gas constant R after the equation

$$C_v = 233.7\ R\ (T/\Theta)^3\ . \qquad (8)$$

With R = 8.31 J K^{-1} mol^{-1} equation (8) transforms to

$$\Theta = 12.48\ T\ C_v^{-1/3}. \qquad (9)$$

The standard entropy of uranium was determined graphically as 45.4 J/(J.mol) for the region from 17.2 to 273.16 K taking into account the Debye entropy at 17.2 K with 0.80 J/(K mol). The temperature 0 °C was chosen instead of 25 °C as our measurements did not extend to this region. The figure obtained is 5 % smaller than the literature value of 47.8 J/(K mol) (ref. 16,26). Our c_p value at 0 °C amounts to 27.8 J/(K mol) instead of 27.2 J/(K mol) for the cited authors.

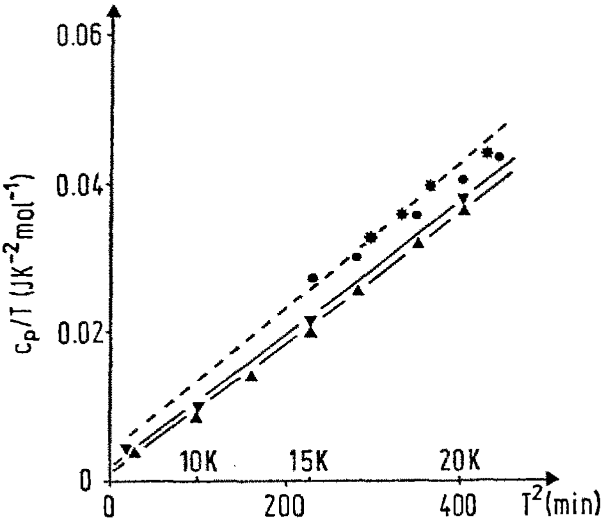

Fig. 5. Plot of c_p/T as function of T^2 at temperatures below 25 K.
✱: this paper (τ_3 = 145x10^{-4} J K^{-2} mol^{-1}); ●: Jones et al. 1952 (τ_3 = 410x10^{-4} J K^{-2} mol^{-1}); ▲: Flotow and Lohr 1960 (τ_3 = 35.6x10^{-4} J K^{-2} mol^{-1}); ▼: Smith and Wolcott 1955 (τ_3 = 54.8x10^{-4} J K^{-2} mol^{-1}).

At low temperatures the lattice contribution C_{la} to C_v follows the Debye T^3-rule, while at higher temperatures it tends towards the equipartition value 3R. In the same sense a characteristic figure must exist for the temperature region between the two extrema. Following the Debye theory the heat capacity of a metal should be describable by a single Debye temperature Θ for all temperatures. Calculating the specific temperature Θ for the obtained C_v values by means of the Debye function gives the $\Theta(C_v)$

TABLE 3

Experimental data for uranium from this paper and from the literature

(Θ and T_o in K; τ in 10^{-4} J K^{-2} mol^{-1}; A in 10^{-6} mol J^{-1})

	this paper	Clusius Piesbergen	Clusius Bühler	Jones et al.	Flotow Lohr	Smith* Wolcott
Θ_g	159	170	165	162	-	-
T_o	181	-	180	183	187	-
Θ'	216	185	(167)	(184)	(187)	-
τ_1	53.6	87.9	59.9	54.0	50.2	-
τ_2	98.4	86.7	-	69.1	67.0	-
τ_3	145	-	-	(420.0)	(35.6)	(54.8)
A	4.25	4.97	-	4.94	(4.94)	-

*cited after Flotow and Lohr (1960)

shown in Table 1 and in Figure 5. It is obvious that the mean value $\Theta(C_v)$ = 190 K is valid only in a small temperature region and that $\Theta(C_v)$ vanishes at a temperature T_o around 181 K. This is due to the fact that at elevated temperatures the contribution of the electrons to the heat capacity plays an important role. Following an argumentation of Clusius and Bühler (ref. 24) and applying their formula (11)

$$\tau_1 = 0.30\ \Theta_D^2/T_0^3 \quad \text{(in cal K}^{-2}\text{ mol}^{-1}\text{)} \quad \text{or} \qquad (10)$$

$$= 1.25\ \Theta_D^2/T_0^3 \quad \text{(in J K}^{-2}\text{ mol}^{-1}\text{)} \qquad (11)$$

one can calculate an approximate value for the proportionality constant τ_1 of the electronic contribution C_{el} to the heat capacity C_v. With T_o = 181 K and Θ_D = 159 K τ_1 amounts to 53.55x 10^{-4} J K^{-2} mol^{-1}, while for the data of Jones et al. (ref. 16) and Flotow and Lohr (ref. 26) values of 53.80x10^{-4} and 50.41x10^{-4} J K^{-2} mol^{-1}, resp., can be estimated (see Table 3). Clusius and Bühler (ref. 24) found a τ_1 = 59.87x10^{-4} J K^{-2} mol^{-1} at a T_o = 180 K. Correcting C_v with these electron contributions renders a smoother curve for the Debye temperature. Optimal fits are obtained by trial with the τ_2 values $98.3\text{x}10^{-4}$, $69.1\text{x}10^{-4}$ and $67.0\text{x}10^{-4}$ J K^{-2} mol^{-1} for our data and that of Jones et al. (ref. 16) and Flotow and Lohr (ref. 26), resp. The different τ_1 and τ_2 values are compiled together with other data in Table 3. Fig. 6 presents the original Θ value and the fitted ones for our data and that of Jones et al. (ref. 16) and Flotow and Lohr (ref. 26).

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At temperatures below 20 K the heat capacity may be divided into two contributions, that of the lattice C_{la} and that of the electrons C_{el} in the following way

$$C_p \approx C_V = C_{la} + C_{el} = a\ T^3 + \tau_3\ T \tag{12}$$

showing the T^3-law of Debye and the linear electronic contribution after Sommerfeld. Plotting C_p/T as function of T^2 yields a linear slope with the constant term τ_3. The coefficient τ_3 lies in the order of $8\text{x}10^{-4}$ J K^{-2} mol^{-1} for typical metals such as silver or copper and increases to $120\text{x}10^{-4}$ J K^{-2} mol^{-1} for transition metals like palladium (ref. 24). Goodman and Shoenberg (ref. 37) postulated a γ_3 value for uranium smaller than 142×10^{-4} J K^{-2} mol^{-1}. Clusius and Bühler (ref. 24) gave a figure of 59.9×10^{-4} J K^{-2} mol^{-1} for uranium, Clusius and Piesbergen (ref. 25) 87.9×10^{-4} J K^{-2} mol^{-1}. From the data of Flotow and Lohr (ref. 26) a value of 35.6×10^{-4} J K^{-2} mol^{-1} can be estimated by means of a C_p/T over T^2-plot. Data of Smith and Wolcott (1955; cited in ref. 26) yield 54.8×10^{-4} J K^{-2} mol^{-1}. As there are only few

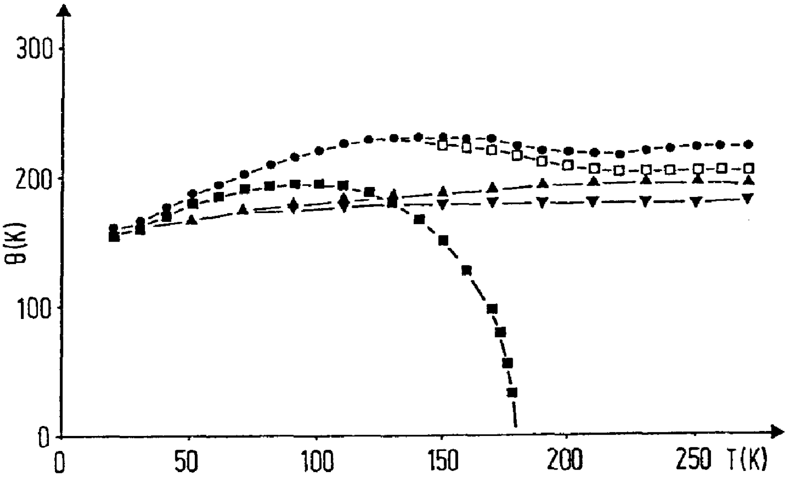

Fig. 6 Debye temperature Θ calculated from c_v as function of temperature. ■: c_v, this paper; ●: $c_v - 98.4\times10^{-4}$ T, this paper; □: $c_v - 92.1\times10^{-4}$ T, this paper; ▲: $c_v - 69.1\times10^{-4}$ T (ref. 16); ▼: $c_v - 67.0\times10^{-4}$ T (ref. 26).

points in our experiments in this temperature region an extrapolation of the C_p/T over T^2-plot is difficult. It leads to an approximative figure of 145×10^{-4} J K^{-2} mol^{-1}. Values found by different authors are compiled in Table 3, the linear relationship of C_p/T to T^2 is shown in Fig. 6 for our data and some selected ones from the literature.

The results presented here are not always in complete agreement with those of other authors. But as many of the older figures are given without explanation it is difficult to find the reason for the differences. The calorimetrically determined C_p values are slightly too high in the upper temperature region, the entropy at 0 °C a bit too low. The characteristic Debye temperature found by the best fit is 30 K higher than those of other authors. Nevertheless it renders a much better approximation than that published by Clusius and Bühler (ref. 24). Some of the deviations might be due to the imperfect uranium specimen used in these experiments. As pointed out above the mass density of the specimen was much lower than expected, mainly caused by shrinkholes. As Piesbergen (ref. 38) observed with two rhenium specimen of different densities a common Debye temperature is obtained only when different electron contributions to the heat capacity are taken into account. On the other hand incorrect determinations of the energy input to the calorimeter are the main errors in low temperature calorimetry. After the passage of such a long time and without having the specimen used in the experiments any longer it is not possible to decide which reason is the most important for the deviations.

Acknowledgments

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