falls liegt also auch bei den bisher bekannten Messungen der spezifischen Wärme des Benzols als Temperaturfunktion[1]) kein Grund vor für die Annahme der Existenz des von MENZIES und LACOSS erwähnten Schnittpunktes bei etwa 44° C.

Zusammenfassung.

Es wurde darauf hingewiesen, dass der Schluss von MENZIES und LACOSS, nach welchem die Temperaturkurven der Dichte, des Brechungsindex bezw. der spezifischen Wärme des flüssigen Benzols zwischen 0 und 70° C. einen Knick aufweisen, sich im Widerspruch befindet mit den Beobachtungen, auf welchen dieser Schluss fusst. Aber auch falls ein Knick in diesen Kurven tatsächlich vorläge, wäre es verfehlt daraus auf Allotropie des flüssigen Benzols zu schliessen.

VAN 'T HOFF-*Laboratorium.*

Utrecht, Januar 1934.

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[1]) Vergl. auch WILLIAMS und DANIELS, J. Am. Chem. Soc **46**, 1569 (1924).

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures.* XIII. *The Specific Heats of Vanadium, Niobium, Tantalum and Molybdenum from 0° to 1500° C.* By F. M. JAEGER and W. A. VEENSTRA.

(Communicated at the meeting of January 27, 1934.)

§ 1. In this paper we shortly communicate the results of the measurements of the specific heats of the metals *vanadium, niobium* and *tantalum,* all belonging to the fifth group and of *molybdenum,* belonging to the sixth group of the periodical system; for details, we must refer to a future publication on this subject in the *Recueil des Travaux des Chimistes des Pays-Bas.* Purest *vanadium* was most kindly furnished us in solidified grains by the *Vanadium Corporation of America* in *Bridgeville* (Pa); *niobium* and *tantalum* in the form of massive bars by the *Fan Steel Company* in *Chicago; molybdenum* in the shape of a compressed bar by the PHILIPS' *Incandescent Lamps Industry* in *Eindhoven.* All metals proved to be practically free from impurities, only traces of iron being present. They all crystallise in the cubic system, with a bodily-centred cell containing two atoms: the edges of the cell are consecutively: $a_0 = 3.04$ Å.; 3,31 Å.; 3,32 Å., and 3,14 Å., the densities: 5,98; 8,3; 16,3; and 10,21 respectively. *Vanadium* melts at 1715° C., *niobium* between 1700° and 1950° C., *tantalum* between 2800° and 3000° C., *molybdenum* at 2622° C. All metals were preliminarily brought into the "stabilized" condition by a suitable

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thermal treatment; they dont show any indication of allotropic changes, nor of retardation-phenomena.

The measurements at each temperature were repeated several times; the values given proved to be reproducible within 0,1—0,2 %, even at the highest temperatures.

§ 2. *Vanadium*. After stabilization the metal yielded perfectly constant values for $\bar{c}_p$, which are expressed by:

$$\bar{c}_p = 0,11846 + 0,156867 \cdot 10^{-4} \cdot t - 0,225132 \cdot 10^{-8} \cdot t^2 + 0,3546 \cdot 10^{-12} \cdot t^3.$$

The true specific heats c_p, therefore, are:

$$c_p = 0,11846 + 0,313734 \cdot 10^{-4} \cdot t - 0,675396 \cdot 10^{-8} \cdot t^2 + 0,14184 \cdot 10^{-11} \cdot t^3$$

and the atomic heat C_p by:

$$C_p = 6,0414 + 0,1600 \cdot 10^{-2} \cdot t - 0,34446 \cdot 10^{-6} \cdot t^2 + 0,7234 \cdot 10^{-9} \cdot t^3.$$

Some values of c_p and C_p thus calculated are collected in Table I.

TABLE I. True specific Heats and Atomic Heats C_p of Vanadium.		
Temperature in °C. :	True specific Heats C_p :	Atomic Heats C_p :
0°	0.1185	6.044
100	0.1215	6.196
200	0.1245	6.349
300	0.1273	6.492
400	0.1300	6.630
500	0.1327	6.768
600	0.1352	6.895
700	0.1376	7.018
800	0.1400	7.140
900	0.1422	7.252
1000	0.1445	7.369
1100	0.1467	7.482
1200	0.1488	7.589
1300	0.1509	7.696
1400	0.1530	7.803
1500	0.1551	7.910

The value of $C_p = 3R$ calories is already reached at —40° C. As no data concerning the compressibility $\varkappa$ and the thermal dilatation α of *vanadium* are available in the literature, no calculation of the corresponding values of c_v and C_v could be made with any degree of certainty. The C_p-t-curve for *vanadium* is reproduced in Fig. 1.

§ 3. *Niobium.* After heating the metal at 1400° C. for five hours in vacuo and slowly cooling, the values of $\bar{c}_p$ proved to remain constant. They can be expressed by:

$$\bar{c}_p = 0{,}06430 + 0{,}386383 \cdot 10^{-5} \cdot t + 0{,}078258 \cdot 10^{-8} \cdot t^2.$$

The true specific heats, therefore, by:

$$c_p = 0{,}06430 + 0{,}772766 \cdot 10^{-5} \cdot t + 0{,}234774 \cdot 10^{-8} \cdot t^2,$$

and the atomic heats by:

$$C_p = 6{,}0120 + 0{,}722533 \cdot 10^{-3} \cdot t + 0{,}21952 \cdot 10^{-6} \cdot t^2.$$

Some of the values of c_p and C_p for a series of temperatures are calculated in Table II and graphically reproduced in Fig. 1.

TABLE II. True specific and Atomic Heats of Niobium.		
Temperature t in °C. :	True specific Heat c_p :	Atomic Heat C_p :
0°	0.06430	6.012
100	0.06510	6.087
200	0.06594	6.165
300	0.06683	6.249
400	0.06777	6.337
500	0.06875	6.423
600	0.06978	6.524
700	0.07086	6.626
800	0.07198	6.730
900	0.07316	6.840
1000	0.07437	6.954
1100	0.07564	7.072
1200	0.07695	7.195
1300	0.07832	7.323
1400	0.07973	7.455

Niobium is somewhat less compressible than *iron* [1]): at 30° C. $\varkappa = 5{,}70 \cdot 10^{-7}$, at 75° C. $\varkappa = 5{,}778 \cdot 10^{-7}$ KG/cM². However, no data

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[1]) P. W. BRIDGMAN, Proceed. Amer. Acad. of Arts and Sciences, **68**, (1933), 28.

for the thermal dilatation of this metal are given in the literature, so that no values for c_v and C_v could be calculated. Also in this case the value of $C_p = 3R$ calories appears to be reached below 0° C.

Fig. 1.

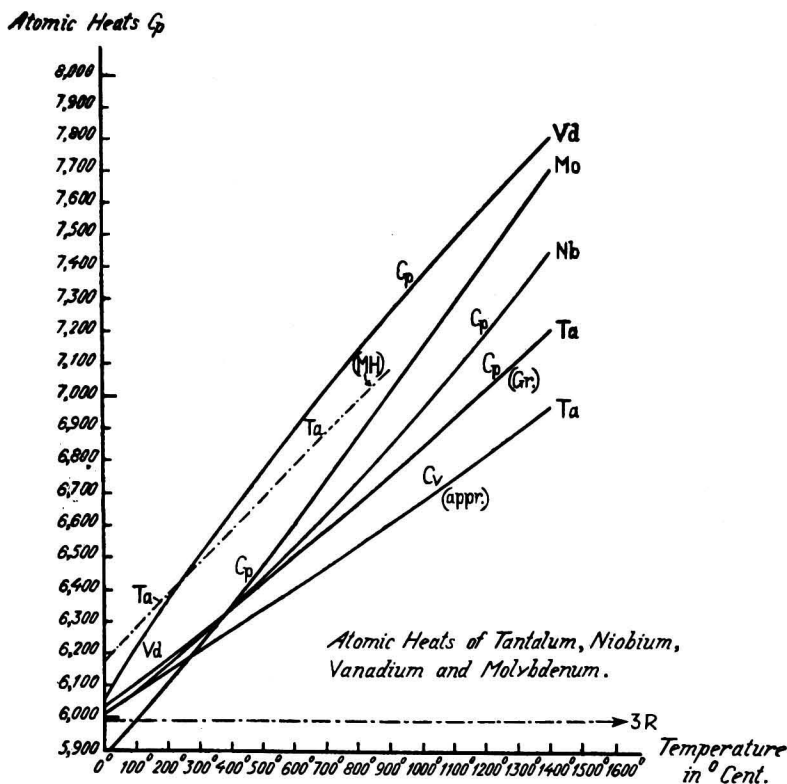§ 4. *Tantalum.* The specific heats of this metal till 900° C. were already determined by MAGNUS and HOLZMANN [1]; their values do, however, rather appreciably differ from our results. The lumps were stabilized at 1400° C. by heating in a vacuum for three and then for six hours and slowly cooling. The mean specific heats $\bar{c}_p$ can be expressed by:

$$\bar{c}_p = 0,033218 + 0,2099 \cdot 10^{-5} \cdot t + 0,10983 \cdot 10^{-9} \cdot t^2 ;$$

the true specific heats c_p, therefore, by:

$$c_p = 0,033218 + 0,4198 \cdot 10^{-5} \cdot t + 0,3295 \cdot 10^{-9} \cdot t^2,$$

and the atomic heats C_p by:

$$C_p = 6,0244 + 0,38066 \cdot 10^{-3} \cdot t + 0,19919 \cdot 10^{-7} \cdot t^2.$$

For a series of temperatures the values of c_p and C_p thus calculated, are represented in Table III.

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[1] A. MAGNUS and H. HOLZMANN, Ann. der Phys., (5), **3**, (1929), 596.

TABLE III. True Specific Heats c_p and Atomic Heats C_p of Tantalum.			
Temperature in °C :	c_p	C_p (this Laboratory):	C_p (MAGNUS: HOLZMANN):
0°	0.03322	6.024	6.174
100	0.03364	6.101	6.275
200	0.03407	6.179	6.376
300	0.03450	6.257	6.477
400	0.03495	6.339	6.578
500	0.03540	6.420	6.679
600	0.03585	6.502	6.780
700	0.03632	6.587	6.881
800	0.03679	6.672	6.982
900	0.03726	6.757	7.082
1000	0.03774	6.844	(7.183)
1100	0.03823	6.933	(7.284)
1200	0.03873	7.024	(7.385)
1300	0.03923	7.115	(7.486)
1400	0.03974	7.207	(7.587)

The c_p-t- and C_p-t-curves are almost straight lines, with a feeble increase of $\left(\dfrac{\partial C_p}{\partial t}\right)$ at higher temperatures. The inclination of the C_p-t-line of MAGNUS and HOLZMANN who found a linear dependency of C_p on t, as well as the absolute values of C_p at corresponding temperatures are both appreciably greater than those following from our measurements. In both cases, however, the value $C_p = 3R$ calories is already reached at a temperature below 0° C.; already at a temperature no less than 1600° C. lower than the meltingpoint, C_p becomes equal to 7,0 calories, without any indication of a slower increase at higher temperatures. An approximate estimation of C_v teaches, that also this number surpasses the value $3R$ calories below 0° C.; see Fig. 1.

§ 5. *Molybdenum.* After heating the metal in a vacuum crucible at 1400° C. during 4, 8 and 12 hours, the values of $\bar{c}_p$ proved not to vary any more. They can be expressed by:

$$\bar{c}_p = 0,061046 + 0,0616043 \cdot 10^{-4} \cdot t + 0,0345454 \cdot 10^{-8} \cdot t^2.$$

The true specific heats, therefore, by:

$$c_p = 0,061046 + 0,1232086 \cdot 10^{-4} \cdot t + 0,103636 \cdot 10^{-8} \cdot t^2$$

and the atomic heats C_p by :

$$C_p = 5,8604 + 0,11828 \cdot 10^{-2} \cdot t + 0,9949 \cdot 10^{-7} \cdot t^2.$$

Some of these values are, for a series of temperatures, calculated and collected in Table IV.

TABLE IV. True Specific Heats c_p and Atomic Heats C_p of Molybdenum.		
Temperature t in °C, :	c_p :	C_p :
0°	0.06105	5.860
100	0.06229	5.980
200	0.06355	6.101
300	0.06484	6.224
400	0.06614	6.349
500	0.06746	6.476
600	0.06881	6.606
700	0.07018	6.737
800	0.07157	6.870
900	0.07297	7.005
1000	0.07440	7.143
1100	0.07585	7.282
1200	0.07732	7.423
1300	0.07881	7.566
1400	0.08033	7.711

The value of $C_p = 3R$ calories is already reached a little above 100° C.; even at a temperature no less than 1100° C. below its meltingpoint; the metal yields a value for C_p of about 8,0 calories, without there being any indication of a less rapid increase of C_p at higher temperatures. The inclination of the curve with respect to the axis of temperatures is appreciably steeper than in the case of Nb and Ta (See Fig. 1). From the measurements of $\varkappa$ by BRIDGMAN [1]) and those of α by DISCH [2]), FINK [3]) and HIDNERT-GERO [4]), the values of C_v *approximately* can be estimated: at 500° C. the value C_v must be about: 6,40, so that, — just as in the case of *tungsten*, — the C_p-t- and C_v-t-curves seem not to deviate strongly from each other [5]).

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[1]) P. W. BRIDGMAN, loco cit.
[2]) J. DISCH, Zts. f. Physik, **5**, 1921), 173.
[3]) C. F. FINK, Trans. Amer. Electrochem. Soc., **17**, 233.
[4]) P. HIDNERT and W. B. GERO, Scient. Papers Bur. Standards, **19**, (1924), 429.
[5]) F. M. JAEGER and E. ROSENBOHM, Recueil d. Trav. chim. Pays-Bas, **51**, (1932), 7, 11.