

# EXPERIMENTAL DETERMINATION OF THE ENTHALPY AND HEAT CAPACITY OF MOLYBDENUM UP TO 2337°C

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**Abstract**—Results of the experimental determination of the enthalpy and heat capacity of molybdenum between 700°C and 2337°C are presented in the form of a table, diagram and equations. Experimental data were obtained by the method of mixtures using a massive calorimeter with an isothermal shell. A sample was heated to a high temperature in a furnace with a tungsten heater, in a vacuum or in an argon medium. The paper deals with some methods of an experimental determination of the enthalpy at very high temperatures. The experimental results are compared with those in the literature. For the determination of enthalpy the limiting accidental error was  $\pm 0.4$  per cent using a thermocouple to measure temperature up to 1300°C, and  $\pm 0.9$  and  $\pm 1.2$  per cent using a disappearing-filament optical pyrometer for temperatures up to 2000°C and 2400°C, respectively.

BECAUSE of its high melting point, mechanical strength and good mechanical machinability, molybdenum finds increasingly wider application in high-temperature engineering. Therefore such important thermophysical properties as enthalpy and heat capacity should be known at very high temperatures. The highest temperatures used in investigations of enthalpy and heat capacities were 1500°C in experiments done by Wüst [1], and 1554°C in experiments done by Jaeger and Veenstra [2, 3].

In the present work, the investigation of molybdenum enthalpy was extended over a temperature range 700–2337°C. The experiments were carried out on an experimental apparatus specially constructed to investigate the enthalpy and heat capacity of solid materials at very high temperatures [4]. The apparatus used the method of mixtures, applying a massive calorimeter and a diathermic method of measuring heat. The sample was heated up to a high temperature in a resistance furnace with a tungsten heater in an argon medium at 1.05 atm, or in a vacuum. The description of this experimental apparatus and the methods of determining the enthalpy up to 2000°C have been published earlier [4, 5]. The methods of investigation and the value of the apparatus were demonstrated when determining the enthalpy of corundum ( $\alpha$  is a modification of

aluminium oxide), which has been applied lately as a standard material in high-temperature calorimetry. Experimental data on the enthalpy of corundum were obtained at 500–2000°C. In the overlapping interval of 500–1550°C, they agree with the most accurate investigations carried out by other authors, within limits of  $\pm 0.5$  per cent [4, 5].

An experimental determination of the enthalpy, carried out on samples turned out of molybdenum rods made according to the method of powder metallurgy, did not exceed 0.04–0.05 per cent according to the semi-quantitative spectral analysis.

To suit the specific conditions of experiments at high-temperatures, given in detail elsewhere [4], ampoules were not used when investigating the enthalpy of molybdenum, and the values of heat losses were calculated when samples fell into the calorimeter. This method was practicable because of the fact that the coefficient of total radiation of molybdenum is known with sufficient accuracy [7, 8]. The evaluation of possible heat losses when samples fall could be carried out with an error of  $\pm 25$  per cent. Thus the greatest error due to these heat losses while determining the quantity of heat added to the calorimeter by the sample does not exceed 0.1 per cent at 2400°C, the highest temperatures

investigated. This error has a lower value than that obtained when determining the change in heat content of an empty ampoule.

The samples used had the form of frustum cones, the sizes of which coincided with an axial recess in a copper block in order to improve the transfer of heat from the sample fallen into the calorimeter. The surface of the samples was thoroughly polished to stabilize radiation and to decrease heat losses as they fell into the calorimeter.

Samples of three sizes with corresponding weights approximately equal to 120, 90 and 60 g were used. The use of three sizes of samples made it possible to obtain the increase in temperature of the calorimetric system within the limits of 3–8°C in the whole investigated range of 700–2400°C, which ensured sufficient accuracy in measuring the quantity of heat added to the calorimeter. The enthalpy of molybdenum was determined on five samples: sample No. 1 was the largest, No. 3 was the middle, and Nos. 4, 4b and 3–4a (see Table 1) were the smallest ones. Sample No. 3–4a was turned out of sample No. 3 after test run No. 26. A blind hole 6–7 mm in diameter, with the depth 2–3 mm larger than half the sample height, was made along the axis in all the samples, to allow the measurements of their temperature by a thermocouple and pyrometer.

The temperatures of the samples were measured up to 1327°C by model second-class platinum–platinum–rhodium thermocouples standardized at the All-Union Scientific-Research Institute of the Measures and Meters Standards Committee of the Council of Ministers of the U.S.S.R. The thermocouple, isolated by a two-channel porcelain straw, was inserted in a sample in such a way that the junction of it was in the centre of the sample. For mutual control the measurement of a temperature was carried out by three thermocouples. In the furnace the samples were suspended on tungsten wires. At the correct moment the wires were burnt through by electrical current, and the sample fell into the calorimeter. The construction of the suspensions of samples has been described in detail elsewhere [4].

Above 1327°C the measurement of the temperature of the samples was carried out by a

disappearing-filament optical pyrometer through a three-edged glass prism with total internal reflexion. The pyrometer was standardized using model first-class temperature lamps at the All-Union Scientific-Research Institute of the Measures and Meters Standards Committee of the Council of Ministers of the U.S.S.R., both with and without a prism having total internal reflexion. The intensity of the current passing through the filament of the pyrometer lamp was measured by a model resistance coil by the compensation method. On measuring temperature by the pyrometer the error was 0.5 per cent for the limits of measurements 900–2000°C and 0.7 per cent for the range 2000–2400°C.

The temperature was measured using a model of an ideal black body made in the blind hole of the sample. For this the hole in the sample was closed from above by a molybdenum disk having a central opening 2.3 mm in diameter for sighting the pyrometer. The disk in the recess was about 13 mm in diameter in the above cross-cut of the sample (marked (2) in Fig. 1). In addition, the end of a molybdenum tube in the suspension, described elsewhere [4], entered the recess. This tube fixed the position of the sample, suspended on tungsten wires, in the furnace. The bottom of the hollow in the black body model was scored with fine, intersecting cuts, and it was covered with fine molybdenum powder to obtain diffuse reflection of radiation.

The use of an ideal black body model made it possible to measure the temperature of a sample by an optical pyrometer more precisely than could be done by measuring brightness temperature and introducing corrections for the monochromatic coefficient of emissivity. When the temperature of the molybdenum samples was measured the greatest value of the correction for the non-blackness of radiation, due to the presence of the sighting hole 2.3 mm in diameter with the depth of the hollow 15 mm at a temperature of 2400°C, was found to be 2°C. The disturbance of the temperature field in the sample wall due to the presence of the sighting hole was negligibly small because of the high heat conduction of molybdenum.

The experimental values make a smooth curve over the range of transition from temperature measurement by a thermocouple to

Table 1. Experimental data on the enthalpy of molybdenum

No. exp. run	Experimental conditions		$t$ , (°C)	$t'_n$ , (°C)	$i_t - i'_n$ , (kcal/kg)	$i_t - i_{0^\circ\text{C}}$ (kcal/kg)	$\frac{\delta t}{\Delta t}$ %
1	20	Sample No. 1 argon screen	699.3	25.56	44.02	45.58	3.99
2	19	" " "	883.3	26.95	57.17	58.82	2.16
3	18	" " "	1010.7	27.34	66.85	68.53	2.81
4	17	" " "	1199.0	28.85	81.30	83.09	4.16
5	1	" vacuum	1327.4	29.95	91.33	93.19	3.77
6	12	Sample No. 3 argon	1432	27.70	99.75	101.51	2.57
7	3	" " screen	1446	27.99	100.89	102.66	2.47
8	4	" " "	1536	28.34	108.58	110.40	2.80
9	2	" " screen	1600	28.02	113.85	115.67	1.74
10	25	" vacuum	1629	28.75	117.04	118.91	4.44
11	5	" argon	1657	28.80	119.16	121.04	3.50
12	13	" " "	1690	29.19	122.53	124.45	3.56
13	6	" " "	1739	29.05	127.02	128.95	4.18
14	14	" " "	1780	28.87	131.07	133.01	4.39
15	26	" " screen	1788	27.41	131.83	133.70	2.85
16	8	" " "	1854	29.85	137.45	139.48	4.91
17	9	" " "	1900	30.06	142.40	144.46	4.23
18	15	" " "	1942	30.25	145.77	147.87	4.25
19	7	" " "	1954	30.53	148.25	150.37	5.18
20	27	Sample No. 3-4a argon	1970	28.20	149.60	151.63	2.35
21	24	Sample No. 4 vacuum	1985	28.44	149.37	151.44	2.89
22	16	" argon	2036	28.81	154.57	156.67	3.81
23	32	Sample No. 4b "	2046	27.29	156.67	158.72	1.41
24	10	" " "	2077	28.84	159.89	160.29	3.78
25	23	" vacuum	2106	28.60	161.30	163.47	5.40
26	30	Sample No. 4 argon	2165	28.21	168.72	170.95	2.80
27	11	" " "	2172	29.27	168.34	170.59	3.18
28	22	" vacuum	2235	28.80	175.79	178.10	6.89
29	21	" " "	2241	29.23	175.97	178.30	4.79
30	31	Sample No. 4b argon	2250	28.07	177.07	179.37	3.08
31	28	Sample No. 3-4a "	2257	29.26	178.73	181.03	3.67
32	29	" " "	2337	29.67	187.75	190.22	2.68

$t$  = temperature of sample in the furnace;

$t'_n$  = final temperature of the calorimeter with regard to the correction for heat transfer;

$i_t - i'_n$  = enthalpy counted out from  $t'_n$ ;

$i_t - i_{0^\circ\text{C}}$  = enthalpy counted out from  $0^\circ\text{C}$ ;

$\frac{\delta t}{\Delta t}$  = relative value of the correction for heat transfer between the calorimetric system and the shell.

measurement by a pyrometer, and an abrupt change in the slope of the smoothing curve of the dependence enthalpy upon temperature was not observed.

It was found on determining the enthalpy above  $2000^\circ\text{C}$  that the tungsten wires on which the sample was suspended in the furnace and the sample itself "stuck" to the molybdenum tube of the suspension, used in experiments for the investigation of corundum [4]. This was

particularly so in experiments carried out in vacuum.

To avoid this, a slightly modified sample suspension was used at temperatures above  $2000^\circ\text{C}$ . The arrangement of it is shown in Fig. 1 against a background of outlines of the tungsten heater (marked (1) in this figure). The sample (2) was suspended in the furnace on two tungsten wires (3), which, in turn, hung on two loops from the same tungsten wires, arranged on

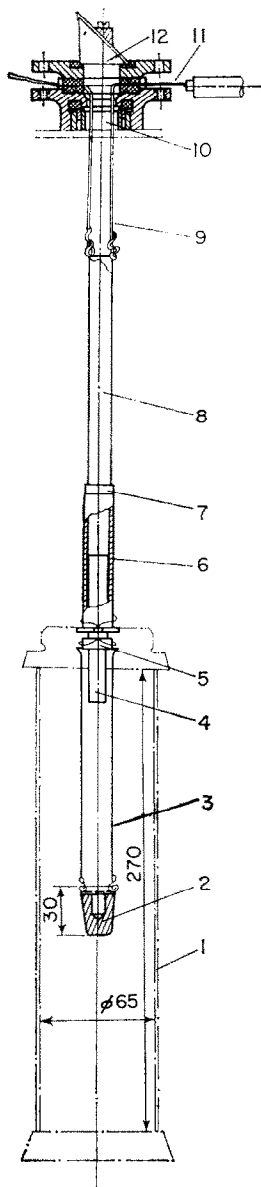


FIG. 1. Suspension of samples in the furnace at temperatures above 2000°C.

the graphite ring (5). The molybdenum tube (8) was shortened up to the lower end of the chuck (6) and the other shorter molybdenum tube (4) was inserted inside the first one to prevent fumes and gases (which sometimes accumulated

in the upper part of the furnace in experiments conducted in an argon medium) from falling into the field of vision of the pyrometer. The small surface of thermal contact between the molybdenum tubes (4 and 8) in the form of some support projections gave protection from burn-up to the mica insulation (7) between the tube (8) and the chuck (6). The burn-up of the loops took place on the graphite ring (5) to which these wires did not stick. The current for the burn-up of these wire loops was supplied from one side to the chuck (6) through the body of the apparatus, and from the other, through the copper wires (9) to the molybdenum tubes (8 and 4) and the ring (5).

Some of the first experimental results had a low temperature value when the enthalpy above 2000°C was determined in the argon medium. It turned out that this discrepancy in the temperature occurred because of fumes and gases which began to form in the furnace at temperature about 2000°C and higher. Entering the field of vision of the pyrometer these absorbed a part of the radiation and thus the measured temperature was lowered. To avoid this in further experiments carried out at these high temperatures the inspection channel (10) was cleared out by argon from above downwards (Fig. 1). Thus during the temperature measurement argon was supplied in a continuous jet from the balloon through the pressure regulator into a metallic tube (11) 1 mm in diameter at such a rate that fumes and gases should be completely removed from the field of vision of the pyrometer, while the sample itself and the furnace were not cooled. The metallic tube for the argon supply to the furnace, as well as the copper wires (9) on which the suspension hung, was sandwiched between two packings of a vacuum rubber. The packings were pressed by a flange attached to which was the glass prism having total internal reflexion (12), through which the sample in the furnace was observed.

The tests were carried out both in argon medium and in vacuum (see Table 1). Two conclusions may be derived from the agreement of the results of enthalpy determination obtained in vacuum and in an inert argon medium at 1.05 atm. Firstly, small gentle cleaning by the

argon jet, used at high temperatures was completely justified, as was proved by control test runs No. 21, 22, 23 carried out in vacuum at temperatures above 2000°C. Secondly, a considerable difference in the form of the temperature calorimeter curves in the main period of tests with vacuum and argon medium did not practically influence the results. This once more proved the conclusion obtained from the graduating tests specially carried out [4], that one may for practical purposes neglect both the thermal inertia of the calorimeter resistance thermometers and the difference in the temperature fields in the copper block which took place on graduating and measuring the enthalpy. Analogous conclusions have been reported elsewhere [6].

After the series of tests Nos. 1–11, covering the temperature range 1327–2172°C, thermal stabilization of the samples No. 1, 3 and 4 was made at 2050°C in a vacuum. For 3 h the samples were heated and then for 1½ h they were slowly cooled. After the thermal stabilization the tests were repeated. No divergence between the tests carried out before the thermal stabilization and after it was observed. Those tests that were carried out at the transition between high temperatures and lower ones also agreed (see the Table). Apparently, in the temperature range investigated there were no irreversible phenomena in the metal neither in essence nor due to quick cooling of a sample in the calorimeter.

During the thermal stabilization in vacuum the weight of the samples decreased by 1.6–1.8 per cent. In tests in a vacuum at temperatures above 1900–2000°C a decrease in the weight of the samples by approximately 0.5–0.6 per cent was also observed during a test due to metal evaporation. This evaporation led to some decrease in the glitter of the polished surface of the samples. During investigations in the argon medium the glitter of the polished surface of the samples was largely preserved. Sometimes, beginning at 1900°C, a very thin friable grey deposit appeared on the upper edge of the samples. This deposit was easily removed, and the samples were polished again before the next test run. Thus, some increase in the weight of the sample was observed because of formation

of the deposit in a number of tests carried out in argon at temperatures above 1600°C: however, at the highest temperatures of investigation, it did not exceed 0.09 per cent. The samples were weighed before and after the tests. The enthalpy was calculated on the weight of the samples after the test runs.

In a number of experiments (see Table 1) a molybdenum screen in the form of a cylinder was used for levelling the temperature field around the sample, which was located inside this cylinder. A good agreement between experimental points obtained with and without using the screen demonstrates that the temperature gradient over the height of the sample was small, and could be neglected.

In accordance with the methods of measurements applied the experiment was carried out in the following order. After the sample had been suspended in the furnace and centred by a plumb line relative to the vertical axis of the furnace, a temperature somewhat lower than 22°C was established in the calorimetric system with the help of a special cooler or heater, which could be introduced into the receiving channel of the copper block of the calorimeter. Then the calorimeter was hermetically attached to the furnace with bolts, the fore-vacuum pump was switched on to evacuate air from the apparatus, and the temperature was equal to that of the calorimetric system set in the thermostat. Thus, thermal conservation in the calorimetric system ready for an experiment was achieved.

When the experiment was carried out in neutral medium, the apparatus was filled with argon up to 1.05 atm after air evacuation. When the experiment was conducted in vacuum, an oil diffusion pump was used to obtain vacuum of the order of  $10^{-2}$ – $10^{-3}$  mmHg. When the corresponding medium in the apparatus had been prepared, the heater of the furnace was switched on and the temperature gradually raised to the given value. Simultaneously, the same temperature is regulated by the thermostat of the calorimeter, so that the relative value of the correction for heat transfer between the calorimetric system and the shell should not exceed 5 per cent from the amount of heat brought by the sample into the calorimeter (see Table 1).

In 10–15 min after the establishment of a constant temperature in the thermostat a first-class potentiometer of the type IIMC-48, with a mirror galvanometer of the type M 21/4, began to record the change in resistance of the two thermometers in the calorimeter, and the record lasted 30–40 min (initial period). Usually by this time the required temperature was established in the furnace and controlled by the thermocouple and pyrometer. The sample was thrown down into the calorimeter when the temperature of the system reached 22°C. Such an initial temperature at the main period was established in all the tests, including graduating ones using methods of measurements developed when carrying out the calorimetric procedure [4, 5].

Before the sample was thrown down the blind

of the special device, which protected the calorimeter from radiation from the furnace, opened and the current burned through the tungsten wire on which the sample was suspended. When the sample fell it passed the "flicker device" [4] which protected the calorimeter from radiation from the furnace when the blind is open, and the falling sample itself opened it for only a negligible period of time.

Before the sample fell into the calorimeter (10) the copper flaps (1) of the calorimeter cover were maintained by the spreaders (4) in the open position (for clearness the lever for closing the cover flaps of the calorimeter has been shown in Fig. 2 against the background of the calorimeter contours. After the sample fell into the calorimeter, the blind of the special blind device, not shown in Fig. 2, was shut quickly

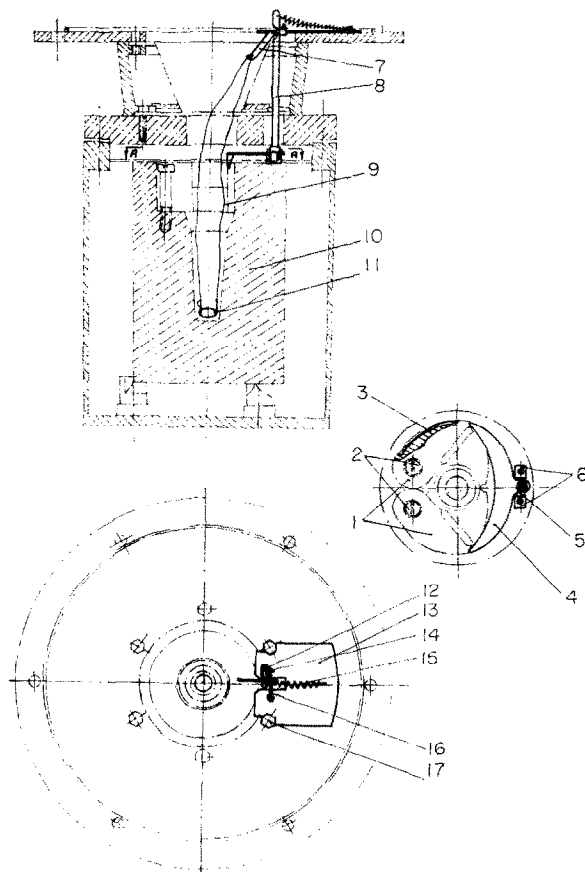


FIG. 2. Mechanism for automatic closing of the calorimeter flaps.

by hand. It touched by the projection the end of the Textolite lever (8) and turned it to the right together with the spreaders (4) around the axis (5) placed on two supports (6). The flaps (1) were released by the spreaders (4) and, rotating around their axes (2) under the action of the plate springs (3), they closed the calorimeter when the sample had fallen.

Since the time from the moment when the sample falls into the calorimeter till the flaps of the calorimeter shut does not exceed 1 s, according to calculation the heat loss by the sample could be neglected for the given construction of the calorimeter. Nevertheless, this assumption needed experimental verification. For this purpose a device was mounted on the plate (13), adjusted with the bolts (17), with the help of which the flaps of the calorimeter were closed automatically and nearly instantaneously when the falling sample hit the molybdenum disk (11). The effect of the falling sample passed through the tungsten wires (9) from the disk (11) to the lever (7). Turning around the axis (12) the lever (7) freed the latch (16), holding the lever (8), from the support (14). Because of the stretched spring, (15) the lever (8) turned together with the spreader (4) around the axis (5) freeing the flaps which shut immediately.

The experimental points obtained when the flaps shut automatically very quickly (test runs No. 32 at  $t = 2046^\circ\text{C}$  and No. 31 at  $t = 2250^\circ\text{C}$ ) agree with the experimental points obtained previously when the flaps were closed by hand. It should be noted that this comparison is made in the least favourable temperature range. From then onward, the tests were carried out only with automatic closing of the calorimeter flaps since this eliminated the possible influence of subjective factors on the results of tests especially at temperatures exceeding  $2000^\circ\text{C}$ .

The main and final periods of the calorimetric procedure lasted from 80 to 200 min depending on the conditions of an experiment (in argon or in vacuum). Particular attention was given to the correct determination of the end of the main period.

During the whole experiment a constant vacuum, or a pressure of 1.05 atm, was maintained in the apparatus.

Thirty-two experimental values for enthalpy

were obtained in the range from 700 to  $2337^\circ\text{C}$ . The results of investigation are given in Table 1. The enthalpy was counted out from  $0^\circ\text{C}$ . The change in the enthalpy from  $0^\circ\text{C}$  to the final temperature of the calorimeter was taken from data given by Kelley [9] with regard to corrections for heat transfer. An empirical equation for enthalpy and the true heat capacity of molybdenum were obtained on the basis of the experimental values for the temperature interval  $700\text{--}2400^\circ\text{C}$ :

$$i_t - i_{0^\circ\text{C}} = 0.05970t + 7.08 \times 10^{-6}t^2 + 7.7 \times 10^{-10}t^3 \quad (1)$$

$$c_p = 0.05970 + 14.16 \times 10^{-6}t + 23.1 \times 10^{-6}t^2 \quad (2)$$

where  $t$  is the temperature ( $^\circ\text{C}$ );  
 $i_t - i_{0^\circ\text{C}}$  is the enthalpy change from  $0^\circ\text{C}$  to the temperature  $t$  (kcal/kg);  
 and  $c_p$  is the true heat capacity (kcal/kg  $^\circ\text{C}$ ).

When converting absolute joules to calories the following conversion factor was adopted: 1 calorie = 4.1840 absolute joule.

The limiting relative error of calculation for the experimental determination of enthalpy was  $\pm 0.4$  per cent for the range  $700\text{--}1300^\circ\text{C}$ ,  $\pm 0.9$  per cent for  $1300\text{--}2000^\circ\text{C}$  and  $\pm 1.2$  per cent for  $2000\text{--}2400^\circ\text{C}$ .

Comparing experimental values obtained for the enthalpy of molybdenum with more trustworthy experimental results of Jaeger and Veenstra [2, 3] in the overlapping range  $700\text{--}1554^\circ\text{C}$ , it was found that in general the discrepancy did not exceed  $\pm 0.5$  per cent. In their investigations Jaeger and Veenstra used the method of mixtures as well as the massive calorimeter. In their investigation pieces of molybdenum practically free from admixtures were placed into a hermetically sealed platinum bulb. The experimental data of Wüst *et al.* [1] in the overlapping temperature range  $700\text{--}1500^\circ\text{C}$  are 3–8 per cent higher than our experimental data for enthalpy. Such high values in this work can be explained both by the non-accurate measurement of a sample temperature in the furnace (the temperature was measured by a thermocouple placed near the sample) and by possible admixtures in

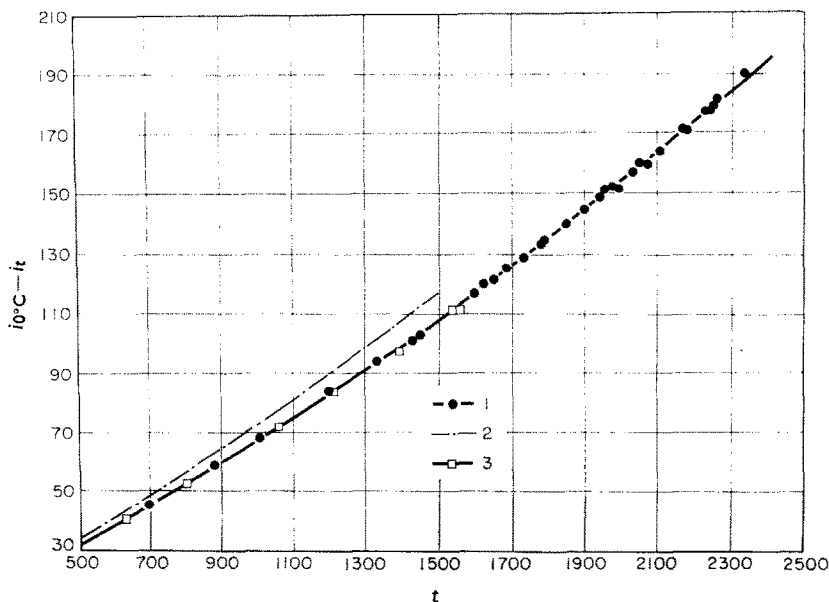


FIG. 3. Dependence of molybdenum enthalpy on temperature

1—authors' data,

2—data of Wüst, Meuthen, Durrer

3—data of Jaeger, Rosenbohm.

molybdenum, chemical analysis of which was not given. In the work by Redfield and Hill [10] the scatter of experimental values for the enthalpy of molybdenum at 200–1100°C was  $\pm 4$  per cent. Our experimental values agreed with other experimental data [10] within the limits of this scatter.

Experimental data on enthalpy and the smoothing curve calculated by equation (1) are given in Fig. 3 (solid line). For comparison data obtained by other investigators are given.

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**Аннотация**—Приведены результаты экспериментального определения энтальпии и теплоемкости молибдена в интервале температур 700–2337°C в виде таблицы, графика и уравнений. Опытные данные получены на экспериментальной установке, работающей по методу смещения при применении массивного калориметра с изотермической оболочкой. Образец нагревался до высокой температуры в печи с вольфрамовым нагревателем в вакууме или в среде аргона. В статье освещены некоторые вопросы методики экспериментального определения энтальпии при весьма высоких температурах. Результаты опытных данных сравниваются с данными других исследователей. Предельная случайная ошибка определения энтальпии при измерении температуры термомпарой (до 1300°C) оценивается в  $\pm 0,4\%$ , а при измерении оптическим пирометром с исчезающей нитью— $\pm 0,9\%$  до 2000°C и  $\pm 1,2\%$  до 2400°C.



**Résumé**—Les résultats expérimentaux donnant l'enthalpie et la capacité thermique du molybdène entre 700°C et 2337°C sont présentés sous forme de table, de diagramme et d'équations.

Les données expérimentales sont obtenues par la méthode des mélanges qui utilise un calorimètre massif dans une enceinte isotherme. L'échantillon est chauffé, à haute température, sous vide ou dans l'argon, dans un four à élément chauffant en tungstène. Cet article décrit aussi quelques méthodes de détermination expérimentale de l'enthalpie aux très hautes températures. Les résultats sont comparés à ceux de la littérature.

Pour la détermination de l'enthalpie, l'erreur limite est de  $\pm 0,4\%$  en utilisant un thermocouple pour la mesure des températures jusqu'à 1300°C et  $\pm 0,9\%$  et  $1,2\%$  en utilisant un pyromètre optique à extinction de filament pour les températures allant jusqu'à 2000°C et 2400°C.

**Zusammenfassung**—Die Ergebnisse experimenteller Untersuchungen der Enthalpie und der spezifischen Wärme von Molybdän zwischen 700°C und 2337°C sind als Tabellen, Diagramme und Gleichungen angegeben. Die Werte wurden nach der Mischungsmethode in einem massiven, isotherm umhüllten Kalorimeter erhalten. Die Erwärmung der Proben auf hohe Temperaturen erfolgte mit Hilfe einer Wolfram-Heizung im Vakuum oder in Argon-Atmosphäre. Einige Methoden der experimentellen Enthalpiebestimmung bei hohen Temperaturen werden besprochen und die Ergebnisse mit jenen der Literatur verglichen. Bis 1300°C ist die Enthalpie mit einer Messunsicherheit von  $\pm 0,4\%$  ermittelt, wobei die Temperatur mit Thermoelementen gemessen wurde; für 2000°C bzw. 2400°C ergab sich ein Fehler von  $\pm 0,9$  und  $\pm 1,2\%$  bei Verwendung eines Glühfadenpyrometers.