Physical Chemistry

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1961

SovietRxiv

Abstract

Full Text

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EXPERIMENTAL DETERMINATION OF THE ENTHALPY OF MOLYBDENUM AT TEMPERATURES OF 700-2337°

Molybdenum is one of the refractory metals that has recently found ever wider application in many high-temperature devices. Nevertheless, its enthalpy and heat capacity have been studied only up to temperatures of the order of 1500° ([1–3]). In the present work, the enthalpy of molybdenum was determined in the temperature interval 700-2337° on an experimental apparatus operating by the method of mixtures with the use of a massive calorimeter with an isothermal jacket ([4–6]). The molybdenum specimen was heated to a high temperature in a furnace with a tungsten heater. The calorimeter and furnace, separated by a cooled shutter device, formed a common volume hermetically isolated from the air; during the experiments this volume either was under a vacuum of about 10^{-3} mm Hg or was filled with argon at a pressure of 1.05 ata. This made it possible to protect the specimens under investigation and the heater from oxidation.

The temperature of the calorimetric system was measured simultaneously by two platinum resistance thermometers. One of these thermometers was wound bifilarly on the side surface of a copper block, and the second—in the form of a spiral of platinum wire—was wound bifilarly on a copper helicoidal frame that was tightly inserted into a blind hole 3.3 mm in diameter in the block. The resistance thermometers were connected in series, and their resistance was measured with a first-class potentiometer of the PMS-48 type paired with a mirror galvanometer of the M21/4 type. The measurement circuit used ensured sensitivity in measuring the resistance of the thermometers down to the unit of the sixth digit.

The constancy of the temperature of the jacket of the calorimetric system was maintained by a photorelay with an accuracy of $\pm 0.001°$. Ampoules were not used in the investigation, taking into account the particular features of determining enthalpy by the method of mixtures at high temperatures ([5,6]). The heat losses of the specimen during its fall into the calorimeter were calculated from the known coefficient of total radiation of molybdenum ([7,8]). In the present

case, this method of determining the heat losses of specimens during the fall leads to a smaller error of investigation than in the case of using ampoules.

The specimens were machined from molybdenum rods obtained by powder metallurgy. The amount of impurities in the specimens, according to semiquantitative spectral analysis, did not exceed 0.04-0.05%. The specimens had the shape of a truncated cone, matching in dimensions the axial recess in the calorimeter. The surface of the specimens was carefully polished. The enthalpy of molybdenum was determined on five specimens, which had masses of about 120, 90, or 60 g. Owing to this, in each case an optimal rise of the temperature of the calorimetric system was achieved throughout the entire temperature interval 700-2340°.

The temperature of the specimens up to 1327° was measured with standard platinum–platinum-rhodium thermocouples of the second grade, the hot junction of which was placed at the center of the specimen. Higher specimen temperatures were measured with an optical disappearing-filament pyrometer; in this case a model of an absolutely black body was created in the specimen. For this purpose a cavity was used, drilled along the axis of the specimen, which was closed at the top by a molybdenum disk having a 2.3 mm diameter hole for sighting the pyrometer. On the bottom of the cavity, fine mutually intersecting notches were made with a steel point, or a layer of fine molybdenum powder was poured on, in order to obtain diffuse reflection of the radiation.

It should be noted that in some preliminary experiments for determining the enthalpy in an argon atmosphere at temperatures above 2000°, underestimated values of the experimental data were obtained because of vapors and gases entering the field of view of the pyrometer. Subsequently, in experiments carried out at temperatures above 2000°, a slight purge of the space between the specimen and the pyrometer with argon was used in order to remove these vapors and gases. This fully justified itself: control experiments carried out in vacuum at temperatures of 2106, 2235, and 2241° agree well with the experimental data obtained when purging was used and the apparatus was filled with argon.

In addition, the design of the specimen suspension in the furnace was changed ([5]), since at 1900–2000° and above, especially in vacuum, sticking of the specimen and of the tungsten wires on which the specimen was suspended to the molybdenum tube of the suspension was observed. In the modified suspension the molybdenum tube was shortened, and the tungsten wires, at the place where they were heated by electric current, were suspended on a graphite ring located in the cold zone of the furnace. The wires did not stick to the ring.

After 11 experiments covering the temperature interval $1327 \div 2172°$, thermal stabilization of the molybdenum specimens was carried out at 2050° in vacuum. The specimens were heated for 3 hours and then cooled for one and a half hours. After thermal stabilization the experiments were repeated. No discrepancies were observed between the experiments carried out before thermal stabilization and after it. Within the permissible experimental error, the experiments ob-

tained on going from high temperatures back to low ones also coincided, as did the experiments carried out in vacuum and in argon.

In experiments at temperatures of 699.3; 1446; 1600, and 1788°, the specimens under study were placed in a molybdenum cylinder 26 mm in diameter and 100 mm high, in order to equalize the temperature field over the height of the heater. The experimental data obtained with and without the use of the molybdenum cylinder agree well with one another. This gives grounds for assuming that the temperature gradient over the height of the specimen is sufficiently small and does not introduce a significant error into the measurement of the specimen temperature.

At the moment when the shutter device for dropping the specimen was opened, the calorimeter was protected from heat radiated from the furnace by an additional shutter in the form of a blinker, the design of which is described in ([5]). The blinker opened only for an instant for the falling specimen.

The leaves of the calorimeter lid closed after the specimen had fallen, approximately one second later, by means of a lever mechanism actuated by the manually closing shutter of the shutter device. The heat loss during the time from the moment the specimen fell into the calorimeter until the moment the leaves closed, according to a calculation for the given calorimeter design, should be negligible. To verify this, a device was constructed which actuated the lever mechanism closing the leaves from the impact of the fallen specimen, i.e., almost instantaneously. The check showed that the experimental points obtained with automatic closing of the leaves coincided with the previously obtained experimental points in the case of manual closing of the leaves. Nevertheless, in subsequent experiments only automatic closing of the leaves was used.

period, since this eliminated possible influence of subjective factors on the experimental results.

The results of the experiments are given in Table 1. In all, 32 experimental points were obtained. Enthalpy was counted from 0°. In processing the experiments it was assumed that 1 cal = 4.1840 absolute joules.

Table 1

Experimental data on the enthalpy of molybdenum

No.	Temp., °C	$i_t - i_0^\circ$C, kcal/kg	No.	Temp., °C	$i_t - i_0^\circ$C, kcal/kg	No.	Temp., °C	$i_t - i_0^\circ$C, kcal/kg
1	699.3	45.58	12	1690	124.45	23	2046	158.72
2	883.3	58.82	13	1739	128.95	24	2077	160.29
3	1010.7	68.53	14	1780	133.01	25	2106	163.47
4	1199.0	83.09	15	1788	133.70	26	2165	170.95
5	1327.4	93.19	16	1854	139.48	27	2172	170.59
6	1432	101.51	17	1900	144.46	28	2235	178.10

No.	Temp., °C	$i_t - i_0^\circ$C, kcal/kg	No.	Temp., °C	$i_t - i_0^\circ$C, kcal/kg	No.	Temp., °C	$i_t - i_0^\circ$C, kcal/kg
7	1446	102.66	18	1942	147.87	29	2241	178.30
8	1536	110.40	19	1954	150.37	30	2250	179.37
9	1600	115.67	20	1970	151.63	31	2257	181.03
10	1629	118.91	21	1985	151.44	32	2337	190.22
11	1657	121.04	22	2036	156.67			

The maximum relative random error of the experimental determination of enthalpy does not exceed ±0.4% when temperature is measured with a thermocouple, and when a pyrometer is used, ±0.9% for the temperature interval 1300—2000° and ±1.2% for 2000—2400°.

The experimental points of Jaeger and Veenstra ([2,3]) in the overlapping temperature range 700—1554° agree with the newly obtained points within ±0.5%. The experimental data of Wüst et al. ([1]) lie above the obtained data by 3—8%, evidently because of insufficient accuracy in measuring the temperature of the samples and contamination of the molybdenum, for which no chemical analysis is given. Redfield and Hill ([9]) determined the enthalpy of molybdenum in the temperature interval 200—1100°, with a scatter of the experimental points of ±4%. Within this scatter there is agreement of the obtained experimental points with the data of ([9]).

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Received
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Note: Figure translations are in progress. See original paper for figures.