hexanol are partially soluble in water [0.6 part/100 water for 1-hexanol and 3.6 parts for cyclohexanol at 20°C (*2*)]. Both cyclohexanol and 1-hexanol have some ability to form hydrogen bonds with water. Again, the cyclic structure is more soluble in water than the straight chain.

Tie lines in the last two systems slope in the opposite direction to the first four systems described. Both cyclohexanol and 1-hexanol have OH groups. Pyridine, being an organic dipole, can associate both with the hydrophilic OH group in the alcohols and with their hydrophobic hydrocarbon chains making cyclohexanol and 1-hexanol better competitors for pyridine than water.

ACKNOWLEDGMENT

D.W.R. wishes to acknowledge the granting of sabbatical leave by the Brooklyn Center of Long Island University during which time these results were prepared for publication. The authors also wish to acknowledge the preliminary data gathered by D. L. Thompson in this laboratory on the systems pyridine-water-*n*-hexane and pyridine-water-cyclohexane.

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RECEIVED for review May 24, 1971. Accepted December 7, 1971.

Enthalpy of Molybdenum and Tantalum from 298–1400K

FRANKLIN L. OETTING and JAMES D. NAVRATIL
The Dow Chemical Co., Rocky Flats Division, P.O. Box 888, Golden, Colo. 80401

High-temperature enthalpies from 298–1400K for molybdenum and tantalum have been determined by a copper block drop calorimeter of the isoperibol type. Agreement between these experimental results and certain compilations in the literature is satisfactory.

During the course of investigating the high-temperature thermodynamic properties of nuclear materials, it was necessary to encapsulate certain of these nuclear materials with either molybdenum or tantalum so that the materials would be compatible with the high-temperature drop calorimetric experiments.

It was therefore necessary to correct the experimental enthalpy measurements for the enthalpy of the encapsulating material. Examination of the enthalpy data available on either molybdenum or tantalum revealed that several choices were possible for the respective enthalpies, differing by several percent. Because of the need for comparatively accurate enthalpy values for the encapsulating materials in order to define accurately the enthalpy of the specific material being investigated, enthalpies of both molybdenum and tantalum in our calorimeter were determined.

EXPERIMENTAL

Calorimeter. The calorimeter used for these enthalpy measurements was a copper block drop calorimeter of the isoperibol type where the enthalpies measured were relative to 25°C (298.15°K). The furnace was a platinum 10% rhodium resistance type where the limiting factor for the highest attainable temperature was the melting point of the furnace resistance winding, 1650°C. The apparatus is operated in an air environment necessitating the outermost capsule to be platinum. It is the incompatibility of certain nuclear materials with platinum at the higher temperatures that requires additional encapsulation of molybdenum or tantalum. The detailed description of this apparatus, as well as the calculation of the temperature rise of the calorimeter, may be found elsewhere (*7*). The reliability of the calorimeter was periodically checked by measurements on the calorimetric standard, aluminum oxide. The standard deviation of these Al_2O_3 enthalpy results was not more than ±0.2% from those reported by the National Bureau of Standards (*7*).

Materials. The molybdenum and tantalum used in this study were in the form of hollow closed cylinders where the tops and bottoms were attached by electron beam welding. The size of these metal cylinders was such that they would slip-fit into a platinum capsule (2.5 cm high; 2 cm o.d.; 0.025 cm wall thickness) which, in turn, was sealed under 200-torr helium pressure by heliarc oxygen-acetylene welding. The molybdenum and tantalum capsules also had a wall thickness of 0.025 cm and weighed 9.2283 grams and 11.5739 grams, respectively.

Emission spectrographic analyses, capable of detecting some 40 metallic elements, as well as oxygen, carbon, and nitrogen, indicated 199 ppm of impurities for molybdenum and 186 ppm of impurities for tantalum. Enthalpy corrections for the impurities were not made on either sample; therefore, both metals were considered to be 100% pure, although in actuality both had a purity of 99.98%. There is no significant error involved in not making the enthalpy correction for the impurities.

RESULTS

A total of 11 drop experiments were taken on molybdenum over the temperature range of 696.36–1380.70°K (all temperatures are based on IPTS-1968). Eight drop experiments were taken on tantalum over the temperature range of 533.76–1383.37°K. The experimental molar enthalpy results are given in Table I (cal = 4.184 J) as well as the smoothed enthalpy results at each experimental temperature. The smoothed results are taken from the Shomate equation (*8*) which connects the high temperature data with existing thermo-

Table I. Experimental Enthalpy Values for Molybdenum and Tantalum

$T°$, K	$H_T° - H_{298}°$ (obs), cal/mol	$H_T° - H_{298}°$ (calcd), cal/mol	Diff, cal
	Mo		
696.36	2437	2470	−33
739.51	2744	2748	−4
786.84	3085	3054	+31
821.79	3312	3281	+31
884.57	3734	3691	+42
915.90	3860	3896	−36
990.45	4453	4385	+68
1034.51	4614	4676	−62
1138.19	5318	5362	−44
1178.85	5583	5632	−49
1380.70	7036	6981	+55
	Ta		
533.76	1466	1468	−2
650.86	2220	2221	−1
774.24	3044	3028	+16
881.58	3724	3741	−17
996.93	4534	4519	+15
1135.20	5438	5466	−28
1264.58	6408	6368	+40
1383.37	7184	7208	−24

dynamic data at 298°K. The solution of the Shomate equation which expresses the enthalpy is:

$$H_T° - H_{298}° = a + bT + cT^2 + dT^{-1}$$

and its derivative which expresses the heat capacity,

$$C_p° = b + 2\,cT - dT^{-2}$$

is based on the two boundary conditions:

$$H_T° - H_{298}° = 0 \text{ when } T = 298.15°\text{K}$$

and

$$C_p° = C_{p_{298}}° \text{ when } T = 298.15°\text{K}$$

These two conditions force the high-temperature data to fit the existing low-temperature data.

The enthalpy equation for molybdenum is given by

$$H_T° - H_{298}° = -2134.3 + 6.384\ T + 1.332 \times 10^{-4}\ T^2 + 6.529 \times 10^4 T^{-1} \text{ cal/mol} \quad (1)$$

and the equation for tantalum is given by

$$H_T° - H_{298}° = -1867.4 + 5.975\ T + 4.179 \times 10^{-4}\ T^2 + 1.452 \times 10^4\ T^{-1} \text{ cal/mol} \quad (2)$$

of which both equations are applicable over the temperature range of 298–1400°K.

The standard deviation of the molybdenum results is ±54 and ±31 cal for the tantalum results when compared to the smoothed curve. It must be noted that these deviations are comparatively large for this calorimeter; however, this is attributed to the sample container ratio, as the encapsulating platinum accounted for over 50% of the measured enthalpy.

DISCUSSION

Molybdenum. The high-temperature thermodynamic properties of molybdenum have been compiled by Stull and Sinke (*9*) and by the JANAF Thermochemical Tables (*5*). The compilation of Hultgren et al., (*2*) is identical to that of Stull and Sinke. The enthalpy values listed for molybdenum in the first two compilations differ by a little more than 1% from 400–1400°K where they join and list nearly identical values. However, the JANAF Tables list several additional references since it was published some 10 years after the compilation by Stull and Sinke. Thus, by inclusion of additional data, the spread in the reported enthalpy values is noticeably increased. Since the JANAF values are the average values of numerous data, and since the values listed by Stull and Sinke were based only on early data, there existed the possibility that either compilation, or both, could possibly be in error.

The smoothed enthalpy values reported in this work on molybdenum do not deviate more than ±0.3% from the values compiled by the JANAF tables from 400–1000°K. From 1000–1400°K, our values tend to become negative by a little over 1% when compared to the JANAF values.

Tantalum. The available enthalpy data for tantalum are in the compilations of Hultgren et al. (*3*) and Stull and Sinke (*10*). Both works rely heavily upon the enthalpy measurements of Hoch and Johnston (*1*) who determined the enthalpy of tantalum from 1400–3000°K. Hultgren et al. extrapolated the experimental enthalpy data of Hoch and Johnston from 1400°K to room temperature. Stull and Sinke, on the other hand, included the early work of Jaeger and Veenstra (*4*) and Magnus and Holzmann (*6*) in their compilation. Comparison of the listed enthalpy data in these two compilations indicates a difference of as much as 2% in the temperature range of 298–1400°K.

Comparison of our smoothed enthalpy values for tantalum with the two compilations shows that the agreement is very good with the tabulated values of Stull and Sinke (*10*) at the lower temperatures. Comparison of our value at the higher temperatures with the experimental values of Hoch and Johnston (*1*) indicates our values to be about 1% higher.

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Received for review June 18, 1971. Accepted October 23, 1971. Work performed under U.S. Atomic Energy Commission Contract AT (29-1)-1106.