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HEAT CAPACITY OF MOLYBDENUM

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REACTOR EXPERIMENTAL ENGINEERING DIVISION

HEAT CAPACITY OF MOLYBDENUM

T. A. Redfield
J. H. Hill

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CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
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SUMMARY

Using a Bunsen ice calorimeter, measurements were made of the changes in enthalpy of molybdenum in the temperature range 200° to 1100°C. The heat capacity was then derived from the enthalpy measurements and found to be 0.0675 calories per gram - degree centigrade over the temperature range investigated. The accuracy of results was determined to be within 5% based on an initial calibration of the equipment using a standard sapphire sample which was obtained from the National Bureau of Standards.

INTRODUCTION

The purpose of this investigation was to measure the heat capacity of molybdenum with an accuracy of better than 5% over the temperature range 200° to 1100°C. This necessitated the experimental determination of the enthalpy-temperature relationship for molybdenum with an accuracy of approximately ± 4%.

METHOD AND PROCEDURE

The method and apparatus are described in detail in ORNL-1040, "The Design and Construction of an Ice Calorimeter", dated June 12, 1951. In brief, the procedure consists of heating the sample, which is sealed in a heat resistant container, to a known temperature in an electric furnace, and then dropping it into an ice calorimeter containing a water-ice mixture. A density change results in the calorimeter due to the melting of ice by heat released from the sample. Since the densities of ice and water are different at 0°C, there is associated with any change in the heat content of the two phase system a proportional change in the total volume of the two phase system. The proportionality constant is calculated from the heat of fusion of water and densities of ice and water at 0°C, and is found to be approximately 880 cal/cc volume change. The volume change is measured on a burette system connected to the calorimeter, and, using the above relation, is converted into heat evolved by the sample in cooling to 0°C. Knowing the relative enthalpy of the container material as a function of temperature, the relative enthalpy of the sample is readily calculated. By repeating the process at a number of temperatures, the heat capacity of the sample can be derived from the defining equation,

$$\left(\frac{\partial H}{\partial T}\right)_p = Cp$$

In this investigation two samples of known weight were machined to fit in 316 stainless steel capsules which were sealed by means of heliarc welds. The capsules with enclosed samples were weighed prior to each run and were alternated. The weight of each sample was assumed to remain constant with all of the weight change occurring in the stainless steel container. Care was taken to allow the capsule temperature to reach an

equilibrium state before it was dropped. The rate of heat leak into the calorimeter was determined prior to dropping to provide an end point after the drop.

Capsule temperatures were measured by a platinum-platinum-10% rhodium thermocouple. At temperatures above 500°C an inert atmosphere of argon was maintained in the furnace to minimize oxidation of the stainless steel capsules. In order to preclude the formation of an appreciable oxide layer and subsequent flaking, capsules were buffed down after each run at the higher temperatures.

RESULTS

The relative enthalpy of molybdenum as a function of temperature using 0°C as a base is shown graphically in Figure 1. The following empirical expression for relative enthalpy change as a function of temperature was determined by the method of least squares.

$$H_t - H_o = 0.0675\ t - 0.37 \quad (200^\circ C \leq t \leq 1100^\circ C)$$

where, t is the temperature in °C.

$H_t - H_o$ = enthalpy change from 0°C to temperature t in calories/gm.

The first derivative of the above expression gives the heat capacity of molybdenum as follows:

$$C_p = \frac{\partial (H_t - H_o)}{\partial t} = 0.0675$$

where, C_p is the heat capacity in calories/gm-°C

DISCUSSION OF RESULTS

Heat capacity results obtained agree closely with those previously reported on molybdenum, particularly in the temperature range 400° to 600°C. A comparison of values for different temperatures is given in Table I.

A linear relationship between enthalpy and temperature was assumed, since a plot of the relative enthalpy values versus temperature in the range 200° to 1100°C was linear within the limits of experimental error.

Several sources of error were ignored in enthalpy determinations since errors were known to be small and not subject to easy quantitative evaluation. Errors due to heat leak and to radiation and convection losses during the dropping process should tend to cancel similar errors present in the stainless steel determinations, with the result that errors in the molybdenum data should be small. Errors introduced by accuracy limitations on temperature and volume readings, evaporation in the burette system, corrosion of capsule and sample, and weighing errors were negligible, considering the accuracy desired. The possibility of any significant error due to impurities in the molybdenum was

eliminated by a spectrographic analysis of the samples after completion of the experimental work. This analysis showed a trace of iron as the only impurity present in the samples.

Previous calibration of the equipment, using a standard sapphire sample obtained from the National Bureau of Standards, had shown that the equipment was capable of better than 95% accuracy in heat capacity determinations, indicating that the net effect of all the above errors introduced less than a 4% error in the values of relative enthalpy.

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TABLE I

MOLYBDENUM - RELATIVE ENTHALPIES

Temperature °C	$H_t - H_o$ cal./gram
208.0	14.69
215.5	14.51
226.0	14.57
244.0	15.31
267.5	16.82
320.0	19.48
353.0	24.62
401.5	26.69
425.0	28.69
449.5	29.51
478.5	32.34
502.0	32.39
553.5	37.03
595.0	39.21
622.1	41.71
663.0	43.86
688.6	44.78
699.2	48.76
743.0	49.37
767.0	52.21
810.0	55.07
834.0	54.70
871.0	58.70
908.0	61.59
940.5	62.50
978.0	65.10
991.4	65.78
1032.0	68.50
1036.0	68.20
1075.3	73.95
1086.0	72.90

TABLE II

COMPARISON OF RESULTS WITH THOSE PREVIOUSLY REPORTED

Temperature °C	C_p (cal/gm-°C)	C_p (cal/gm-°C) Previously Reported*	Percent Deviation
200	0.0675	0.0637	+ 5.9
400	0.0675	0.0664	+ 1.7
600	0.0675	0.0689	- 2.0
800	0.0675	0.0715	- 5.6
1000	0.0675	0.0742	- 9.0

* K. K. Kelly, Bureau of Mines Bulletin 476, "High Temperature Heat Content, Heat Capacity, and Entropy Data for Inorganic Compounds".

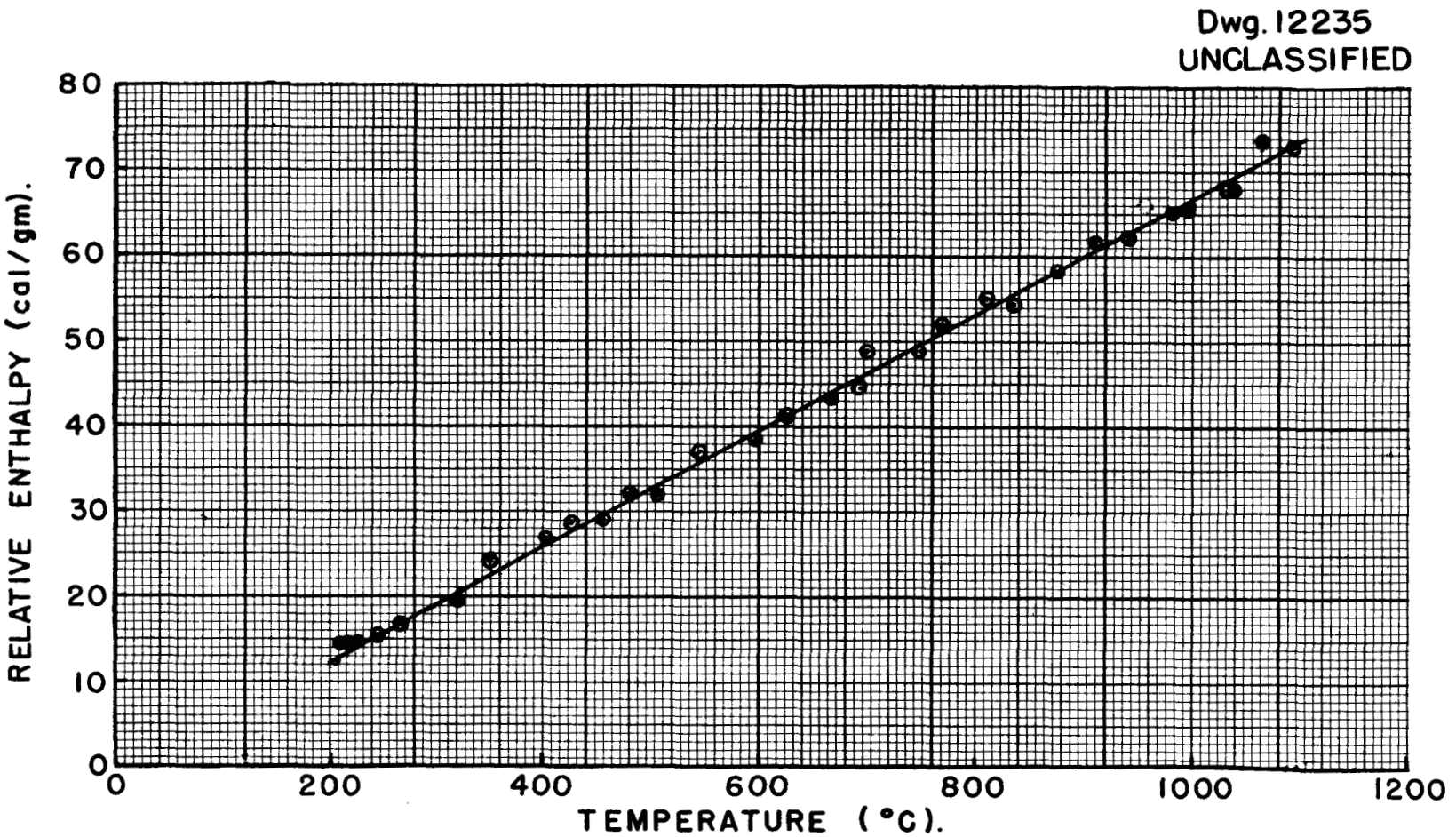

FIGURE 1. MOLYBDENUM - RELATIVE ENTHALPY AS A FUNCTION OF TEMPERATURE.