Heats of Fusion and Transformation for Some Metals and Compounds

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The heats of fusion and allotropic transformation for Ca, Ce, Mg, Pb, Sn, Zn, $CaMg_2$, $MgZn_2$, CeZn, $CaZn_2$, $CaCl_2$, and $ThCl_4$ were measured with an adiabatic calorimeter and the results presented.

A COMMERCIAL ADIABATIC CALORIMETER marketed by the Rigaku-Denki Co. Ltd., Tokyo, Japan, was employed in the measurement of the heats of fusion and transformation of a number of pure metals and compounds. The apparatus, generally, is referred to as an SHM and DTA apparatus since it can be employed for specific heat measurements (SHM) or for differential thermal analysis (DTA). In the SHM operation of the calorimeter, the specimen is heated at a constant wattage by means of a small resistance heater inserted in the specimen while, ideally, adiabatic conditions are maintained between the sample and a surrounding nickel sphere. The temperature of the sphere is adjusted automatically by controlling the power input to external furnace windings. A similar apparatus has been employed by Mukaibo *et al.* (*8, 9*) in the determination of the specific heat of uranium carbide and in the determination of the heat of oxidation of UO_2 to U_3O_7 and to U_3O_8. Some of the early developmental work on this calorimeter was carried out by Nagasaki and Takagi (*10*).

In the present work, heats of fusion and transformation were of primary interest and no attempt was made to evaluate the heat capacity of the materials studied. The heats of fusion of a number of pure metals were measured and compared with previously reported values. These data were helpful in evaluating the performance of the calorimeter and in estimating the uncertainty in the measurements made. Other tests were conducted, also, to evaluate the performance and reliability of the calorimeter.

EXPERIMENTAL PROCEDURE AND MATERIALS

The general arrangement of specimen and thermocouples in the calorimeter employed in this investigation is shown in Figure 1. The sample, 1, was enclosed in a welded tantalum crucible, 2, 1.0 inch in diameter by 1.5 inches high. The sample was heated by a Kanthal resistance heater, 9, wound on a four-hole alundum thermocouple insulator; the lower half of the winding shown is nickel lead-wire which was incorporated in the heater design to minimize heat loss along the lead-wires. The heater-well was made from a 1/4-inch diameter tantalum tube closed at one end and welded to the base of the tantalum crucible at the open end. The crucible was surrounded by a platinum radiation shield, 5, and was electrically insulated from the shield and from the grounded nickel sphere. The sample temperature was measured by a chromel-alumel thermocouple, 13, spot welded to the tantalum crucible. The temperature difference between the nickel sphere and the base of the platinum radiation shield was measured by a differential thermocouple, 14; one junction was spot welded to the shield and the other was embedded in Sauereisen cement in a small hole in the wall of the nickel sphere. The differential e.m.f. between these two junctions was automatically controlled to within ±3 μv. which corresponds to a temperature variation of ±0.08° C.

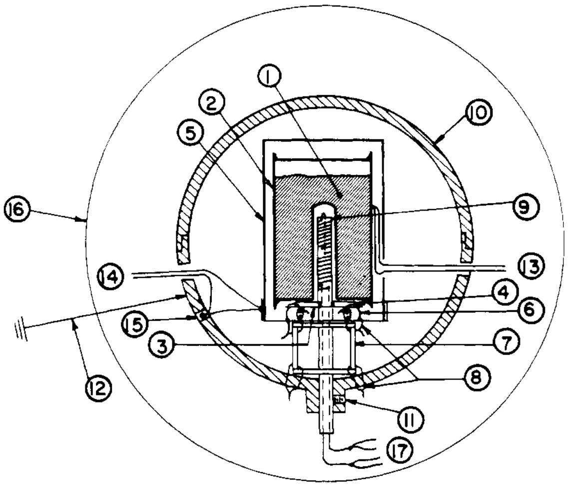

Figure 1. Details of adiabatic calorimeter

1. Sample
2. Tantalum crucible
3. Nickel base plate
4. Insulating spaghetti (0.060-inch diameter)
5. Platinum radiation shield
6. Insulating spaghetti (0.150-inch diameter)
7. Quartz stand
8. Nickel binding wire
9. Internal heater
10. Nickel adiabatic ball (three-inch diameter)
11. Set screw
12. Adiabatic ball ground wire
13. Temperature measuring thermocouple
14. Differential thermocouple
15. Ball junction of differential thermocouple
16. External furnace
17. Nickel heater leads

The control of this differential e.m.f. did not ensure adiabatic conditions, or negligible heat exchange between the nickel sphere and the sample, and the magnitude of the heat exchange was sensitive to the placement of the two junctions of the differential couple. These observations indicated that the temperature was not uniform over the surface of the platinum radiation shield. Consequently, maintaining the two junctions of the differential couple at the same temperature did not assure adiabatic conditions. This difficulty was overcome by inserting a variable microvoltage source ("bucking pot or bias-potentiometer") in

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series with the output of the differential thermocouple. With this arrangement it was possible, by adjusting this microvoltage source, to reduce the heat exchange between the sample and its surroundings to a negligible amount. In operation, this was accomplished by shutting off the constant power input to the specimen and observing the change in sample temperature with time while the adiabatic control section of the apparatus was operative. If, with the differential couple e.m.f. equal to zero, the average temperature of the nickel sphere was hotter than the average temperature of the platinum shield, a slow gradual increase in sample temperature was observed; a slow decrease in temperature was observed for an inverse average temperature difference. The μv. bias-potential was adjusted until the temperature drift was considered negligible. In measuring the heat of fusion of a material, this adjustment was made at two temperatures, one 15 to 25 degrees below and one 15 to 25 degrees above the melting temperature. In subsequent determinations, a mean bias potential setting, considered appropriate for the melting temperature, was employed. The apparatus was set to measure the time, at constant power input to the sample, required to raise the sample temperature 2° C. The time for each 2° C. temperature rise as a function of sample temperature was automatically recorded on a strip chart recorder. In some of the samples melting occurred over a small temperature range, and the recorded base line for temperatures above and below the melting temperature was helpful in correcting the total heat input during fusion for the heat required to raise the sample temperature. The same procedure was employed in measuring heats of transformation. Details on the operation of the various control units have been described elsewhere (*3*).

Although the calorimeter could be adjusted, by means of the bias potentiometer setting, to give negligible heat exchange between the sample and the surrounding nickel sphere, as described above, the assumption could not be made that conditions remained adiabatic after the sample-heater power was turned on. To check possible deviations from adiabatic conditions, the heat of fusion, as a function of sample-heater power setting, was measured for zinc, $CaZn_2$, and $CaCl_2$. Extrapolation of the data to zero power gave the true heat of fusion. These data permitted an evaluation of the uncertainty for heats of fusion obtained at a given power setting. The power setting normally used was in the range of 0.9 to 1.2 watts.

Some properties of the materials investigated are summarized in Table I. The metal samples were machined from ingot stock to fit the tantalum crucible. In the case of intermetallic compounds and the salts, the desired amount of sample, in the form of lumps, was charged into a longer tantalum crucible with heater-well welded in place. The crucible was sealed by arc-welding on a preformed cap under an argon atmosphere. The charge was heated then in a furnace to above its melting point to consolidate it around the heater-well; the top empty portion of the tantalum container was cut off and the crucible again resealed with a new tantalum cap to give essentially the sample-crucible configuration shown in Figure 1.

RESULTS AND DISCUSSION

The results obtained, along with literature values for comparison, are summarized in Table II. Double entries are made for calcium, cerium, and $ThCl_4$, and the heat of fusion and heat of allotropic transformation are given for each. Assessing the uncertainties in the values obtained in the absence of standards or reference materials with well defined heats of fusion is difficult. Presumably, some of the pure metals chosen should be good standards. However, a search of the literature indicates considerable uncertainty in their heats of fusion and the basis for the accepted values is somewhat arbitrary. In assessing available data for tin, Stull and Sinke (*14*) select 1720 cal. per gram-atom for the heat of fusion whereas Hultgren, *et al.* (*5*), in a somewhat more recent evaluation, give 1670 cal. per gram-atom. In neither case is a probable error assigned to the value selected. The latter authors do give an estimate of the uncertainty in some of their selected values, for example bismuth, magnesium, and zinc were assigned the uncertainties shown in Table II. In general, the data obtained in the present work do not show any trend relative to the accepted values, some are higher and some are lower than the literature values. Maintaining

Table I. Source of Materials and Purity

Material	Source	Chemical Analyses, P.P.M.[a]
Al	Reynolds Metal Co., 99.99+% pure	
Bi	Oak Ridge National Lab., 99.999% pure	
Ca	Ames Laboratory, 99.9+% pure	C-200, N-50, O-100, Fe-5, Mg-250
Ce	United Mineral and Chemical Corp., 99.5% pure	Electron beam melted; Ca-50, Cu-50, Mg-400, Fe-300, Si-300, O-300, N-5, H-5
Mg	Ames Laboratory, 99.9+% pure	N-13, C-195, Trace Si, Mn, Fe, Al, Cu, and Ca
Pb	Cominco Products Inc., 99.999% pure	
Sn	Leytess Metal and Chemical Corp., 99.999% pure	
Zn	Bunker Hill, 99.99% pure	
$ThCl_4$	Ames Laboratory, 99.8% pure	C-35, O-1050, N-40, Al-50, Cr-140, Fe-50, Ni-30
$CaCl_2$	J. T. Baker Chemical Co. Reagent grade dried under HCl	

[a] Carbon and nitrogen analyses were determined by combustion and Kjeldahl methods, respectively. Metallic impurities were determined either by spectrographic or chemical analyses. Oxygen, hydrogen, and nitrogen for cerium were determined by the vacuum fusion method. In the case of $ThCl_4$, the carbon, nitrogen, and oxygen contents for the salt were based on analyses of the thorium metal produced from the same batch of salt.

Table II. Heats of Fusion and Transition

Material	No. of Determinations	ΔH, Cal./mole	Std. Dev.	Literature Values ΔH, Cal./mole	Literature Values Temp., °K.	Literature Values Ref.
Al	4	2630	8	2570	932	(*5*)
Bi	9	2755	18	2600 ± 100	544.5	(*5*)
Ca, fus.	6	2040	42	1970	1123	(*5*)
trans.	6	222	6	60	737	(*5*)
Ce, fus.	6	1305	53	1238	1077	(*5*)
trans.	5	715	3	700	1003	(*5*)
Mg	5	1970	16	2140 ± 50	923	(*5*)
Pb	6	1175	9	1140	600.6	(*5*)
Sn	4	1645	16	1670	505	(*5*)
Zn	9	1755	20	1765 ± 80	692.7	(*5*)
$MgZn_2$	4	9690	26		863	(*4*)
$CaMg_2$	6	11745	172		987	(*4*)
CeZn	2	6975	175		1098	(*1*)
$CaZn_2$	12	9206	176		977	(*6*)
$ThCl_4$, fus.	4	14690	314		1042	(*12*)
trans.	3	1200	138		679	*a*
$CaCl_2$	11	6790	190	6780	1055	(*7*)

[a] Not previously reported.

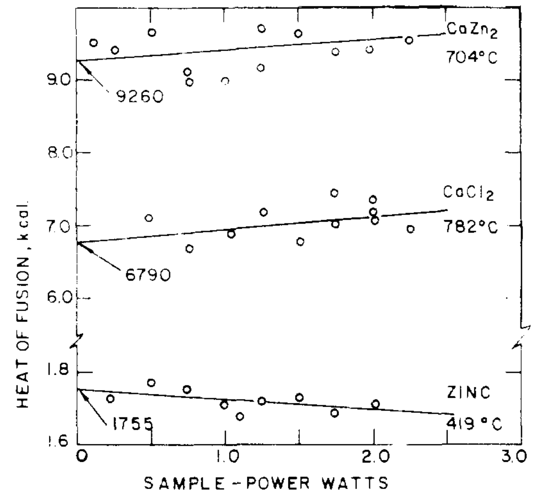

Figure 2. Dependence of the heat of fusion on sample-power input

adiabatic control became increasingly difficult on increasing the temperature above 700° C., and attempts to determine the heat of fusion for silver, 960° C., proved unsatisfactory. Some premelting was observed in $ThCl_4$, $CaZn_2$, cerium, and magnesium. The heat absorbed was estimated and included in the heat of fusion. This premelting, probably, was due to small amounts of impurities, or nonstoichiometry in the case of $CaZn_2$, and was less than 1.5% of the total heat of fusion.

The heats of fusion for zinc, $CaCl_2$, and $CaZn_2$ were measured as a function of the power input to the sample as shown in Figure 2. Extrapolation of the data to zero power input should yield the true heat of fusion. The standard deviations for these intercepts are given in Table II. The other heats of fusion were measured at a constant sample-power input in the range of 0.9 to 1.2 watts. The data in Figure 2 indicate that the probable error in the measured heats of fusion is within ±3.0%.

Stansbury (*13*), working with a similar adiabatic calorimeter, has found that a Dauphinee (*2*) thermocouple comparator circuit gives better control than the differential thermocouple arrangement shown in Figure 1. The data for $CaZn_2$ were obtained with this modification. However, the largest source of error, in the present measurements, is believed to be a nonuniform temperature distribution over the nickel sphere surrounding the sample and particularly, differences in temperature between the top and bottom halves. Possible methods for reducing this effect are under consideration.

The transformation in $ThCl_4$ at 406° C. (679° K.) has not been reported previously. The authors found that exposure of the salt to the atmosphere before the sample was sealed in a tantalum container, or on heating to 850° C. in tantalum, either reduced the magnitude of the heat of transformation or made this heat too small to detect. The sample, which yielded the data given in Table II, was heated repeatedly to a maximum temperature of 780° to 790° C. When subsequently heated in a differential thermal analysis apparatus to 850° C., the sample gave strong thermal arrests at 406° and 769° C. but no longer gave thermal arrests at 406° C. on cooling or on reheating. The reason for this behavior is uncertain. The salt was discolored somewhat and may have been contaminated with some tantalum. However, the inside of the crucible showed no visual evidence of attack. No anomalous behavior was observed in the other materials, and melting or transformation temperatures were in good agreement with the literature values given in Table II, with the exception of the transformation and melting temperatures for calcium, which were observed to be 448° and 839° C., respectively, in agreement with Peterson and Fattore (*11*).

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Dissociation Constants of Pyridinepentacarboxylic Acid and Other Pyridinecarboxylic Acids

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By using the potentiometric titration method, with glass and calomel electrodes, the dissociation constants of pyridine, six substituted pyridines, and eight pyridinecarboxylic acids, including pyridinepentacarboxylic acid, have been measured at 25° C.

THE DISSOCIATION constants of a number of dicarboxylic acids have been measured. Those of some tricarboxylic acids are known—for example, citric acid (*2*) and isocitric acid (*9*)—but few polycarboxylic acids of higher degree have been studied. One of these is benzenehexacarboxylic acid (mellitic acid), the six dissociation constants of which have been elucidated by Maxwell and Partington (*11*). An analogous example is pyridinepentacarboxylic acid where the pyridinium ion affords the sixth stage of dissociation. The authors now have prepared this acid and studied its dissociation constants. In addition, a number of other pyridine derivatives have been made and their dissociation constants measured.

MATERIALS

The samples of pyridine, 2,6-dimethylpyridine, and 2,4,6-trimethylpyridine were obtained commercially and triply distilled to give fractions of b. p. 114-15°, 142-43°, and 162-64° C., respectively.

A sample of 3,5-dicyanopyridine was recrystallized three times from water to give thin flakes, m. p. 112-13° C.

The remaining compounds for this study were prepared by known methods and are described in Table I.

The criterion used for all compounds was chromatographic purity, using an ascending paper system (Whatman No. 3), developed with the upper phase of the mixture 1-butanol-acetic acid-water (4 : 1 : 5) and sprayed with bromocresol green (0.5% in 95% ethanol adjusted to pH 8.0-9.0 with 0.1*N* sodium hydroxide).

The analytical data for pyridinepentacarboxylic acid, given in Table I, are not in good agreement with the calculated values. The authors suspect this was due to difficulty in drying the compound. Therefore, the dipotassium salt was prepared. Calcd: C, 31.1; H, 1.1; N, 3.7%. Found: C, 31.3; H, 1.4; N, 3.7%. This was dissolved in water containing 2 moles of hydrochloric acid per mole of the dipotassium salt to give a solution for electrometric titration.

MEASUREMENTS

Values of pK were determined by potentiometric titration, using glass and calomel electrodes. The temperature of the system was maintained at 25° C. The glass electrode was standardized with aqueous 0.05 molal potassium tetraoxalate (pH 1.68), 0.05 molal potassium hydrogen phthalate (pH 4.01), and the equimolal mixture of 0.025 molal potassium dihydrogen phosphate and 0.025 molal disodium hydrogen phosphate (pH 6.86).

The results are given in Table II. The first seven entries refer to monobasic acids; thus, although pyridine is itself a base, the pK value quoted is that of the conjugate acid and the dissociation process is:

$$BH^+ \rightleftarrows H^+ + B$$

The pK value of the pyridinium ion, BH^+, is given by the equation:

$$\mathrm{pK} = \mathrm{pH} + \log m_1/m_2 + \log \gamma_{BH^+}/\gamma_B$$

where m_1 is the molality of pyridinium ion and m_2 that of pyridine at any stage in the titration of a solution of pyridinium hydrochloride with sodium hydroxide. γ designates an activity coefficient and, for the dilute solutions used in this work, it suffices to write:

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