Conf-730920-1

To be presented at the Symposium on Physico-Chemical Techniques
at High Temperatures, in Austria, September, 1973.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

CONF-730920--1

AN ASSESSMENT OF THE ACCURACY OF THE HIGH TEMPERATURE
HEAT CAPACITY OF SOLID METALS

C. R. BROOKS AND E. E. STANSBURY

Chemical and Metallurgical Engineering Department

The University of Tennessee

Knoxville, Tennessee 37916 U.S.A.

Abstract

Comparison of the values of the reported high temperature heat capacity of solid metals frequently shows wide variance, usually increasing with increasing temperature. Unfortunately measurements on specimens made from the same stock material frequently show deviations well outside the uncertainty claimed by the investigators. Typical data are presented to illustrate the significance of the problem. It is clear that the origin of most of the differences lies in unrecognized errors in the experimental techniques. Possible sources of errors and the practicality of establishing a metal as a heat capacity standard are discussed.

Introduction

Although measurements of the heat capacity of solid materials at high temperatures (e.g., above 300 K) have become increasingly sophisticated, unacceptable discrepancies in the values remain. The major origin of these discrepancies is unknown and unrecognized heat transfer. Careful investigators report reproducibility, based on data obtained under wide range of operating variables (e.g., heating rate, sample size), and assess determinate errors associated with measurable quantities (e.g. voltage). The combination of the reproducibility and the determinate errors allows at least an estimate of the absolute accuracy of the measurements. However, the data of equally careful investigators differ frequently by an amount far outside the accuracy claimed by each. A method to clarify the issue is to measure the heat capacity, by different methods and calorimeters, using the same material (preferable from the same source) and look for statistical convergence to the true value. One should then be able to reveal those techniques which have undiscovered errors in them.

In this paper we illustrate the points stated above by examining the heat capacity values of selected metals. The possibility of establishing standards for heat capacity measurements on metals is discussed.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fey

1. Aluminum Oxide

Probably the substance most widely used for measurement of the heat capacity in order to assess the accuracy of a technique is aluminum oxide. This choice stems from the decision to use it for a standard for low temperature (below 300 K) calorimetry. The United States National Bureau of Standards (NBS) in particular, has made detailed measurements (Ginnings and Furakawa, 1953; Furakawa et al., 1956; Ditmar and Douglas, 1971); subsequently, the temperature range of measurements and comparison was extended above 300 K. The NBS has continued to make measurements on aluminum oxide using both adiabatic and drop calorimeters, the reproducibility of these measurements being excellent. The NBS has also supplied this material (called Calorimeter Conference Standard) to calorimetrists to permit an extensive compilation of heat capacity values. Other investigators (notably Martin and Snowdon, 1966, 1970 and Macleod, 1967) reported results and Ditmars and Douglas (1971) have published a comparison of the reported values. Over the range 300-1200 K the maximum deviation is about $\pm 0.6\%$. We have made measurements (Brooks et al., 1968) on an aluminum oxide sample which was a single piece (about 0.25 kg mass), fabricated to our required geometry. The purity was stated to be about 99.5%. Our data showed a scatter of about $\pm 0.5\%$ (consistent with our technique), and a curve fitted to these data lies within the scatter of the data summarized by Ditmars and Douglas. Thus other aluminum oxide samples yield heat capacity data quite close to those of the Calorimeter Conference samples.

An important disadvantage of using aluminum oxide as a standard is that it cannot be fabricated easily into the shapes specific techniques require. This undesirable characteristic makes many metals (and alloys) attractive as alternate standards. A principle objective of this paper is to examine the heat capacity values of some pure metals with this application in mind.

2. Aluminum

Aluminum appears to be a possible standard material for an intermediate temperature range (300-800 K). It is readily available, can be easily fabricated, and can be obtained in quite high purity. Figure 1 shows some of the heat capacity data of aluminum. From 300 to 600 K the spread in the data is within about $\pm 2\%$, but above 600 K the deviation widens. To illustrate the difficulty in assessing calorimetric

errors, we can compare our data (Brooks and Bingham, 1968) and those of Leadbetter (1968). It is seen that at 500 K the two curves differ by about 5%, well outside the limit of error stated by the investigators. Both Leadbetter and we have measured on aluminum oxide with close agreement (e.g., better than $\pm 1\%$) with the NBS data. Further, both Leadbetter (1968) and we (Cordoba and Brooks, 1971) have measured the heat capacity of solid lead and obtained an agreement to within 2%. This example nicely illustrates the difficulties in assessing the absolute accuracy of a given calorimetric technique.

Fig. 1. The Heat Capacity of Aluminum as obtained by several investigators.

3. Iron

The heat capacity of iron has been measured by numerous investigators, using dropping, adiabatic and pulse calorimeters. It is clear from a comparison of data (Kollie, et al., 1969) since 1949 that the deviation of the results increases markedly above the Curie temperature, and that there is even greater deviation in the face-centered cubic (fcc) phase. From 370 to about 950 K, the data agree within $\pm 3\%$; in the vicinity of the Curie temperature, the deviation becomes as great as $\pm 10\%$, and in the fcc region the deviation is about $\pm 6\%$. It is clear that the phase transformation complicated the measurements.

4. Platinum and Gold

The relative inertness, high purity, and fabricability of platinum and gold make them attractive as possible heat capacity standard materials. These advantages are offset by their cost. Fig. 2 shows the heat capacity data of gold. Over the range 500-1200 K the values differ by about 6%, well outside the accuracy claimed by the investigators. It is significant that the data Cordoba and Brooks (1971a) and of Ferrier (1972) were obtained on samples made from the same

Platinum could be used as a standard to as high as 1800 K. The data, shown in Fig. 3, differ by about 4% over the range 300-1700 K. The values of Vollmer (1965) and of Yeh and Brooks (1972) were obtained using samples made from the same platinum source.

Fig. 2. The Heat Capacity of Gold as obtained by several investigators.

Fig. 3. The Heat Capacity of Platinum as obtained by several investigators.

5. Tantalum

Refractories metals such as tantalum can be used to temperatures approaching 3500 K. Fig. 4 shows the heat capacity of tantalum from 100 to about 3300 K. The three upper curves extending above 2500 K are based on the pulse technique, and these results differ by an amount within their estimated accuracy. Hoch and Johnston (1961) using a drop calorimeter, report values above 1500 K considerably lower than the other data.

Fig. 4. The Heat Capacity of Tantalum as obtained by several investigators. The bar at the end of each curve is a measure of the accuracy stated by the investigators.

Discussion

There are a number of sources of errors contributing to scatter in the measured heat capacities of metals. Some of these clearly can be eliminated as not contributing significantly to the wide deviations. For example, measurements of voltage, time interval and specimen mass are usually sufficiently precise not to require consideration here. Temperature measurements are based on signals from thermometers which are calibrated directly; frequently values derived from standard calibration tables are used. Errors in the temperature measurement are critical since the heat capacity calculation involves a temperature interval. However, if the error varies slowly and uniformly with temperature, the error in the interval can be quite small. The International Temperature Scale used does enter into comparisons of data; Douglas (1969) has discussed the problems of converting data from one temperature scale to another. This effect is sufficient to account for differences of the order of 0.3% in the heat capacity, but not the larger discrepancies.

In general, errors in measurements of voltage, mass, time, in converting thermometer readings to temperature, and in the choice of the temperature scale, cannot account for the wide variation in experimental values of the heat capacity. A most obvious additional source of error in the experimental technique is unaccounted for heat exchange by the specimen. Such errors have been discussed by several authors (West, 1963; West and Westrum, 1967; Wollenberger, 1970) and will not be considered in this paper. Instead, we will limit our considerations to the purity of the sample as an origin of the heat capacity variations.

Chemical purity and structural homogeneity of the specimen are considerations in comparing heat capacity data. The level of impurity content to be considered here is less than one per cent, and the impurities may be in solution in the matrix or present as second phases, or both. The effects of impurities on the measured heat capacity manifest themselves in several ways.

a) If the impurities are present in solid solution, they will affect the heat capacity in two ways. Their presence will alter the energy absorbing mechanisms of the lattice and electrons. However, in the temperature range above the Debye temperature, this effect is negligible for the range of purity usually encountered.

Of greater consequence is the additional heat effect associated with the exchange of lattice positions by solute and solvent atoms. Solid solutions generally deviate from random arrangements of the atoms on the lattice sites; if the number of solvent atoms about a solute atom is greater than the random number, the solid solution is short range ordered (SRO). Otherwise the solid solution shows clusters of solute atoms. As temperature increases, the clustering or SRO decreases, and the solid solution approaches a completely random solution. On cooling from a high temperature, solute-solvent atom exchanges tend to occur to establish the equilibrium degree of SRO or clustering. However, a temperature is reached below which the atom mobility is so restricted that such exchanges effectively cease. Upon reheating in a calorimeter from a terminal temperature (e.g., 300 K) atom exchanges to decrease the degree of SRO are initially suppressed due to low atom mobility. A temperature is reached, however, where the atom exchange rate causes a significant decrease in SRO, with an accompanied energy absorption. Thus the heat capacity appears greater than that which would be obtained if the only heat absorption were due to lattice vibration and electron excitation. For solid solutions on which heat capacity measurements have been made to reveal this effect, the solute concentration must be relatively high (e.g., greater than 5%), so that this impurity effect in the present consideration can be neglected (Brooks, 1970).

If the presence of the impurities causes the formation of a second phase, and the phase is stable with temperature (i.e., will not dissolve upon heating), then the effect on the measured heat capacity can be determined from a knowledge of the heat capacity of this phase and the amount present. Again, for the range and type of impurities

usually encountered, this effect is probably negligible.

b) If the solubility of the second phase is temperature dependent, and the rate of solution of the precipitate upon heating is sufficiently rapid, then some of the heat to the specimen will be absorbed as the precipitate dissolves. This effect can be significant. For example, Fig. 5 shows the heat capacity of a zirconium alloy, having an initial hydrogen (H_2) content of 0.0115 wt. %. The sample was in a vacuum of about 10^{-4} Torr during measurement. Upon heating, the zirconium hydride dissolved, with an energy absorption causing a rise in the heat capacity (solid curve) until about 300°C ; above this temperature the alloy is a single phase solid. The alloy was then heated for several hours at 800°C in a vacuum better than 10^{-4} Torr, which removed most of the hydrogen. The heat capacity values (points in Fig. 5) then showed no rise in the range 100 - 300°C . We have observed the same effect in titanium (Prabhakar and Brooks, 1973), which also was removed by proper vacuum annealing of the metal.

Fig. 5. The Heat Capacity of Zircaloy-2. The solid line represents the data for the as-received condition; the data point represent the data after a vacuum anneal. (Brooks and Stansbury, 1966).

c) The effects of impurities on the heat capacity near solid state phase transformations, or transformations such as the Curie transformation, must be considered. For iron the data show increased deviation as the Curie temperature is approached, the spread being about 10% (Kollie et al., 1969) below the Curie temperature and almost 15% above. It is doubtful that these wide discrepancies are due to the effect of impurities on the Curie temperature, but instead are more likely associated with temperature gradients in a specimen which is assumed to be isothermal when the transformation begins (Kollie, 1969).

d) As the melting point is approached, the heat capacity may show deviations associated with an effect frequently called "premelting".

contribution to the heat capacity. Further, the impurity content in solution may allow melting by entrance into the two phase liquid-solid region; this depends on the phase relations for the particular system. The rate at which this occurs may also be a factor (Martin, 1970).

Closure

The practicability of establishing a metal as a heat capacity standard can be examined in view of the preceding discussion. The expected variations in the purity of a metal do not affect significantly the heat capacity, as long as temperature ranges in which structural and phase changes occur are avoided. Thus metals such as copper, gold and platinum should be quite suitable in the range 300-1300 K. For higher temperatures, refractory metals can be employed. The heat capacity data of aluminum oxide show that careful measurements, using different calorimetric techniques, are capable of yielding data of excellent accuracy, and there is no obvious reason that such accuracy cannot be approached for a metal.

Acknowledgements

This research was supported by the United States Atomic Energy Commission under Contract At-(40-1)-3291. Appreciation is expressed to Dr. Albert Ferrier for allowing us to use his unpublished gold data.

References

- Brooks, C. R., and Stansbury, E. E., (1970), European Conference on Thermophysical Properties of Solid Materials At High Temperatures, Zentralstelle fur Atomkerenergie-Dokumentation, Karlsruhe.
- Brooks, C. R., and Stansbury, E. E., (1966), J. Nucle. Mat., 18, 233.
- Brooks, C. R., and Bingham, R. E., (1968), J. Phys. Chem. Solids, 29, 1553.
- Brooks, C. R.; Norem, W. E.; Hendrix, D. E.; Wrights, J. W. and Northcutt, W. G.; (1968), J. Phys. Chem. Solids, 29, 565.
- Cezairliyan, A., McClure, J. L., and Beckett, C. W., (1971), J. Res. N. B. S., 75A, 1.
- Clusius, K., Losa, C. G., and Franzosini, P., (1957), Z. Naturforschg. 12, 34.
- Cordoba, G., and Brooks, C. R., (1971a), phys. stat. sol. (a), 6, 581.
- Cordoba, G., and Brooks, C. R., (1971b), phys. stat. sol. (a), 7, 503.
- Ditmars, D. A., and Douglas, T. B., (1971), J. Res. N. B. S. 19 75A, 401.

- Douglas, T. B., (1969), J. Res. N. B. S., 73A, 451.
- Eastman, E. L., Williams, A. M., and Young, T. F., (1924), J. Am. Chem. Soc., 46, 1178.
- Ferrier, A. (1972), unpublished research.
- Franzosini, R., and Clusius, K., (1963), Z. Naturforschg., 18a, 1243.
- Furukawa, G. T., Douglas, T. B., McCoskey, R. E., and Ginnings, D. C., (1956), J. Res. Nat. Bur. Stds., 57, 67.
- Geballe, T. H., and Giaque, W. G., (1952), J. Am. Chem. Soc., 74, 2368.
- Giauque, W. F. and Meads, P. F., (1941), J. Am. Chem. Soc., 63, 1897.
- Ginnings, D. C., and Furukawa, G. T., (1953), J. Am. Chem. Soc., 75, 522.
- Hoch, M., and Johnston, H. L., (1961), J. Chem. Phys., 65, 855.
- Jaeger, F. M., Rosenbohm, E., and Bottems, J. A., (1932), Proc. Royal Acad. Amsterdam, 35, 772.
- Jaeger, F. M., and Veenstra, W. A., (1934), Rec. Trav. Chim., 53, 677.
- Jaeger, F. M., and Rosenhohm, E., (1939), Physica, 6, 1123.
- Kendall, W. E., Orr, R. L., and Hultgren, R., (1962), J. Chem. Engr. Data, 7, 516.
- Kollie, T. G., 1969, Ph.D. Dissertation, The University of Tennessee.
- Kollie, T. G., Barisonia, M., McElroy, D. L., and Brooks, C. R., (1969), High Temperatures - High Pressures, 1, 167.
- Kraftmakher, Ya.A., and Lanina, E. G., (1965), Soviet Phys. Solid State, 7, 92.
- Leadbetter, A. J., (1968), J. Phys. C. (Proc. Phys. Soc.), 1, 1481.
- Lowenthal, G. C., (1963), Australian J. Phys., 16, 47.
- MacDonald, R. A., (1967), J. Chem. and Engr. Data, 12, 115.
- Macleod, A. C., (1967), Trans. Far. Soc., 63, 300.
- Macleod, A. C., (1972), J. Chem. Thermo., 4, 391.
- Martin, D. L., (1970), Can. J. Phys., 48, 1327.
- Martin, D. L., and Snowdon, R. L., (1966), Can. J. Physics, 44, 1449.
- Pochapsky, J. E., (1963), Acta Met., 1, 1303.
- Prabhakar, K., and Brooks, C. R., (1973), unpublished research.

- Rasor, W. S., and McClland, J. D., (1960), J. Phys. Chem. Solids, 14, 17.
- Skelskey, D., and Sype, J. V., (1970), J. Appl. Physics, 41, 4750.
- Stansbury, E. E., and Brooks, C. R., (1969), High Temperatures-High Pressures, 1, 289.
- Taylor, R. E., and Finch, R. A., (1964), J. Less-Common Metals, 6, 283.
- Vollmer, O., (1965), Inaugural-Dissertation zur Erlangung des Doktorgrades, der Universitat zu Koln.
- Vollmer, O., and Kohlhaas, R., (1968), Z. Metallkde., 59, 273.
- West, E. D., (1963), J. Res. N.B.S., 67A, 331.
- West, E. D., and Westrum, E. F., (1967), in Experimental Thermodynamics, J. P. McCullough and D. W. Scott, eds., Butterworths, London.
- Wollenberger, H., (1970), phys. stat. sol. (a), 2, 511.
- Wust, F., (1918), Forschungarbeiten gebiete Ingen., 204, i
- Yeh, C. C., and Brooks, C. R., (1972), unpublished research.