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DIFFERENTIAL SCANNING CALORIMETER STUDIES OF THE HEAT CAPACITIES OF COPPER DIFLUORIDE AND GOLD

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ABSTRACT

A commercial differential scanning calorimeter has been modified to yield heat capacity data which appear to be accurate to within ±2% or better. Using this instrument the constant pressure heat capacities of Au, 350 to 750 K, and CuF_2, 330 to 710 K, have been determined. Values of $\bar{C}_p^\circ$ and $\bar{H}_T^\circ - \bar{H}_{298}^\circ$ from 298 to 1000 K are presented for CuF_2.

INTRODUCTION

The thermodynamic functions of solid CuF_2 at elevated temperatures are based on estimated heat capacities[1]. To reduce the uncertainty associated with these data, needed for our studies of $CuF_2(g)$ and CuF(g) and its polymers[2], experimental values were desirable. The reactivity of CuF_2 required the use of gold sample containers. However, there is a lack of consistency between reported values for the heat capacity of Au at elevated temperatures[3–5]. That is, the most recent data[3] are 6% greater at 400 K than those reported previously while the 300 K values from refs. 3 and 4 are 3% less than the "best" value[6]. Since it appeared necessary and possible to determine the heat capacity of Au to within ±2% with the apparatus described herein, a redetermination of C_p(Au) above ambient temperature was undertaken.

EXPERIMENTAL

A commercial differential scanning calorimeter was used[7] but several modifications were necessary to achieve satisfactory accuracy and precision. These included substituting platinum covers for the standard aluminum sample holder covers, altering the temperature programmer to achieve linear scan rates, and thermostating the sample holder assembly. Using Pt covers eliminated shifts in the baseline due to changes in cover emissivity. Linearizing the temperature scale, entirely an electronic modification[8], eliminated the difference between the programmed rate $\dot{T}_p$ and true scan rate $\dot{T}_t$. After this modification the value of $(T_t - T_p)$ for transitions in various calibrants scanned at 10 K min^{-1} was found to be 0.6 at the melting point of Ga

(302.9 K), − 0.1 at the transition of NH_4NO_3 (398.4 K), − 0.5 at the m.p. of KNO_3 (400.8 K), 1.5 at the m.p. of In (427.8 K), 1.1 at the m.p. of Sn (505.1 K), 0.0 at the m.p. of Cd (594.3 K), 1.1 at the m.p. of Pb (606.7 K), and 0.4 at the m.p. of Zn (692.7 K) where (temperature) is the literature transition temperature, IPTS-68[9]. Thus, at $\dot{T}_p = 10$ K min^{-1} the observed temperature led the true temperature by 0.5±1K between 303 and 693 K. There is no reason to expect this relation to fail below 303 K or above 693 K but the lack of suitable calibrants prevented testing this. For $\dot{T}_p = 5$ K min^{-1} the observed temperature led the true temperature by 1.0 K. At 20 K min^{-1} the lag was 1.1 K. Other rates were not used.

Thermostating the sample holder assembly greatly improved baseline stability as others also noted[10]. To record the DSC output we used a 10 mv recorder which was calibrated for linearity and accuracy to ±0.01 mv with a Leeds and Northrup No. 7554 test facility.

Large output signals were kept on-scale with a range expander accessory which was similarly calibrated. Only the X1 and X2 sensitivity ranges were used and these gave consistent results.

Calibration of the DSC was based on the equation[11] $k = \dot{T}_p\, C_{R,T}/V_{R,T}$ where k is the sensitivity constant, $C_{R,T}$ is the heat capacity of a reference material at temperature T and $V_{R,T}$ is the net deflection from the baseline at T caused by the presence of the reference material in the sample holder. As reference material we used 38.823 mg of α-Al_2O_3[12]. $C_{R,T}$ values were taken from the literature[13]. To eliminate any effect of thermal lag as well as uncertainty regarding the baseline position the calibration and gold measurements were made using short, bidirectional scans. For example, to find $V_{400\ K}$ the interval 395 to 405 K was scanned upwards and the deflection 405 K was recorded after a stable baseline was achieved. Then the interval was scanned downward and the deflection 395 K was found. This process was repeated as necessary to average random variations down to 1% of the net deflection. $V_{400\ K}$ was taken as the average of $V_{395\ K}$ and $V_{405\ K}$.

To eliminate hydrolysis of CuF_2 which is very rapid above 450 K all joints in the DSC were carefully sealed until a vacuum of better than 1×10^{-6} mm Hg could be attained in the sample chamber and all associated plumbing. After evacuation the DSC was filled with N_2 dried over $CaSO_4 \cdot 0.5H_2O$. This atmosphere was used for all experiments. To maintain constant, atmospheric pressure the system was vented through the drying agent during experiments.

From measurement of $V_{R,T}$ at 400 K it was found that $k = 0.1010$ cal K V^{-1} sec^{-1}, reproducible to within 0.5%. The value of k was independent of temperature although the reproducibility above 600 K was poorer.

Unknown heat capacities $C_{S,T}$ were then found using eqn 1[14] in which one measures the difference in heat capacity between the sample and the reference material:

$$C_{S,T} = C_{R,T} + (V_S - V_R)_T \frac{k}{\dot{T}} \qquad (1)$$

In the context of eqn (1) "sample" refers to pure Au in the form of standard DSC sample pans, reported to be at least 99.99% pure[14], for finding $C_{p,\,Au}$ or CuF_2 in an Au pan for finding $C_{p,\,CuF_2}$. Analysis of CuF_2 by electrodeposition gave 100.0% of the theoretical Cu and by titrimetry gave 100.0% of the theoretical F. The X-ray powder pattern for the CuF_2 was in agreement with that reported for crystalline CuF_2[15].

RESULTS

The results of several hundred measurements on Au are summarized in Table 1.

TABLE 1

HEAT CAPACITY OF SOLID GOLD AT ONE ATM

T(K)	350	400	500	600	700	750
$\bar{C}_p^{\circ}$ (cal K^{-1} mol^{-1})	6.11	6.17	6.19	6.25	6.39	6.51

The tabulated values are averages for bi-directional scans at $\dot{T}_p = 5$ and 10 K min^{-1} over intervals from 4 to 20 K.

The results for crystalline CuF_2 are shown in Table 2.

TABLE 2

HEAT CAPACITY OF CuF_2 (c) AT ONE ATM

$T(K)$	$C_{Au} \div C_{CuF_2}$ (cal $K^{-1} \times 10^3$)	$C_{p}^{\circ}{}_{,CuF_2}$ (cal K^{-1} mol^{-1})	Sample[a]
300	12.10	16.06	a
340	12.31	16.51	a
350	12.34	16.56	a
360	12.51	16.92	a
370	12.61	17.14	a
380	12.65	17.21	a
390	12.72	17.35	a
400	12.82	17.59	a
410	12.91	17.75	a
420	12.97	17.86	a
430	13.00	17.93	a
440	13.08	18.11	a
450	13.18	18.31	a
480	11.46	18.70	b
540	11.60	19.04	b
600	11.72	19.30	b
650	11.99	19.95	b
710	12.19	20.31	b

[a] Sample a was 0.160580 g of Au and 0.045137 g of CuF_2; sample b was 0.163458 g of Au and 0.034352 g CuF_2.

To minimize the chance of hydrolysis of the CuF_2 by the inevitable traces of moisture leaking into the DSC, the data above 450 K were taken at more widely spaced intervals. Several scans from 450 to 770 K revealed no evidence of first or second order transitions in this region, so C_p and $H_{T_2} - H_{T_1}$, must vary smoothly over the range of this study.

DISCUSSION

The typical uncertainty in individual values of $(V_s - V_R)$ was 2% although by averaging at least three values the noise-related part of this error was reduced somewhat. Including a possible 0.5% error in k brings the uncertainty in the $(V_S - V_R)k/\dot{T}$ term in eqn (1) to 2.5%. In comparison, the uncertainty in C_R, arising only in the weight and heat capacity measurements of the reference material, is entirely negligible. Since for the Au studies the $(V_S - V_R)k/\dot{T}$ term was always negative and 30% or less of the C_R term, the C_{Au} values should be uncertain by no more than 1%.

In the CuF_2 studies C_R again could be taken as exact while the $(V_S - V_R)k/\dot{T}$ terms were positive and no more than 50% of C_R so the C_S values should be uncertain by 1% or less. Then considering that the gold pans constituted under 40% of the value of C_S, it can be concluded that the $\bar{C}_{CuF_2}$ values in Table 2 are in error by no more than 2%.

Although it was not possible to directly determine the heat capacity of Au at 300 K, any resonable extrapolation agrees within 1% with the value from ref. 6. Above 300 K the Table 1 values agree within experimental error with those from ref. 4 but not with those from ref. 3.

Graphical integration and smoothing was used to obtain the values listed in Table 3.

The smoothed data show a greater temperature dependence than do the JANAF estimates. For example, at 300 K the JANAF heat capacity is 8.5% greater than that in Table 3 but at 800 K the JANAF value is 5.4% less.

The data in Table 2, fitted to an equation of the form $\bar{C}_p = a + bT - cT^{-2}$

TABLE 3

SMOOTHED VALUES OF $\bar{C}_p°$ AND $\bar{H}_T° - \bar{H}_{298}°$ FOR CuF_2(c)

T(K)	$\bar{C}_p°$ (cal mol^{-1}K^{-1})	$\bar{H}_T° - \bar{H}_{298}°$ (cal mol^{-1})
298	15.40	—
300	15.46	31
400	17.58	1,696
500	18.72	3,569
600	19.58	5,486
700	20.38	7,480
800	21.12	9,550
900	21.8	11,690
1000	22.4	13,900

by a least squares method in which all points were weighted equally, are described by

$$\bar{C}_p^\circ = 21.475 - 5.822 \times 10^{-4}\,T - 5.7654 \times 10^5\,T^{-2} \tag{2}$$

While eqn (2) is convenient to use, its applicability is limited to the experimental temperature interval, 330–710 K.

Sublimation pressure measurements made here[2] indicate $\Delta\bar{S}^\circ_{\text{subl}} = 39.32 \pm 0.8$ cal K^{-1} mol^{-1} at 950 K. Recalculating $\bar{S}^\circ_{950K}$ for CuF_2 (g) to conform with the matrix isolation spectroscopic results[16] gives 73.9 ± 0.2 cal K^{-1} mol^{-1}, so the entropy of crystalline CuF_2 at 950 K is 34.7 ± 1.0 cal K^{-1} mol^{-1}. With the Table 3 data this can be corrected to 298 K. The value found is 13.0 ± 1.5 cal K^{-1} mol^{-1}, allowing 0.5 cal K^{-1} uncertainty as a result of the correction to 298 K. The JANAF value for 298 K is 16.4 cal K^{-1} mol^{-1}. There is an obvious need for low temperature heat capacity measurements of CuF_2 and for additional information on the structure of CuF_2(g).

Despite the successful performance of the equipment, it appears that baseline reproducibility would show considerable improvement if the sample holders were plated with an inert, low emissivity material such as rhodium, platinum or gold.

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