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Temperature calibration of a simultaneous TG/DTA apparatus

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Abstract

Three sets of reference materials were used to calibrate the temperature of a Seiko TG/DTA320 apparatus. They are magnetic standard materials (Perkin–Elmer Co.), first-order solid_1 to solid_2 transition materials (certified NIST–ICTA materials) and melting-point standard materials. The temperature range of the calibration is between 100 and 1100°C. The calibrations of temperature among the three sets of standards show some significant differences at higher temperatures.

INTRODUCTION

Temperature calibration is of foremost importance for thermal analysis. The simultaneous thermo-gravimetric/differential thermal analyzer (TG/DTA) allows us to calibrate using both phase transitions (DTA standard) and magnetic transitions (TG standard). It is interesting to compare the different kinds of calibration for a single apparatus. Two sets of phase transition materials have been used as DTA standards. One consists of metals using their melting points, the other of compounds with a first-order solid_1 to solid_2 transition. The latter are the NIST–ICTA certified reference materials [1]. These reference materials are KNO_3, $KClO_4$, Ag_2SO_4, SiO_2, K_2SO_4, K_2CrO_4, $BaCO_3$, and $SrCO_3$. The metals are In, Sn, Pb, Zn, Al, Ag, Au and Cu. For the magnetic transitions, Alumel, Ni, Nicoseal, Perkalloy, Fe and Hisat were used. The results of the calibration are expressed as the temperature differences between the observed transition temperatures and the generally accepted values. The areas of the DTA curves associated with each phase transition were normalized to unit energy and also investigated.

EXPERIMENTAL PROCEDURES AND RESULTS

Simultaneous thermogravimetric/differential thermal analysis is a technique which performs TG and DTA measurements on a single sample at the

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same time as this sample is subjected to a programmed temperature cycle. The Seiko TG/DTA320 is one module of their SSC5200 thermal analysis system. It covers the temperature range from room temperature to 1500 °C. It uses a horizontal differential system balance mechanism for TG measurement and the thermocouples for the DTA measurements are platinum–platinum rhodium 13%. These thermocouples are welded to the bottom of the platinum sample holder.

The DTA calibration procedure is essentially the same as that used for the usual DTA measurement. The onset temperatures of the DTA events were accepted as the observed phase transition temperatures. For TG calibration, a permanent magnet was placed above the sample and reference holder but outside the furnace. This resulted in some apparent weight loss for a magnetic sample, due to the magnetic field gradient, before the magnetic transition temperature was reached. To achieve an apparent weight loss of 10–30% (depending on the material), the permanent magnet was placed on a quarter-inch-thick ceramic mat that sat directly on top of the TG/DTA furnace. According to standard convention for the magnetic transition, the final temperatures of the TG events were taken as the observed magnetic transition temperatures. Figure 1 is an example of a calibration run in which SiO_2, Fe and Perkalloy were placed on the sample pan and K_2CrO_4 was placed on the reference pan. Four transition temperatures were measured in a single run and measuring inconsistencies were reduced.

At first, four heating rates (2, 5, 10 and 20°C min^{-1}) were used but there were no systematic differences in the observed transition temperatures, so a 10°C min^{-1} heating rate was adopted. The purge gas was nitrogen at 100 ml min^{-1}. However, carbon dioxide and nitrogen with 5% hydrogen were also used. Carbon dioxide was used to shift the decomposition of $SrCO_3$ to higher temperatures. To prevent oxidation (our nitrogen always contains some

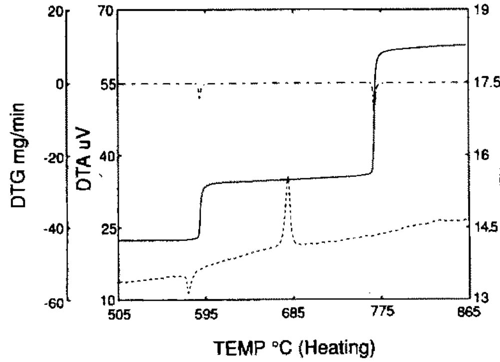

Fig. 1. Heating curve for the simultaneous TG, DTG and DTA of Perkalloy 11.5 mg, Fe 6.4 mg, K_2CrO_4 35.6 mg, and SiO_2 30.0 mg at 10°C min^{-1} in N_2 at 100 ml min^{-1}. See text for sample arrangement: ———, TG; ·–·–·; DTG; - - - - - -, DTA.

oxygen) of Hisat and Cu, nitrogen with 5% hydrogen was used. Table 1 is a compilation of the observed values for the various conditions used.

All of the transition temperatures have been measured at least three times. Consistent results were obtained and the average value reported. All measured melting temperatures of In and Sn are within 0.5°C of their mean values. For Au, the melting temperatures were between 1052 and 1056°C in thirteen measurements (there are only four significant figures in temperature measurement) and the mean values was 1054.3°C. So all of the measurements were within the standard limit of error (see discussion section).

TABLE 1

Summary of sample, atmosphere, container, measured and reference transition temperature

Sample	Atmosphere	Sample container	$Temp._{mea}$	$Temp._{ref}$
In	N_2	Al	156.6	156.6
Sn	N_2	Al	231.9	231.9
Pb	N_2	Al	326.3	327.5
Zn	N_2	Al	417.9	419.5
Zn	N_2	Al_2O_3	418.6	
Al	N_2	Al_2O_3	657.7	660.3
Ag	N_2	Al_2O_3	951.7	961.8
Au	N_2	Al_2O_3	1054.0	1064.4
Au	CO_2	Al_2O_3	1054.6	
Au	N_2 with 5% H_2	Al_2O_3	1054.3	
Cu	N_2 with 5% H_2	Al_2O_3	1075.2	1084.5
Alumel	N_2	Pt	159	163
Ni	N_2	Pt	357	354
Nicoseal	N_2	Pt	443	438
Perkalloy	N_2	Pt	588	596
Fe	N_2	Pt	765	780
Hisat	N_2 with 5% H_2	Pt	985	1000
KNO_3	N_2	Al	130.2	128.1
$KClO_4$	N_2	Al	300.2	299.7
Ag_2SO_4	N_2	Al	426.0	426.9
SiO_2	N_2	Pt	568.3	573.9
K_2SO_4	N_2	Pt	579.4	583.9
K_2SO_4	N_2	Al_2O_3	579.9	
K_2SO_4	CO_2	Pt	579.6	
K_2SO_4	CO_2	Al_2O_3	579.3	
K_2CrO_4	N_2	Pt	665.7	665.9
$BaCO_3$	N_2	Pt	799.8	805.9
$BaCO_3$	N_2	Al_2O_3	804.2	
$BaCO_3$	CO_2	Pt	809.6	
$BaCO_3$	CO_2	Al_2O_3	809.6	
$SrCO_3$	N_2	Pt	926.0	923.9
$SrCO_3$	N_2	Al_2O_3	923.3	
$SrCO_3$	CO_2	Pt	922.5	
$SrCO_3$	CO_2	Al_2O_3	923.1	

DISCUSSION

Figure 2 is a plot of the temperature correction measured versus temperature for the results at 10°C min^{-1}. For the melting points of metals, the new International Temperature Scale of 1990 (ITS-90) [2] was used as reference except for Pb [3]. For the first order transition temperatures, "Thermochemical data of pure substances" [3] was the reference. For the magnetic transition temperatures, the recommended Perkin–Elmer TG calibration list was used [4]. The results between different standard materials were significantly different and will be discussed later.

The TG/DTA was pre-calibrated with In and Sn which explains why the temperature corrections for these two were essentially zero. The thermocouple for temperature measurement is the thermocouple (sample side) used for the DTA measurement. According to the "Thermocouple Reference Table" [5], the standard limit of error for this thermocouple (type R) is ±1.4°C between 0 and 538°C and ±1/4% between 538 and 1482°C. Careful annealing and avoiding subsequent quenching are important for consistent temperature measurement. A quenched thermocouple would cause an error of −10°C around 1000°C and of 2°C around 200°C.

For Au, nitrogen, carbon dioxide and nitrogen with 5% hydrogen were used as purge gases and no significant difference was found among them (see Table 1). As a result, nitrogen with 5% hydrogen should not affect the melting temperature of Cu as compared to pure nitrogen. An alumina pan was used for Cu, Au, Ag and Al. An aluminum pan was used for the other metals. For Zn, an alumina pan raised its apparent melting point by 0.7°C. This difference was taken as within the level of experimental error.

For magnetic standard materials, platinum and alumina pans were used and no significant difference was found between them. After these samples

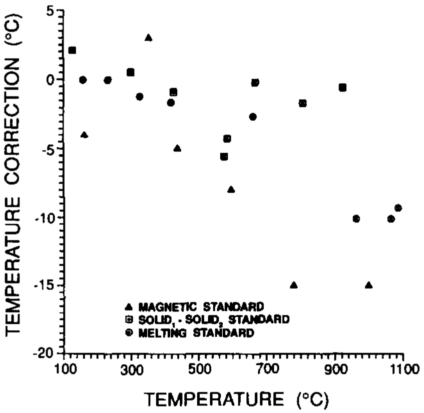

Fig. 2. Observed temperature corrections as a function of temperature for 10°C min^{-1} in purge gas at 100 ml min^{-1}.

were annealed, some of the measured values were still around within ±2°C of the mean values agreeing with the earlier work [4]. The mean values, however, are quite different. These variations were greater than expected.

The International Confederation for Thermal Analysis (ICTA) and the National Institute of Standards and Technology (NIST) have recommended using the first-order solid$_1$ to solid$_2$ transition temperatures of KNO_3, $KClO_4$, Ag_2SO_4, SiO_2, K_2SO_4, K_2CrO_4, $BaCO_3$ and $SrCO_3$ for comparison temperatures [1]. Since the thermodynamic transition temperatures of this set of materials are not certified standards, the reported transition temperatures would be expected to show some differences. Surprisingly, most are within about 1°C except for $BaCO_3$. The reference [3] used here reported that value to be 805.85°C and that used by ICTA [6] listed it as 810°C. Using this latter value gives a significantly improved value for the correction in comparison with the melting point standards.

The transition temperature of K_2SO_4 is very stable, with either a platinum or alumina pan. Similarly, carbon dioxide and nitrogen gave the same result. However $BaCO_3$ and $SrCO_3$ show a dependence on the purge gas and pan. Table 1 indicates the extent of this variation. For $BaCO_3$, a platinum pan and carbon dioxide gave 809.6°C, a platinum pan and nitrogen 799.8°C, an alumina pan and carbon dioxide 809.6°C, and an alumina pan and nitrogen 804.2°C. For $SrCO_3$, a platinum pan and carbon dioxide gave 922.5°C, a platinum pan and nitrogen 926.0°C, an alumina pan and carbon dioxide 923.1°C, and an alumina pan and nitrogen 923.3°C. These differences are probably related to the degree of carbonate decomposition and the resulting formation of oxide, oxycarbonate, or carbonate eutectics. It is not, however, related to the thermal properties of the purge gases since all purge gases gave the same melting temperature for Au.

In Fig. 2, the results with the alumina pan and nitrogen were used. The temperature correction between the melting points of metals and the first-order solid$_1$ to solid$_2$ transition temperatures are quite different. This is probably due to the difference between isothermal transition temperatures and dynamic transition temperatures, as we have noticed the mean onset temperatures of solid$_1$ to solid$_2$ given by NIST–ICTA certificate are different from their equilibrium ones [1]. In addition emissivities will play an increasing role at higher temperatures as radiative thermal transport becomes dominant.

Figure 3 shows the areas of the DTA events normalized to unit energy. The enthalpy changes associated with each process were obtained from "Thermochemical data of pure substances" [3]. The DTA signal of the apparatus is the difference in the thermoelectric voltages between the two thermocouples, units of μV. The DTA unit was converted to °C by dividing by the Seebeck coefficient [5] which is temperature dependent. Future values of unknown enthalpy may be estimated by dividing the observed areas, obtained under these identical conditions, by the product of the appropriate

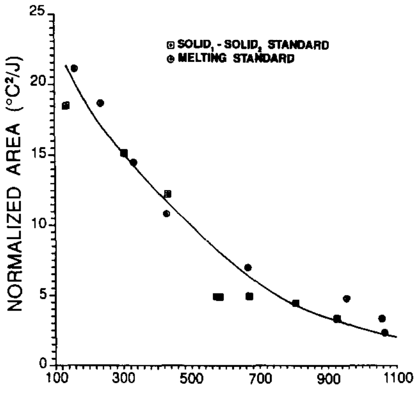

Fig. 3. Observed factors for the conversion of measured areas into the actual heat absorbed. 10°C min^{-1} in a flow of gas at 100 ml min^{-1}.

value from Fig. 3 and the sample weight. The line drawn in Fig. 3 is a smooth curve, hand-drawn through the experimental points.

The observed trend is that the normalized area decreases rapidly with increasing temperature. This is the expected trend which distinguishes DTA from DSC. If thermal conductivity is the only means of heat transfer during a DTA event and the purge gas is the only medium, the transport properties of an ideal gas predict that the thermal conductivity coefficient K is proportional to $T^{3/2}$ [7] and the area should be inversely proportional to $T^{3/2}$. This is an approximation as radiation is a significant means of heat transfer at higher temperatures and the heat capacity of the system is not constant over the entire temperature range.

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