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CALORIMETRIC RESPONSE OF THE DU PONT 1200 °C DIFFERENTIAL THERMAL ANALYZER

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The probable calorimetric accuracy of the Du Pont 1200 °C cell has been described. With proper attention to technique, calorimetric precision of about $\pm$ 2% can be obtained with a slightly larger deviation of about $\pm$ 5% in accuracy. The heat flow calibration constant, *E*, is linear with temperature, and its value is two to four times that of commercial scanning calorimeters.

A number of calorimeters are available to assess the heat response of various materials; among these are the adiabatic [1], Boersma [2], and differential scanning calorimeters [3, 4]. Chiu [5] has described the excellent temperature accuracy and atmosphere control possible with the Du Pont 1200 °C DTA cell. Furthermore, his work has shown that the 1200 °C cell can be used as a calorimeter. This communication relates the calorimetric response of the Du Pont 1200 °C Differential Thermal Analyzer and its comparison with results from existing calorimetric data.

Experimental

The 1200 °C cell was used as a module to the Du Pont 900 Thermal Analyzer. Three runs each of pure metal samples of tin, lead, zinc, aluminum, and silver, as well as potassium nitrate and potassium chloride, A.C.S. reagent grade, were carried out for the establishment of the heat flow calibration constant and the reported heats of fusion.

A multi-range, time base recorder was attached to the Y-axis terminals in the rear of the 900 console, causing the spread of the heat of fusion over a large area for accurate planimetering. The 1200 °C cell is shown in Fig. 1. Platinum cups inserted over platinum-rhodium thermocouples and surrounded by an alumina tube were heated with a Kanthel-wound, resistance furnace. The proper positioning of the alumina tube, platinum cups and furnace are essential to obtaining proper baseline performance. The baseline positioning of the cell was achieved using alumina in each cup. Sample size was selected so that a reasonable peak area was obtained during the fusion corresponding to a Y-axis deflection of 0.02 millivolts per inch chart paper. The heating rate was 20° per minute.

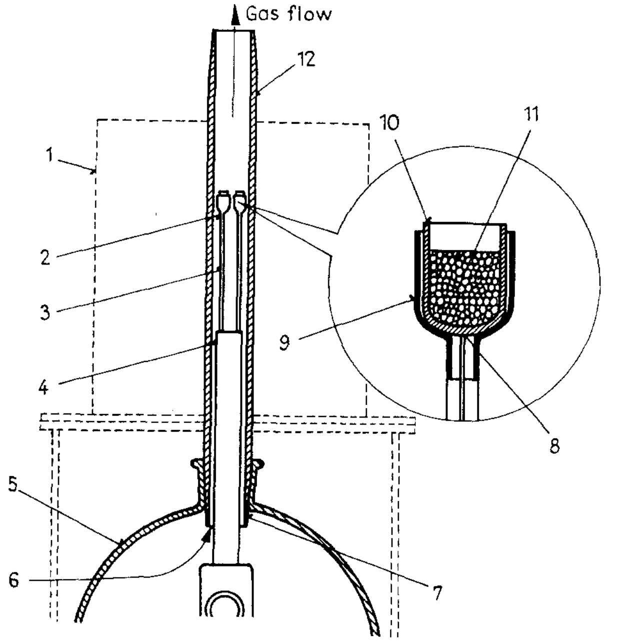

Fig. 1. Cup cell, cross-section. 1: furnace; 2: shoulder; 3: ceramic insulator; 4: ceramic support; 5: bell jar; 6: gas flow; 7: tapered joint; 8: thermocouple junction; 9: platinum cup; 10: liner; 11: sample; 12: alumina furnace tube

Results

The inherent resistance of a calorimeter to heat flow may be manifested as a constant in the equation:

$$E = 60 \frac{\Delta HMC}{\Delta T_s A}$$

where ΔH is the heat constant of the sample (millicalories per milligram), E is the heat flow calibration constant (millicalories per millivolt per second), A is the peak area (inch^2), ΔT_s the Y-axis sensitivity (millivolts per inch), M the sample mass (mg), and C the chart speed (inch per min).

In Table 1 and Figure 2 are shown the values of E, the heat flow constant, at various temperatures calculated from the above equation.

The heat flow constants in Table 1 are slightly higher than those for existing commercial differential scanning calorimeter cells. The values of Table 1 indicate that the 1200 °C calorimeter is 2 to 5 times less sensitive than existing differential scanning calorimeters.

The plot in Fig. 2 indicates a linearly increasing thermal resistance in proportion to the increasing thermal resistance of air. When E is expressed in terms of milli-

Table 1

Heat flow constants, millicalories per millivolt per second

Tin	0.297
Lead	0.317
Aluminum	0.450
Silver	0.567

calories per °C per minute, this relationship is asymptotic at high temperatures, whereas the resistance to heat flow expressed in Fig. 2 is essentially linear when expressed in millicalories per millivolts per second.

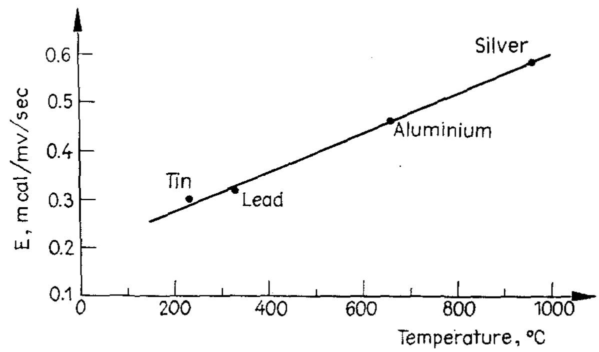

Fig. 2. 1200 °C cell heat flow calibration curve

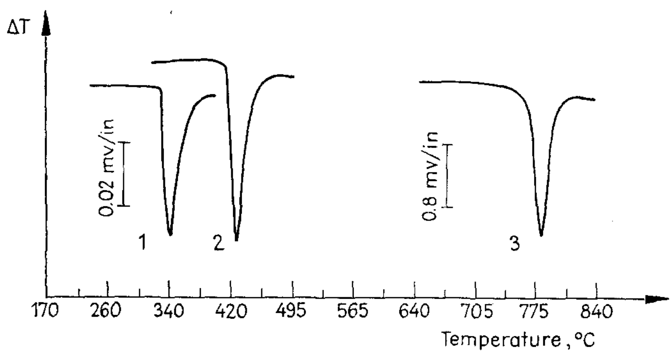

Fig. 3. Melting endotherms. 1: KNO_3, 37.380 mg; 2: Zn, 33.490 mg; 3: KCl, 27.880 mg; atmosphere: air; heating rate: 20°/min; reference: alumina

After calibration with tin, lead, aluminum, and silver, samples of potassium nitrate, zinc, and potassium chloride were run; the results are shown in Figure 3, illustrating the sharp endotherms obtained from these pure materials and spanning the temperature range 300° to 800°. Table 2 contains the calorimetric data for three runs of each material in the 1200°C cell, compared to existing literature data for these three materials.

Table 2

Heats of fusion, calories per gram

Sample	1200 °C cell	Literature*	Calorimetric precision, %
Potassium nitrate, KNO_3	24.3±0.6	25.4	±2.5
Zinc	27.3±0.5	28.1	±1.8
KCl	71.9±1.3	74.1	±1.8

* Handbook of Chemistry and Physics, Chemical Rubber Co., Cleveland, Ohio, 32nd Ed., 1950, p. 1914.

Whereas the calorimetric accuracy of the Du Pont 1200°C cell is slightly less than that of adiabatic and scanning calorimeters, the results from this work evidence the use of this cell for accurate high temperature calorimetric work, for most available calorimeters have lower temperature ceilings than the cell used in this work.

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Résumé — Etude de la précision calorimétrique probable d'une cellule Du Pont de 1200°C. On peut réaliser avec attention soignée une précision d'environ ±2% avec une déviation légèrement plus grande, d'environ ±5% en exactitude. La constante de calibration du courant de chaleur, *E*, est linéaire à la température. Sa valeur fait deux jusqu'à quatre fois celles des calorimètres enregistreurs commerciaux.

Zusammenfassung — Die mit der Du Pontschen 1200°C Zelle erreichbare kalorimetrische Genauigkeit wurde erörtert. Durch geeignetes Verfahren kann eine Präzision von ± 2%, mit einer etwas höheren Abweichung von ±5% in der Genauigkeit erzielt werden. Die Kalibrationskonstante des Wärmestromes *E* ist mit der Temperatur linear und ihre Werte betragen das zwei- bis vierfache derjeniger der handelsüblichen Scanning-Kalorimeter.

Резюме — Описана вероятная калориметрическая точность элемента (cell) ду Понта 1200 °C. При тщательной работе на приборе был достигнут расброс калориметрических измерений около ±2%, и около ±5% точности. Постоянная калибрования потока тепла, E, являющаяся линейной по температуре, в два — четыре раза больше значения константы имеющихся в продаже приборов ДШЦ.