Thermochimica Acta, 149 (1989) 123–131
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DETERMINATION OF THE SPECIFIC HEAT FUNCTIONS OF PYX AND KP BY DSC

GAO XIANG and LAO YUNLIANG

Dept. 8, Beijing Institute of Technology, P.O. Box 327, Beijing (China)

(Received 14 November 1988)

ABSTRACT

A new method for measuring specific heat by DSC is proposed. The specific heat functions of PYX (2,6-bis(picryl amino)-3,5-dinitropyridine) and KP (potassium picrate) have been measured using this and two other methods. The source of errors is analysed, and a formula proposed which represents the relationship between the true value and the measured value. The errors of the specific heats derived using the three methods are discussed, and a comparison is made which shows that the new method is the best for use with energetic materials such as PYX and KP for which the sample weight has to be small when specific heat is measured.

INTRODUCTION

Energetic materials have a wide application in areas such as aviation, space flight, oil prospecting and drilling, etc. in which high temperatures are involved. Evaluation of the thermal performance of energetic materials at high temperatures has therefore become more urgent and more important. Generally, this can be done through solving a heat conduct equation: $C_p \, \mathrm{d}T/\mathrm{d}t = -K\,T + \mathrm{f}(T)$. This requires knowledge of certain physicochemical parameters of the materials involved, one of which is the specific heat.

There are several methods for the measurement of specific heat [1–4]. Compared with other methods, the DSC method has the advantages that only a small weight of sample is required, and the operation is rapid, simple and convenient. Also, it is a direct method. O'Neill [3] has concluded that the error in measurement of a specific heat by this method is 0.3% or less. As only a small weight of sample is required the method is also ideal for measuring specific heats of substances which are energetic and involve some danger of explosion.

PRINCIPLES AND METHODS

When the per unit mass of a given substance at a given temperature rises by 1 K, a certain quantity of heat will be absorbed. This quantity of heat is

0040-6031/89/$03.50

called the specific heat of the substance at that temperature. The DSC method obtains the specific heat function of a sample by measuring the heat flux–temperature diagram for a given temperature programme. To obtain the relation between heat flux and the specific heat of the sample, the following assumptions need to be made: (1) that the temperature in the inner sample is uniform (no gradient of temperature); (2) that the temperature at which the sample is maintained is equal to the stove temperature programme throughout the entire experimental period. These two assumptions can be satisfied by adding a thermal contact area between the sample and the crucible, using samples of small particle size, using a small thickness of sample, etc.

The relationship between heat flux and the specific heat of a sample is

$$(\mathrm{d}H/\mathrm{d}t) = mC_p\, \mathrm{d}T/\mathrm{d}t \qquad (1)$$

where m is the mass of the sample, C_p is the specific heat of the sample, $\mathrm{d}T/\mathrm{d}t$ is the heating rate of the temperature programme, and $\mathrm{d}H/\mathrm{d}t$ is the heat flux.

From eqn. (1)

$$C_p = (\mathrm{d}H/\mathrm{d}t)/(m\, \mathrm{d}T/\mathrm{d}t) \qquad (2)$$

Specific heat C_p can be calculated directly using eqn. (2), but errors introduced by the instrument and the operation will mean that the accuracy of C_p measured in this way will be poor. O’Neill has therefore proposed another method. For a standard reference material

$$(\mathrm{d}H/\mathrm{d}t)' = C_p'm'\, \mathrm{d}T/\mathrm{d}t \qquad (3)$$

Dividing eqn. (1) by eqn. (3), we obtain

$$C_p = C_p'(m'/m)(\mathrm{d}H/\mathrm{d}t)/(\mathrm{d}H/\mathrm{d}t)' \qquad (4)$$

Equation (4) takes into account errors produced during the measurement, and minimizes these with the aid of the specific heat of the standard reference material.

The present authors here propose another method by which errors can be reduced.

Subtracting eqn. (3) from eqn. (1), we obtain

$$C_p = \left(\mathrm{d}H/\mathrm{d}t - (\mathrm{d}H/\mathrm{d}t)' + m'C_p'\, \mathrm{d}T/\mathrm{d}t\right)/(m\, \mathrm{d}T/\mathrm{d}t) \qquad (5)$$

Equations (4) and (5) both reduce measurement errors with the aid of a standard reference material, but as they have different forms, the results they give are also different.

EXPERIMENTAL

The instrument used was a P-E7 Series differential scanning calorimeter. The standard reference substance was Al_2O_3, and the samples were of PYX

(2,6-bis(picryl amino)-3,5-dinitropyridine) and KP (potassium picrate). The temperature range was 60–290 °C for PYX and 60–230 °C for KP.

An isothermal baseline is taken at a low temperature. After this has become stable, the temperature is increased according to a heating programme within a certain temperature range, and a second isothermal baseline taken at a higher temperature. These two baselines and the baseline within the temperature range are stored in the computer system. A sample and the standard reference substance are then put in a crucible, the procedure is repeated, and the heat flux–temperature diagram recorded. When picking up the data, the effect of the baseline must be subtracted. The specific heat of the sample can then be obtained using eqn. (2), (4) or (5).

All samples were put into aluminum crucibles. The masses of the aluminium crucibles were kept as similar as possible for each group of experiments. The mass difference was 0.02 mg. The error introduced through difference of crucible masses can be ignored. The sample mass was about 3 mg for KP, with 4 mg of Al_2O_3, and about 3 mg for PYX, with 5 mg of Al_2O_3.

The instrument was calibrated using the melting points of standard substances. The temperature error of the instrument is less than 0.5 K. The sensitivity of measurement of heat flux was 0.01 mW.

DISCUSSION OF ERRORS

The errors during measurement can be divided into two kinds of variation, one systematic, and the other random. Systematic errors arise from the non-linear property of the calorimeter, which is within 1%, and the temperature errors after calibration, which can be reduced when the temperature is kept within a narrow temperature range. Random errors arise from baseline noise, the reproducibility of the temperature programme, errors in weighing the samples, etc. These depend on the characteristics of the machine and the operation, and cannot be foreseen. Poor thermal contact between sample and crucible, and poor temperature distribution within a sample can also create errors. These two kinds of error, and errors created by the non-linear property of the machine and extension of temperature are proportional to the quantity of heat flux. Baseline noise and the reproducibility of the temperature programme are not usually related to heat flux.

So measurement error can be divided into two other kinds of variation: that which is proportional to heat flux, and that which remains constant. Thus $\mathrm{d}H/\mathrm{d}t$ as determined by the machine can be written as

$$\mathrm{d}H/\mathrm{d}t = rm\hat{C}_p \, \mathrm{d}T/\mathrm{d}t + \mathrm{a} \qquad (6)$$

where $m\hat{C}_p \, \mathrm{d}T/\mathrm{d}t$ is the true value of the heat flux, $\hat{C}_p$ is the true value of the specific heat, and $1 - r$ represents the amount of error proportional to the heat flux. If $r = 1$, heat flux has no contribution to the error. The larger the value of $1 - r$, the greater the contribution of heat flux to the error. The symbol a represents the error which is not related to heat flux, and can be considered to be a constant. Errors created by calculating specific heat using eqns. (2), (4) and (5) will be analysed below.

Inserting eqn. (6) into eqn. (2), we obtain

$$C_p = r\hat{C}_p + \mathrm{a}/(m\ \mathrm{d}T/\mathrm{d}t) \tag{7}$$

where

$$\hat{C}_p = (C_p - \mathrm{a}/(m\ \mathrm{d}T/\mathrm{d}t))/r \tag{8}$$

and C_p is the measured value of specific heat.

The error is

$$E_1 = (1 - r)C_p/r - \mathrm{a}/(rm\ \mathrm{d}T/\mathrm{d}t) \tag{9}$$

Inserting eqn. (6) into eqn. (4), we obtain

$$C_p = \left(r\hat{C}_p\ \mathrm{d}T/\mathrm{d}t + \mathrm{a}/m\right)/\left(r\ \mathrm{d}T/\mathrm{d}t + \mathrm{a}/(m'C_p')\right) \tag{10}$$

where

$$\hat{C}_p = C_p + \left(C_p\mathrm{a}/(m'C_p') - \mathrm{a}/m\right)/(r\ \mathrm{d}T/\mathrm{d}t) \tag{11}$$

The error is

$$E_2 = (C_p - C_p'm'/m)\mathrm{a}/(m'C_p'r\ \mathrm{d}T/\mathrm{d}t) \tag{12}$$

Inserting eqn. (6) into eqn. (5), we obtain

$$C_p = r\hat{C}_p - rm'C_p'/m + m'C_p'/m \tag{13}$$

where

$$\hat{C}_p = (C_p - (1 - r)m'C_p'/m)/r \tag{14}$$

The error is

$$E_3 = (C_p - m'C_p'/m)(1 - r)/r \tag{15}$$

It can be seen from the representations of E_1, E_2 and E_3 that the error created by the first method depends on the sample mass m, the rate of temperature rise $\mathrm{d}T/\mathrm{d}t$ and parameters r and a, and cannot be reduced to zero; the error created by the second method depends on m', m, r, a and $\mathrm{d}T/\mathrm{d}t$, and if m and m' are such that $m'C_p' = mC_p$, then the error can be reduced to zero; and the error created by the third method depends on r and m/m', and can similarly be reduced to zero if $m'C_p' = mC_p$.

We measure specific heat within a temperature range, so it is difficult to find a standard reference to satisfy $m'C_p' = mC_p$ at every temperature point, but we can use a substance whose specific heat function is close to that of the measuring substance as a standard reference. Because of the difference

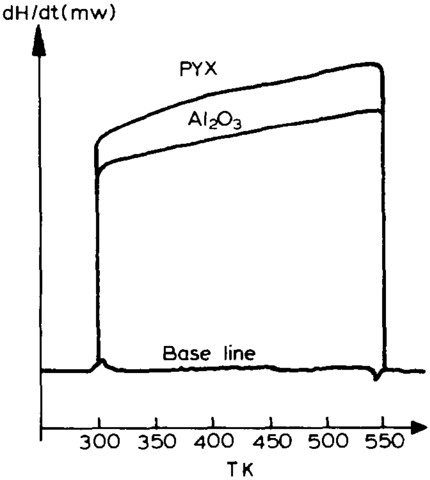

Fig. 1. Heat flux plot for PYX.

between the specific heat functions of different substances, $m'C_p' = mC_p$ should be satisfied at the middle point of the temperature range when specific heat function is calculated using eqns. (3) or (5), which will reduce the error transmitted to the two sides to a minimum. If the specific heat is determined using eqn. (5), only the ratio of m to m' need be controlled in order to reduce the error, which is extremely practical when measuring the specific heat of an energetic material, where a large mass can be dangerous. Enlarging the sample mass is sufficient to reduce the measuring error when determining specific heat using eqns. (2) and (4). So eqn. (5) is the best of the three equations for determining the specific heat function of an energetic material by DSC.

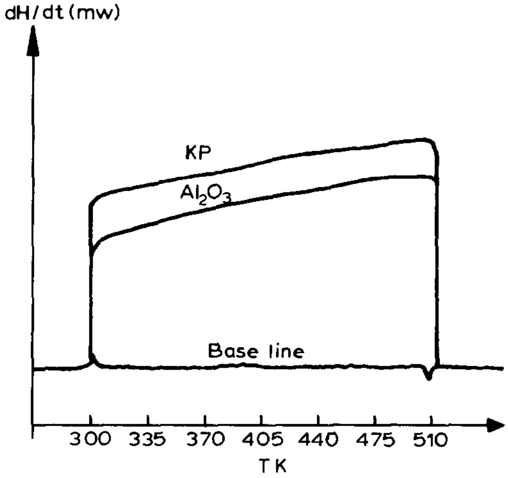

Fig. 2. Heat flux plot for KP.

RESULTS

Figure 1 is a typical diagram of heat flux varying with temperature of PYX and Al_2O_3, and of the baseline during its own temperature range.

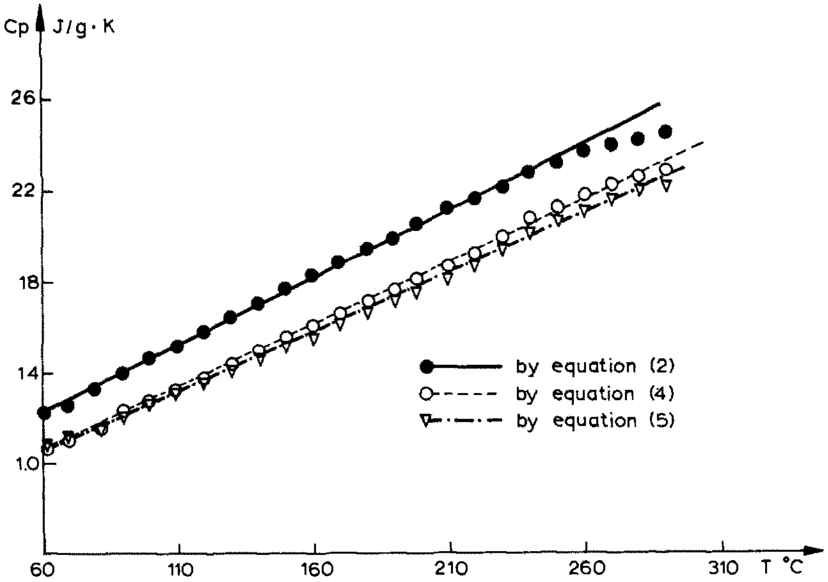

Fig. 3. Specific heat plot for PYX.

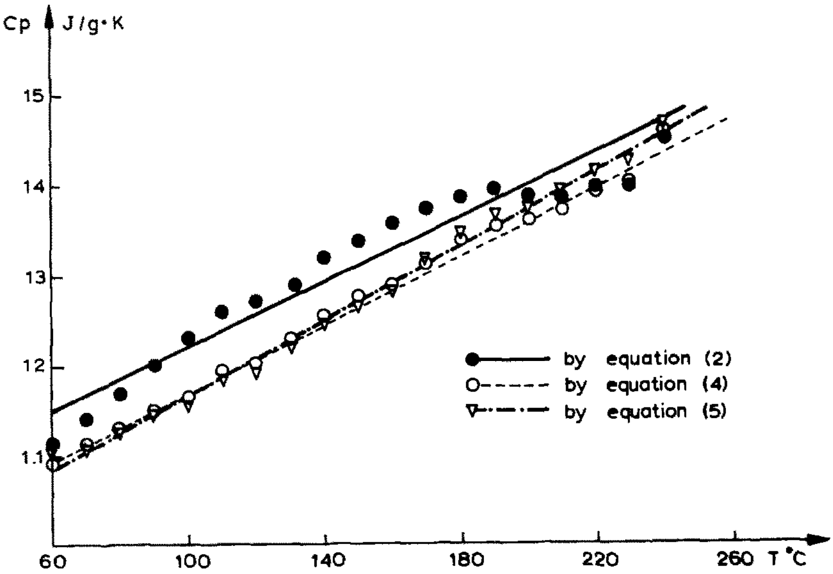

Fig. 4. Specific heat plot for KP.

TABLE 1

Specific heat values for Al_2O_3

Temperature (K)	C_p ($J g^{-1} K^{-1}$)	Temperature (K)	C_p ($J g^{-1} K^{-1}$)
333	0.8330	453	0.9920
343	0.8500	463	1.001
353	0.8665	473	1.010
363	0.8828	483	1.018
373	0.8977	493	1.026
383	0.9119	503	1.034
393	0.9252	513	1.041
403	0.9381	523	1.049
413	0.9497	533	1.056
423	0.9610	543	1.062
433	0.9718	553	1.069
443	0.9820	563	1.075

Figure 2 corresponds to KP and Al_2O_3, and the baseline. Figures 3 and 4 are specific heat diagrams for PYX and KP determined separately by the three equations. The specific heat function of the reference material is similar to those for the two substances under investigation, and $m'C_p' = mC_p$ at the middle point of the temperature range. There is little difference between the

TABLE 2

Measured values for specific heat of PYX

Temperature (K)	C_p ($J g^{-1} K^{-1}$)			Temperature (K)	C_p ($J g^{-1} K^{-1}$)		
	Eqn. (2)	Eqn. (4)	Eqn. (5)		Eqn. (2)	Eqn. (4)	Eqn. (5)
333	1.218	1.069	1.067	453	1.929	1.660	1.704
343	1.256	1.112	1.112	463	1.979	1.705	1.753
353	1.317	1.155	1.158	473	2.041	1.756	1.809
363	1.388	1.204	1.211	483	2.093	1.799	1.855
373	1.450	1.246	1.252	493	2.153	1.876	1.912
383	1.508	1.302	1.315	503	2.200	1.941	1.982
393	1.573	1.345	1.364	513	2.264	2.003	2.065
403	1.637	1.394	1.418	523	2.302	2.051	2.115
413	1.695	1.453	1.480	533	2.348	2.102	2.166
423	1.759	1.505	1.539	543	2.377	2.142	2.212
433	1.823	1.547	1.587	553	2.408	2.181	2.240
443	1.877	1.602	1.644	563	2.425	2.208	2.270

Regressive equation by (2): $C_p = (-6.033 + 5.534 \times 10^{-2}\ T) \times 10^{-1}$, $r = 0.997$.
Regressive equation by (4): $C_p = (-6.771 + 5.172 \times 10^{-2}\ T) \times 10^{-1}$, $r = 0.9991$.
Regressive equation by (5): $C_p = (-7.799 + 5.482 \times 10^{-2}\ T) \times 10^{-1}$, $r = 0.9992$.

TABLE 3

Measured values for specific heat of KP

Temperature (K)	C_p (J g^{-1} K^{-1})			Temperature (K)	C_p (J g^{-1} K^{-1})		
	Eqn. (2)	Eqn. (4)	Eqn. (5)		Eqn. (2)	Eqn. (4)	Eqn. (5)
333	1.117	1.093	1.110	433	1.358	1.290	1.285
343	1.143	1.114	1.109	443	1.373	1.318	1.320
353	1.170	1.130	1.130	453	1.386	1.339	1.344
363	1.203	1.150	1.144	463	1.394	1.355	1.365
373	1.232	1.166	1.155	473	1.386	1.362	1.377
383	1.260	1.195	1.186	483	1.385	1.372	1.393
393	1.272	1.201	1.190	493	1.398	1.392	1.415
403	1.290	1.230	1.223	503	1.398	1.403	1.428
413	1.321	1.255	1.248	513	1.451	1.462	1.467
423	1.341	1.274	1.269				

Regressive equation by (2):$C_p = 0.5655 + 1.767 \times 10^{-3}$ T, $r = 0.9762$.
Regressive equation by (4); $C_p = 0.4154 + 2.023 \times 10^{-3}$ T, $r = 0.9965$.
Regressive equation by (5): $C_p = 0.438 + 1.966 \times 10^{-3}$ T, $r = 0.9961$.

specific heat functions determined using eqns. (4) and (5), but that obtained using eqn. (2) is much greater. This difference is clearly due to the introduction of greater error through the use of eqn. (2). We propose that the values for specific heat function determined using eqns. (4) and (5) are more accurate, and that the value obtained using eqn. (5) is the most accurate. Table 1 lists the specific heat values obtained for Al_2O_3 within 60–290 °C. The specific heat values for PYX and KP determined using the three equations are given in Tables 2 and 3 respectively. It can be seen that within these temperature ranges the relation between temperature and the specific heat values for PYX and KP is linear.

CONCLUSIONS

(1) The method proposed here for the measurement of the specific heat of a material by DSC is simple and sufficient, and has the advantage that it can greatly reduce measurement error.

(2) The equation $\mathrm{d}H/\mathrm{d}t = rmC_p\mathrm{d}T/\mathrm{d}t + \mathrm{a}$ has a distinct physical meaning and is a sufficient tool for analysing the errors.

(3) The specific heat function of the energetic material PYX is $(-7.799 + 5.482 \times 10^{-2}\ \mathrm{T}) \times 10^{-1}$ (temperature range 60–290 °C).

(4) The specific heat function of the energetic material KP is $0.4154 + 2.023 \times 10^{-3}$ T (temperature range 60–240 °C).

REFERENCES

1 D. Ginnings and R.J. Corruccini, J. Res. Natl. Bur. Std., 38 (1947) 593.
2 E.F. Westrum, Jr., J.B. Hatcher and D.W. Osborne, Chem. Phys., 21 (1953) 419.
3 M.J. O'Neill, Anal. Chem., 38 (1968) 1331.
4 Thermophysical Properties of Specific Heat, TPRC Data Series, 1970.