ELSEVIER

Thermochimica Acta 392–393 (2002) 251–257

thermochimica acta

www.elsevier.com/locate/tca

An overview of calibration materials used in thermal analysis—benzoic acid

S.F. Wright*, P. Phang, D. Dollimore, K.S. Alexander

Department of Chemistry, College of Pharmacy, University of Toledo, 2801 W. Bancroft Street, Toledo, OH 43606-3390, USA

Received 29 December 2000; accepted 28 April 2001

Abstract

There are a number of substances used to calibrate various instruments with benzoic acid being an IUPAC recommended calibration material. It has gained recognition as a reference material because it exhibits an ''ideal'' behavior. Hence, benzoic acid is often used to aid in determining the enthalpy of sublimation values for various organic substances. In this study, the thermal behavior of benzoic acid is observed from a simultaneous thermogravimetry–differential thermal analysis (TG–DTA) unit. A series of tests under various experimental conditions is performed, and the results allow for the determination of the enthalpy of sublimation values for benzoic acid. The purpose of this study is to investigate the influence of experimental parameters, such as sample preparation procedures, heating rates, atmospheric conditions, and gas flow rates, on the calculated enthalpy of sublimation values. Enthalpy of vaporization for benzoic acid was also calculated.

Keywords: Sublimation; Evaporation; Thermogravimetry; Calibration material; Benzoic acid

1. Introduction

Sublimation is the direct conversion from a solid to a gas without first melting and changing the chemical composition. Evaporation is the transition from a liquid to a gas without an alteration in the chemical composition. These processes are affected by the following factors of the material: vapor pressure, molecular weight, temperature, and the amount of the surface exposed. For both processes, the enthalpy ΔH can be calculated. The enthalpy of a process is based on the molecules building up enough kinetic energy on the surface of a solid or a liquid to overcome the intermolecular forces of attraction and escape into the gas phase with an increase in temperature. The energy that is supplied to offset the cooling effect brought about by the escaping molecules is the enthalpy of the process. The enthalpy of sublimation is greater than the enthalpy of evaporation due to the fact that sublimation takes place from the solid phase and requires more energy to make the transition to the gas phase.

In the area of thermal analysis, thermogravimetry (TG) has been well established as a rapid and reliable technique for the monitoring of sublimation and evaporation processes of substances [1,2]. When a temperature program is employed using a thermogravimetric analyzer, the mass loss of the sample from an unchanging surface area in a regulated atmosphere is recorded. The resulting data can be illustrated as a TG plot, where mass loss is plotted against temperature or

* Corresponding author. Tel.: +1-419-530-1520; fax: +1-419-530-4033.
E-mail address: shontellf@hotmail.com (S.F. Wright).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00108-9

time. If the derivative of the percentage of mass loss is taken, these values create a differential TG (DTG) curve when they are plotted against temperature.

At any rate in many cases, the information obtained from TG alone is insufficient in the thermal characterization of a material. TG only reveals information about a process that involves a mass change. On the other hand, differential thermal analysis (DTA) will produce an endothermic or an exothermic peak based on the physical characteristics and chemical changes of the sample as it undergoes heat treatment. In DTA measurements, the difference in temperature experienced by the sample during regimes of heating and atmosphere control is compared to a reference and recorded versus time or temperature. As a result, a simultaneous TG–DTA unit can be used since the sample is studied under the same experimental conditions for both techniques, and standard reference materials for DTA can be used for the calibration of temperature.

Benzoic acid has been used as a calibration material in TG to aid in the thermal characterization of substances that either sublime, evaporate, or both because of its so-called "ideal behavior" [3]. The phrase "ideal behavior" refers to the well-characterized points of melting and evaporation, which are reproducible when studied using a calorimeter. Different techniques have been used to characterize the enthalpies of sublimation and evaporation for benzoic acid [3,4]. The enthalpy of sublimation for benzoic acid has been characterized using TG isothermally. When analyzed with a simultaneous TG–DTA unit, benzoic acid has been reported to go through an evaporation process from a liquid to a vapor and that no sublimation occurs [5]. In this study, a simultaneous TG–DTA unit will permit the identification of the regions of the TG curve, which corresponds to sublimation and evaporation.

2. Experimental

Benzoic acid, a certified A.C.S. Fisher Chemical, was obtained from Fisher Scientific Company with a purity rating of >99.5%. The benzoic acid samples were studied using a simultaneous TG–DTA unit from TA Instruments, model 2960. A platinum crucible was used to hold 5–22 mg of the sample. An empty platinum crucible was used as the reference. The inner diameter of the sample crucible was 6.066 mm. Studies were conducted in an atmosphere of dry air. Various flow rates (25, 50 and 100 ml/min) were used in the studies. An electronic flowmeter purchased from J & W Scientific was used to regulate the gas flow rates. A rising temperature method over the temperature range of ambient to 300 °C was utilized. The heating rates for these experiments were also varied at 2, 5 and 10 °C/min. Sample preparation involved packed samples, crushed samples and crystalline samples.

2.1. Sample preparation

In this study, the benzoic acid samples were prepared for analysis by various sample preparation procedures. The purpose of this endeavor was to observe the changes in the sublimation kink on the TG curve and relate them to the effects of sample preparation methods. Three different types of samples were used in the study: packed, crushed and crystalline. The packed samples involved compacting powdered samples into a platinum crucible using a scoop spatula. Benzoic acid samples were also pulverized with a glass mortar and pestle to obtain powdered samples. This was done to obtain uniform particle sizes within the samples. The last type of sample analyzed involved using the benzoic acid, as provided by the manufacturer. These samples exist as white crystalline forms.

3. Results and discussion

3.1. Calculations

The vapor pressure curve of benzoic acid was constructed using the Langmuir equation:

$$\frac{\mathrm{d}m}{\mathrm{d}t}\frac{1}{a} = p\alpha\left(\frac{M}{2\pi RT}\right)^{1/2} \tag{1}$$

where the rate of mass loss per unit area $((\mathrm{d}m/\mathrm{d}t)(1/a))$ is in units of kg/(s m^2), the vapor pressure (p) is in units of Pa, the vaporization constant (α) has no units, the molecular weight of the evaporating species (M) is in units of kg/mol, the gas constant (R) is in units of J/(K mol), and the absolute temperature (T)

is in units K. Using Eq. (1), a form of Langmuir equation better suited for the analysis of the TG data can be achieved.

$$p = kv \tag{2}$$

In Eq. (2), k replaced $\alpha^{-1}(2\pi R)^{1/2}$, and v is replaced by $(T/M)^{1/2}((\mathrm{d}m/\mathrm{d}t)(1/a))$. It has been demonstrated that k is independent of the sample, dependent of the instrument, and can be used in the calibration of substances where the vapor pressures are unknown [6,7]. The value of v is dependent on the sample and independent of the instrument. The effect that temperature had on vapor pressure of benzoic acid was expressed using the Antoine equation in the following form:

$$\log p = A - \frac{B}{C+T} \tag{3}$$

In Eq. (3), A–C are the Antoine constants taken in a certain temperature range for the evaporating species. For benzoic acid, the values of A–C in the temperature range of 405 and 523 K are 7.80991, 2776.12, and −43.978, respectively [8]. These constants were taken in the temperature range for the evaporation process. The Antoine constants were not available in the temperature range for the sublimation process, so the vapor pressure for this process could not be calculated using this method. With the aid of Eq. (2), the linear relationship of p and v was plotted, and the slope was equal k. The value of k for the evaporation processes was determined and used in Eq. (2), to calculate the vapor pressure for the sublimation process. The value of k is dependent on the instrument used and not the sample involved. In this paper, it will be shown that the k of the evaporation

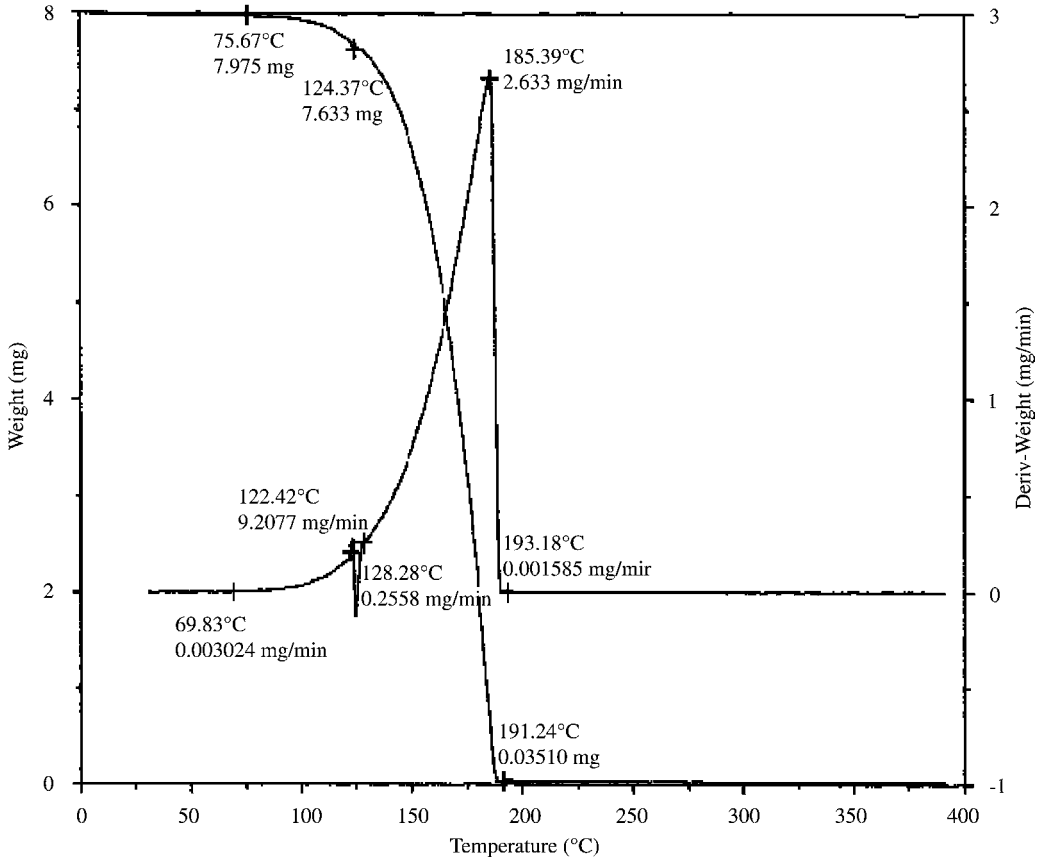

Fig. 1. TG–DTG plot of benzoic acid illustrating the sublimation kink air at a flow rate of 100 ml/min and a heating rate of 10 °C/min to 400 °C (particle size: 7.9816 mg).

process can be used in the calibration of substances, which undergo sublimation. The enthalpies of sublimation (ΔH_{sub}) and vaporization (ΔH_{evap}) were calculated based on the slope from the graph of ln v and $1/T$ using the Clausius–Clapeyron Eq. (5).

$$\ln v = \text{constant} - \frac{\Delta H}{RT} \quad (5)$$

A plot of ln v versus $1/T$ provided a slope, which was equivalent to $-\Delta H/R$.

4. Results

Three plots displaying the sublimation and evaporation processes of benzoic acid were constructed using the data obtained from the simultaneous TG–DTA unit: weight versus time (TG, Figs. 1 and 2), dm/dt versus time (DTG, Fig. 1), and temperature difference versus time (DTA, Fig. 2). The TG plot indicated that the mass loss was gradual. The DTG plot reflected the characteristic evaporation shape and followed a zero-order. Using the TG plot, the sublimation process of benzoic acid was considered to take place from the beginning of mass loss to the beginning of the sublimation kink. The sublimation kink on the TG plot roughly corresponds to the melting point peak on the DTA plot. At the point of melting shown in the DTA plot, there is a corresponding kink in the TG plot. In the DTA plot for benzoic acid, there was one endothermic peak in a lower temperature region, which is taken to be the melting point (T_m) and one endothermic peak in the upper temperature region, which is taken to represent evaporation. When the DTA plot was superimposed on the TG plot, it was determined that the evaporation process occurred between the points of melting and evaporation. On the DTG plot, the maximum rate of evaporation (T_f) is considered to be the peak.

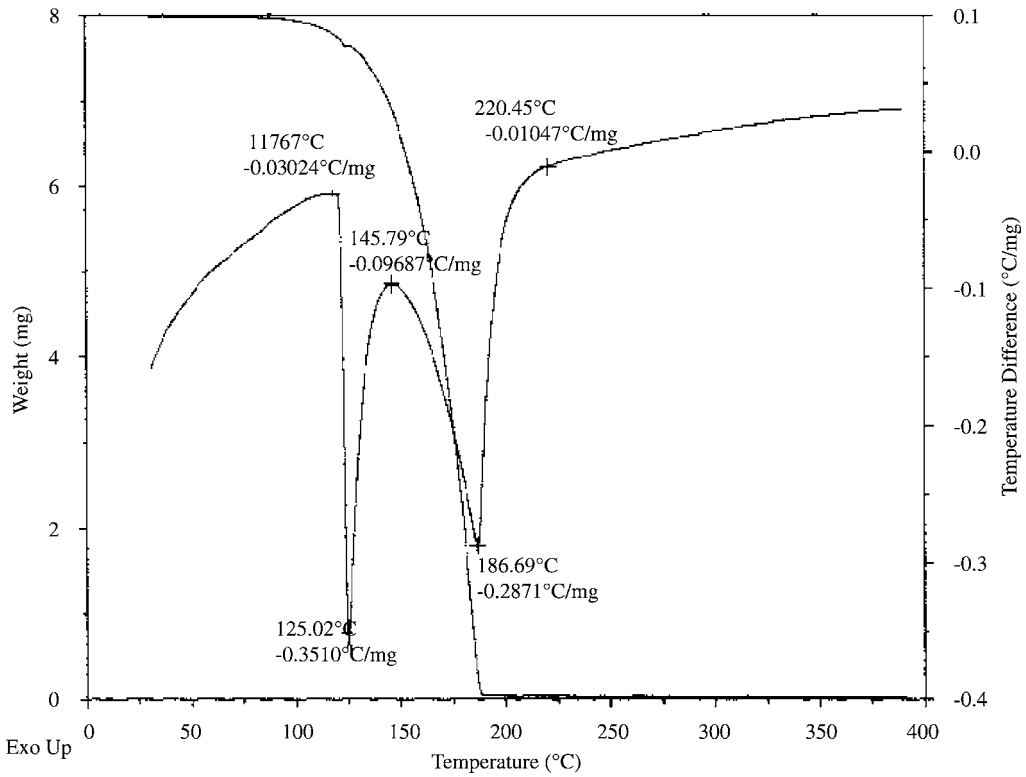

Fig. 2. A typical TG–DTA plot of benzoic acid air at a flow rate of 100 ml/min and a heating rate of 10 °C/min to 400 °C (particle size: 7.9816 mg).

As shown in Fig. 1, it was observed that the sublimation kink on the TG was most prominent for crystalline samples. The irregular particle sizes contributed to uneven melting, and hence, sublimation was easily observed. For crushed samples, the sublimation kink was least distinct. This observation may be attributed to the uniform particle sizes of the sample. The melting event of the crushed sample was even and, hence, the sublimation kink was not as pronounced. The resulting TG curve for packed samples exhibited the presence of a minor kink.

The Antoine equation allowed for the calculation of the vapor pressure (p) with respect to temperature for the evaporation process. Then, p was plotted against v. A sample plot is shown in Fig. 3. From this graph, the slope was taken to be k, which was used in Eq. (2) to estimate the vapor pressure for the sublimation process. The enthalpy for each process was determined using the Clausius–Clapeyron Eq. (5). ΔH_{sub} and ΔH_{evap} were calculated from the slope of the $\ln v$ versus $1/T$ plot. A sample graph is shown in Fig. 4. The values of T_m and enthalpy are listed in Tables 1–3

Table 1
Physical data and enthalpies at various heating rates with a flow rate of 100 ml/min of dry air

β (°C/min)	T_m[a] (°C)	ΔH (kJ/mol)	
		Sublimation[b]	Evaporation[c]
2	122.4	91.33 ± 0.91	60.56 ± 0.61
5	123.1	92.34 ± 0.92	66.05 ± 0.66
10	123.7	91.29 ± 0.91	65.40 ± 0.65

[a] T_m is the melting point from the DTA plot.
[b] The ΔH_{sub} value reported in literature was 89.70 ± 1.00 kJ/mol [4].
[c] The ΔH_{vap} value reported in literature was 65.89 ± 0.09 kJ/mol [3].

based on the various heating rates (β), flow rates, and sample preparations. The ΔH_{sub} and ΔH_{evap} results reported in Tables 1–3 takes in consideration the accuracy of the balance measurements (±1%). The average values of ΔH_{sub} and ΔH_{evap} were 91.11± 1.4 kJ/mol and 66.08 ± 2.0 kJ/mol (mean ± S.D., $n = 6$) at a heating rate of 10 °C/min and a flow rate 100 ml/min using crystalline samples.

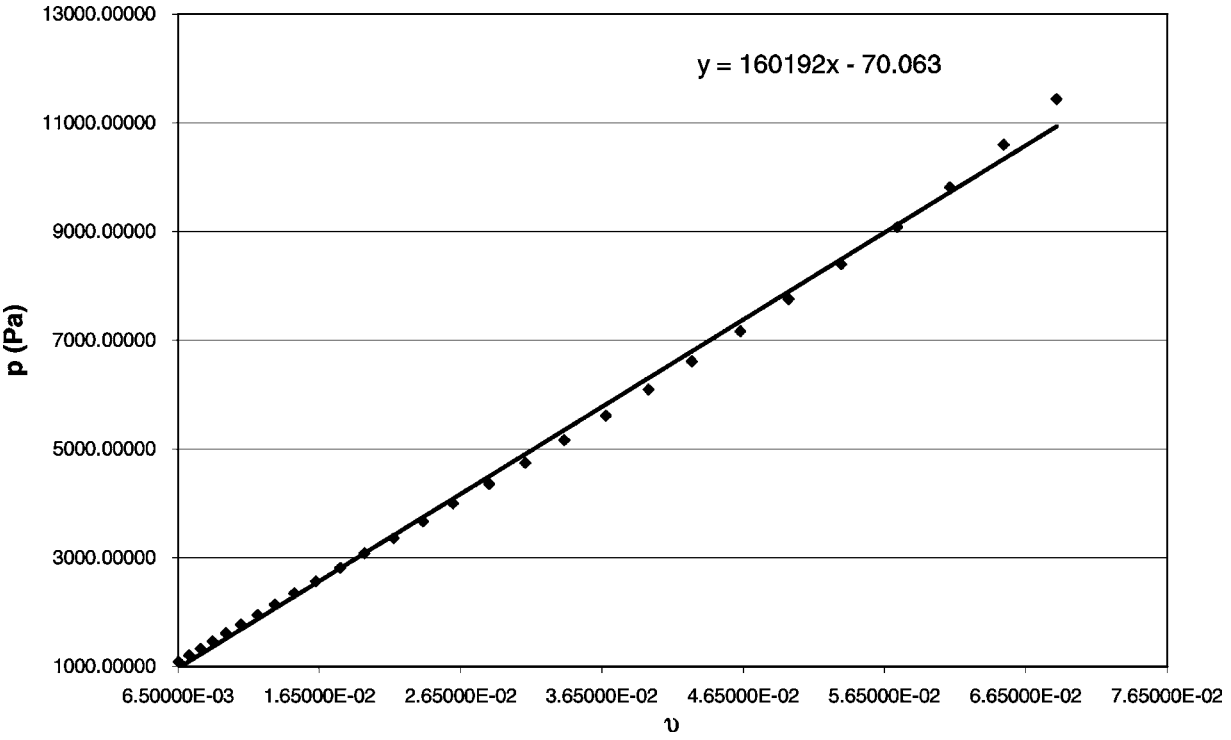

Fig. 3. Sample Langmuir plot. The determination of sample independent variable (k) for the evaporation process (10 °C/min, 100 ml/min).

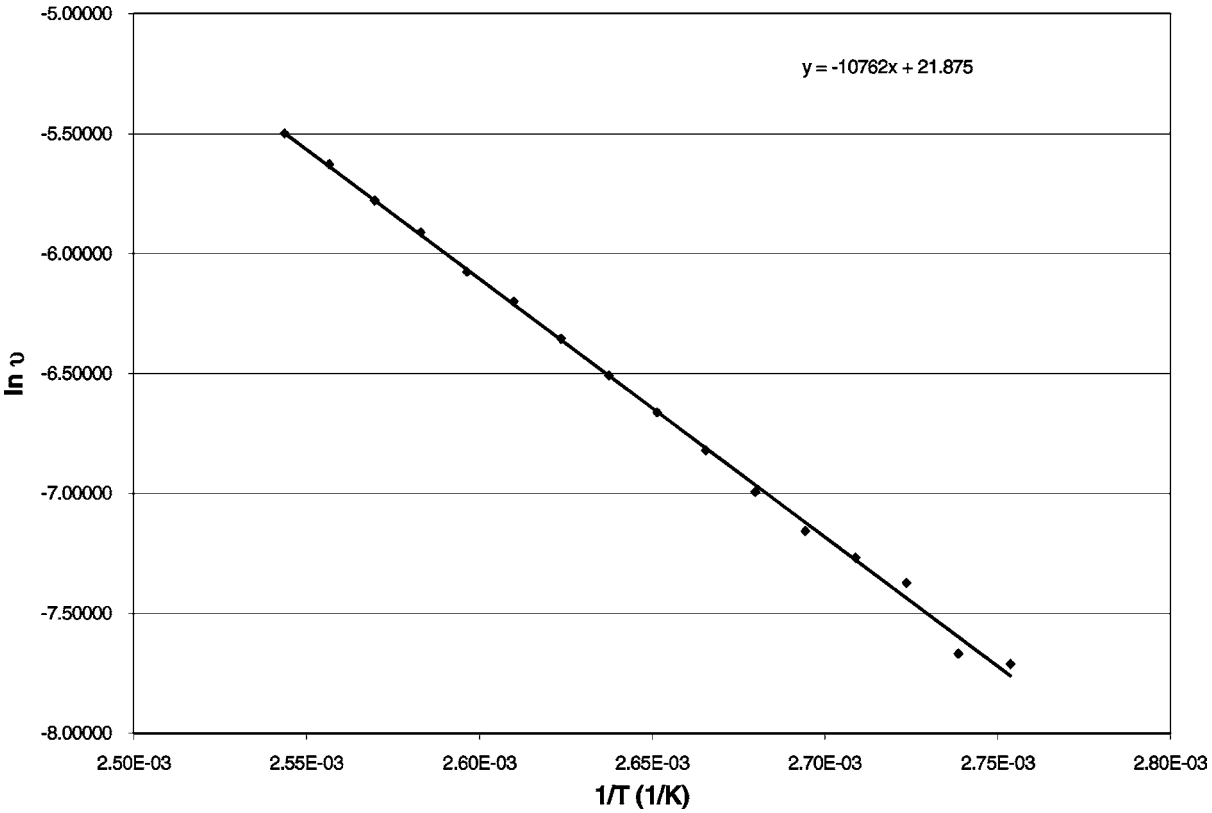

Fig. 4. Sample Clausius–Clapeyron plot. Enthalpy of sublimation (10 °C/min, 100 ml/min).

Table 2
Physical data and enthalpies at various flow rates with a heating rate of 10 °C/min

Flow rate (ml/min)	T_m (°C)	ΔH (kJ/mol)	
		Sublimation	Evaporation
25	123.7	92.24 ± 0.92	67.67 ± 0.68
50	123.7	89.61 ± 0.90	67.54 ± 0.68
100	123.7	89.63 ± 0.89	66.78 ± 0.67

Table 3
Physical data and enthalpies based on sample preparations with a flow rate of 100 ml/min and a heating rate of 10 °C/min

Sample preparation	T_m (°C)	ΔH (kJ/mol)	
		Sublimation	Evaporation
Crystalline	125.0	89.48 ± 0.89	67.24 ± 0.67
Crushed	123.7	91.38 ± 0.91	66.84 ± 0.67
Packed	125.7	87.73 ± 0.88	65.48 ± 0.65

5. Conclusion

Benzoic acid has been confirmed as a calibration material in TG to aid in the characterization of substances that either sublime, evaporate, or both. The simultaneous TG–DTA unit has been established as an excellent tool for detecting the sublimation and evaporation processes of benzoic acid. The sublimation and evaporation processes of benzoic acid followed a zero-order, and the evaporation process was represented by endothermic peak based on the DTG plots. The sublimation process took place in the range of 80–118 °C and the evaporation process in the range of 122–215 °C. The ΔH_{sub} and ΔH_{vap} values of benzoic acid were in close agreement with the values found in literature. The ΔH_{sub} and ΔH_{vap} values remained consistent as the experimental parameters were varied. Before the calculations could be performed on the sublimation data, the data had to be calibrated using the k obtained from the evaporation calculations.

Based on this fact, the sublimation process of benzoic acid would not meet the standards of a good calibration technique when using a simultaneous TG–DTA unit. The evaporation process has been established for years as a reliable calibration technique. This investigation confirms that benzoic acid is a valuable calibration material in the area of thermal analysis.

References

[1] S.J. Ashcroft, Thermochim. Acta 2 (1971) 512.
[2] P. Aggarwal, D. Dollimore, J. Therm. Anal. 50 (1997) 526.
[3] C.G. De Kruif, J.G. Blok, J. Chem. Thermodyn. 14 (1982) 201.
[4] R. Sabbah, An. Xu-wu, J.S. Chickos, M.L. Planas Leitao, M.V. Roux, L.A. Torres, Thermochim. Acta 331 (1999) 93.
[5] D. Dollimore, C. O'Connell, Thermochim. Acta 324 (1998) 33.
[6] D.M. Price, M. Hawkins, Thermochim. Acta 315 (2000) 19.
[7] D. Menon, D. Dollimore, K. Alexander, A TG–DTA study of sublimation of nicotinic acid, in: Proceedings of the 28th North American Thermal Analysis Society Meeting, Orlando, FL, October 2000, pp. 237–239.
[8] R.M. Stephenson, S. Malanowski, Handbook of Thermodynamics of Organic Compounds, Elsevier, New York, 1987.