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A THERMAL ANALYSIS STUDY OF HYDROXY BENZOIC ACID DERIVATIVES USING RISING TEMPERATURE THERMOGRAVIMETRY

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Abstract

Hydroxy benzoic acids were subjected to rising temperature thermogravimetric analysis. After optimizing the procedural variables, the kinetics of decomposition was determined and methyl paraben was taken as the calibration compound to characterize the evaporation patterns for the *ortho* and *meta* derivatives. The E_{act} values for *ortho*, *meta* and *para* derivatives were 64.8, 78.2, and 119.1 kJ mol^{-1}, respectively. The Antoine and Langmuir equations were utilized to determine the coefficient of evaporation k, which was 124525±0.8, units being in the SI system. The vapor pressure plots were generated for the *ortho* and *meta* derivatives; ΔH_{vap} for these two compounds were obtained as 66.7 and 80.4 kJ mol^{-1}, respectively.

Keywords: Antoine equation, Arrhenius equation, benzoic acids, evaporation, kinetics, Langmuir equation, thermogravimetry

Introduction

Benzoic acid derivatives find wide application in the pharmaceutical, chemical and food industry. *Ortho* hydroxy benzoic acid, commonly known as salicylic acid, is a pharmaceutically active antipyretic agent and *para* hydroxy benzoic acid and its derivatives form the majority of the pharmaceutical analgesics and antipyretic agents. Chemically, they also are the parent compounds to most of the preservatives that are in use in the food industry. Chemical characterization of these compounds is necessary to predict their behavioral patterns during manufacturing and other industrial processes. The purpose of this study is to look into the effect of heat treatment on these compounds. The variability in the effects can be determined by performing the calculations for the kinetics of their decomposition, and second, by applying suitable evaporation methodology in order to evaluate the vaporization characteristics for the compounds. The kinetics of evaporation and/or decomposition has to be applied as and when necessary.

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Evaporation can be stated to be the transition from the liquid phase to the vapor phase, without a change in chemical composition. Factors such as vapor pressure of the substance, molecular mass, amount of exposed surface area, etc. can alter the evaporation patterns. The primary influencing factor, however, is the rising temperature conditions to which the preservatives are being subjected. The evaporation parameters can be determined by the rate of mass loss as the substance undergoes the phase transition from liquid to vapor. This can be achieved with a rising temperature program in thermogravimetric analysis.

A decomposition reaction is defined as a chemical process in which a chemical is degraded into a simpler species. Such reactions include processes in which the crystal lattice structure is destroyed, such as melting, evaporation, sublimation, as well as chemical reactions that result in the formation of a new compound [1]. In all solid-state decompositions, the transformation occurs in an area of enhanced activity, referred to as the reaction interface or the boundary between the reactant and the product [1]. The decomposition of substances can be described on the basis of chemical kinetic principles. Such kinetics are described as zero order, first order or pseudo first order reactions. In solid-state reactions, contrary to conventional chemical kinetic studies, the concentration is not monitored, because it does not vary in a manner that can be correlated with changes in the quantity of the remaining reactant [1]. The fraction reacted (α) is a better measure for performing the calculations in such reactions.

As a substance undergoes phase transition from liquid to vapor, determining the rate of mass loss can monitor the evaporation process. This is achieved by thermogravimetry, using a linear rising temperature program [2]. The TG curve that shows a plot of mass *vs.* temperature or time is converted into a DTG curve, which measures the rate of mass loss (dm/dt) *vs.* temperature. The shape of the DTG plot, then, would be instrumental in assigning a preliminary kinetic mechanism to the process. In the case of an ideal zero order mechanism, the DTG plot shows a maximum value for (dm/dt) at a point where all the material is exhausted, so the return of the DTG curve to the baseline is very abrupt and perpendicular in nature. The fraction evaporated (α) is calculated using the following equation:

$$\alpha=(m_i-m_t)/(m_i-m_f) \tag{1}$$

where, m_i and m_f are the initial and final masses in milligrams, respectively [2]. The mass at the specific time is represented as m_t. The data points are obtained from the rising portion of the DTG plot [3]. If a plot of α *vs.* time or temperature were constructed, a sigmoidal shaped curve would be obtained. If evaporation occurs, the fraction evaporated would be obtained as the product of the time and the coefficient of evaporation (k_{vap}), which can be represented as follows:

$$\alpha=(k_{vap})t \tag{2}$$

At constant temperature, (k) is equal to ($d\alpha/dt$) [3]. The rate of evaporation is represented by (dm/dt). For zero order rate processes, the coefficient of evaporation can be calculated by dividing (dm/dt) by the cross sectional area of the crucible used for the sample. In the present study the evaporation takes place from the liquid interface for two of the three compounds studied. When $\ln k_{vap}$ is plotted *vs.* $(1/T)$, a straight line is obtained, with a slope equal to (E_{vap}/R), where, (E_{vap}) is the activation energy of evaporation and (R) is the universal gas constant. Such plots are consistent with the Arrhenius equation:

$$k_{vap}=Ae^{-E_{vap}/RT} \tag{3}$$

or

$$\ln k_{vap}=\ln A_{vap}-E_{vap}/RT \tag{4}$$

where, A_{vap} is the pre-exponential factor. For other decomposition mechanisms, the results can be correlated to a set of models, which are based on nucleation, diffusion, reaction order or geometrical factors of the reactant-product interface [4]. The reaction rate in solid-state decomposition is given by:

$$d\alpha/dt=kf(\alpha) \tag{5}$$

where, $f(\alpha)$ is a function of (α) and (t) is the time [5]. This can be made to relate to the temperature by:

$$d\alpha/dT=(d\alpha/dt)(dt/dT)=[kf(\alpha)]/\beta \tag{6}$$

where, β is the heating rate, in degrees per second [6]. This equation can be transformed to the form:

$$k=[(d\alpha/dT)\beta]/f(\alpha) \tag{7}$$

The term $f(\alpha)$ can be obtained from the tables of different mechanisms. For zero order, it is equal to one, and for first order, it is equal to $(1-\alpha)$ [5]. Using the Arrhenius method:

$$\ln[(d\alpha/dT)\beta/f(\alpha)]=\ln A-E/RT \tag{8}$$

A plot of $\ln[(d\alpha/dT)\beta/f(\alpha)]$ *vs.* $1/T$ can be utilized to determine the Arrhenius parameters. A summary of various $f(\alpha)$ expressions can be obtained from Table 1 [4].

In a moderate pressure range, the Antoine equation is an excellent empirical tool, primarily used for curve fitting purposes [7]. It can be written as:

$$\ln P=a-b/(T+c) \tag{9}$$

where P is the vapor pressure, T is the absolute temperature, $a=2.303\ A$, $b=2.303\ B$, and $c=C$. Here A, B, and C are the Antoine constants at a given temperature range, obtained from the book by Stephenson and Malanowski [8]. It is mainly used to evaluate the temperature dependence of vapor pressure. The Antoine constants have been recorded for methyl paraben and the values are: $A=5.23662$, $B=1159.34$ and $C=-220.03$, for a given temperature range of 446–517 K. The value of P was obtained at each temperature point from 446–501 K, the temperature range being decided upon from the rising portion of the DTG curve.

The Langmuir equation can explain the evaporation phenomenon:

$$dm/dt=(P)(\alpha)(M/2\pi RT)^{1/2} \tag{10}$$

where (dm/dt) is the rate of mass loss per unit area, (P) is the pressure, (α) is the vaporization constant, (T) is the absolute temperature, (R) is the universal gas constant and (M) is the molecular mass of the evaporating vapor. The objective is to determine the vaporization constant in the presence of a purge gas [9].

Table 1 Solid-state rate expressions for deceleratory α-time curves

	$g(\alpha)=kt$	$f(\alpha)=(1/k)(d\alpha/dt)$
Geometrical models		
R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
Diffusion mechanisms		
D1	α^2	$(1/2)\alpha$
D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	$[-\ln(1-\alpha)]^{-1}$
D3	$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
D4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$
Reaction order		
F1	$-\ln(1-\alpha)$	$1-\alpha$
F2	$(1-\alpha)^{-1}$	$(1-\alpha)^2$
F3	$(1-\alpha)^{-2}$	$1/2(1-\alpha)^3$

Langmuir spent considerable time discussing the value of the vaporization constant and was of the opinion that it is unity if the initial conditions were those of a vacuum but did not exclude the fact that it may have different values from unity. For the use of the Langmuir equation for the TG data, one must assume the fact that (α) is a constant that is not unity in the presence of a purge gas. The Langmuir equation holds true for a certain rate of mass loss in volatilization from a given container exposing a constant area of interface. It depends a lot on the experimental set up and is independent of the vapor being examined, provided it is not associated.

Equation (5) can be rewritten as:

$$P=\alpha^{-1}(2\pi R)^{1/2}(T/M)^{1/2}(dm/dt)=k\nu \tag{11}$$

where, $k=\alpha^{-1}(2\pi R)^{1/2}$ and $\nu=(T/M)^{1/2}(dm/dt)$.

Since ν would be a constant for a given set of experiments, the plot of P *vs.* ν would give the value of k. Alternatively, if we take the logarithm of the above equation, then a plot of $\log P$ *vs.* $\log\nu$ would give the value of $\log k$ [10].

In the set of experiments performed, the instrument was calibrated with methyl paraben as the standard, which gave the value of k. The pressure *vs.* temperature plot was performed. This coefficient of vaporization value thus obtained would be theoretically constant and independent of the substance used. This value was taken for *ortho* and *meta* hydroxy benzoic acids. Equation (11) could be effectively utilized for each substance as the ν-value for each substance would be a constant and substituting the *k*-value will give the corresponding pressure values at each temperature. The vapor pressure plots were then obtained from the data.

The enthalpy of vaporization (ΔH_{vap}) can be calculated for each of the compounds from the Clausius–Clapeyron equation, the final form of which is as follows:

$$\log(p_2/p_1)=[\Delta H_{vap}/(2.303R)][(T_2-T_1)/T_1T_2] \tag{12}$$

where, p_2 and p_1 are the corresponding vapor pressures at temperatures T_2 and T_1 respectively and R is the universal gas constant.

Experimental

Reagents

Methyl paraben was obtained from Fischer Scientific Co. (lot number 762258); Salicylic acid was obtained from Sigma Chemical Co. (lot number 52H3418); Meta hydroxy benzoic acid was obtained from Sigma Chemical Co. (lot number 33H7709); and para-hydroxy benzoic acid was obtained from Sigma Chemical Co. (lot number 121H0539). The purity of the compounds was in accordance with the USP standards and was used as received.

Equipment

The SDT 2960, simultaneous TG-DTA, TA Instruments, with Thermal Analyst 2000, TA operating system version 1.0 was used. An electronic flowmeter from J & W Scientific, Model ADM, was used to regulate the flow of dry nitrogen (purge gas) through the samples.

Procedure

Rising temperature experiments were performed on the sample and readings were taken at every 1°C to give accuracy to the results. The runs were conducted in a temperature range from ambient to 400°C. The heating rate was fixed at 10°C min^{-1}. Nitrogen was used as the purge gas and its flow rate was fixed at 100 mL min^{-1}. An open, 110 μL platinum crucible with a cross sectional area of 0.34 cm^2, was used to contain the sample and an empty platinum crucible of equivalent area was used as the reference. The sample size was chosen so as to cover the base of the crucibles uniformly and to about one-third of its capacity.

Data from the DTG plot of methyl paraben was first used to construct the Arrhenius plot from which the activation energy was obtained. From the Clausius–Clapeyron plot for methyl paraben, the latent heat of evaporation was obtained. The Antoine and Langmuir equations were then used to obtain the coefficient of evaporation (k), from which the vapor pressure curve was constructed. The Antoine constants were reported in the literature and were as follows: A=5.23, B=1159.34, and C= –220.03, for a temperature range of 446–499 K. Calculations for the kinetics were performed and the decomposition for *ortho* (salicylic acid) and *meta* hydroxy benzoic acids were determined to be zero order in nature. *Para* hydroxy benzoic acid followed a first order mechanism and therefore, was not subjected to evaporation kinetics. The vapor pressure curves for *ortho* and *meta* hydroxy benzoic acids were constructed by taking into account the (*k*) value obtained from methyl paraben, as the coefficient of evaporation is independent of the sample.

Results and discussions

Thermal analysis and determination of kinetics

From the TG-DTG curves of *ortho*, *meta* and *para* hydroxy benzoic acids (Fig. 1), the rising portions of the DTG curves were taken and the kinetics were determined. The Arrhenius plots are seen in Fig. 2. *Ortho* and *meta* hydroxy benzoic acid follow zero order kinetics, which are non-activated processes. Their latent heats of evaporation values closely correspond to their energy of activation values; the Clausius–Clapeyron plots for *ortho* and *meta* hydroxy benzoic acids are seen in Fig. 3. For *ortho* hydroxy benzoic acid, intramolecular hydrogen bonding is observed and there is no association between two adjacent molecules. Thus, a zero order evaporation process is observed. For the *para* derivative, intermolecular hydrogen bonding is observed that result in an association between adjacent molecules [11]. Greater thermal energy is needed to break such hydrogen bonding and thus a zero order evaporation process is not observed. The energy of activation for *para* hydroxy benzoic acid is 119.1 kJ mol^{-1}, which is far greater than 64.8 and 78.2 kJ mol^{-1} for the *ortho* and *meta* derivatives, respectively. Thus, the decomposition of *para* hydroxy benzoic acid is not a non-activated process and requires considerably more thermal energy than its

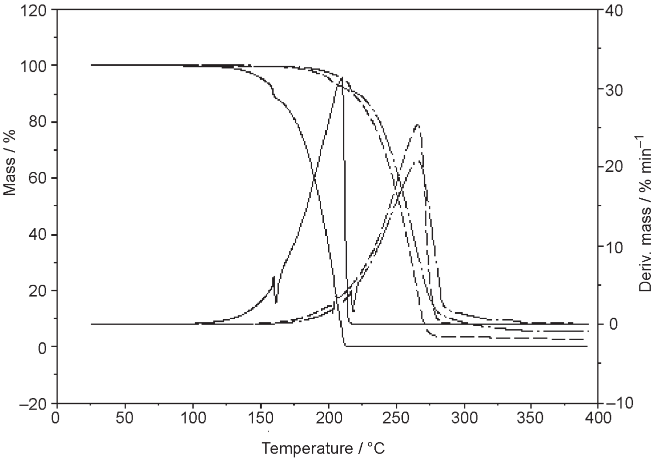

Fig 1 TG-DTG curves for *ortho* (—), *meta* (---) and *para* (– · –) hydroxy benzoic acids

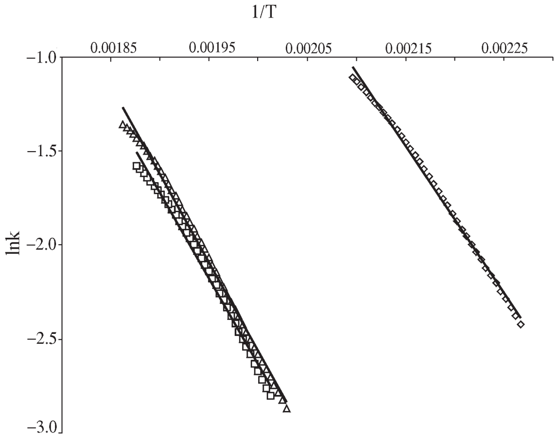

Fig. 2 Calculation for the activation energy; Arrhenius plots for *ortho* (◊), *meta* (Δ), and *para* (□) hydroxy benzoic acids

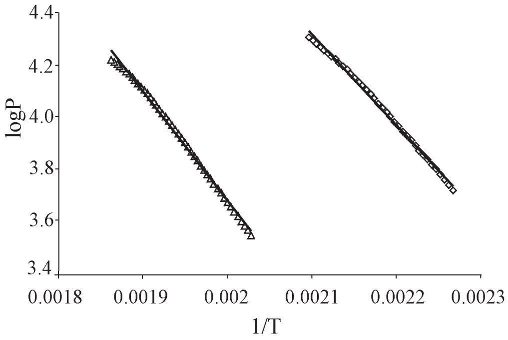

Fig. 3 Clausius–Clapeyron plots for *ortho* (◊) and *meta* (Δ) hydroxy benzoic acids

homologues to undergo decomposition. A summary of the values for the activation energy and latent heats of evaporation are seen in Table 2.

Table 2 Summary of the values for E_{act} and ΔH_{vap} for the compounds studied

Compound	E_{act}/kJ mol^{-1}	ΔH_{vap}/kJ mol^{-1}
Ortho hydroxy benzoic acid	64.8	66.7
Meta hydroxy benzoic acid	78.2	80.4
Para hydroxy benzoic acid	119.1	–
Methyl paraben	75.1	77.1

Construction of vapor pressure curves

Methyl paraben was taken as the calibration compound and the TG-DTG curve for methyl paraben is seen in Fig. 4. A plot of log$P$ *vs.* logν (Fig. 5) was used to obtain

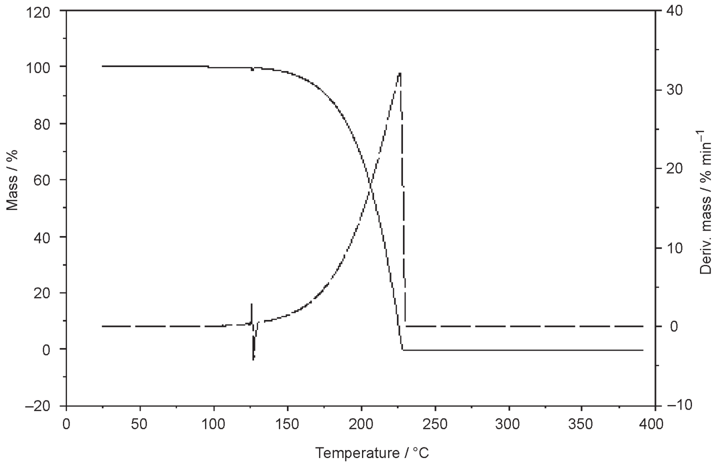

Fig. 4 TG-DTG curve for methyl paraben

the value of (*k*) from the Langmuir equation. The coefficient of evaporation (*k*) obtained from methyl paraben was determined to be 124525±0.8, units being in the SI system. The vapor pressure curves for methyl paraben was constructed from the Antoine constants reported in the literature and are seen in Fig. 6. The vapor pressure curves for salicylic acid and *meta* hydroxy benzoic acid are seen in Fig. 7.

The value of (k)

The coefficient of vaporization (*k*) is perhaps the most important parameter in the Langmuir equation that is being utilized in such studies. This parameter is a constant, and is independent of the material being studied. In a recent study Price and Hawkins have reported the value of (*k*) in the CGS system of units [12]. In this study, it was deemed best to use S.I. units in a uniform manner and the value for *k* was found to be 124525±0.8 Pa $kg^{1/2}$ $mol^{1/2}$ s^{-1} m^{-2}. This is in good correlation with the reported value of *k* in the literature. This study confirms that it is prudent to keep the units in the SI system and thus the value of *k* is in the vicinity of $1.2\cdot10^5$. It must be mentioned however, that after converting the *k*-value obtained by Price and Hawkins to our units, reasonable agreement was observed.

The value of α

Using the Langmuir equation, the *k*-value is inversely proportional to (α). Langmuir had opined that the value of (α) is unity under vacuum conditions [9], though he did not categorically state that it cannot change under the influence of a purge gas. It is important to note that the experimental design utilized in this study would have a multicomponent atmosphere. First, there is nitrogen as the purge gas and second, the compound being investigated is itself vaporizing and continuously adding to the par-

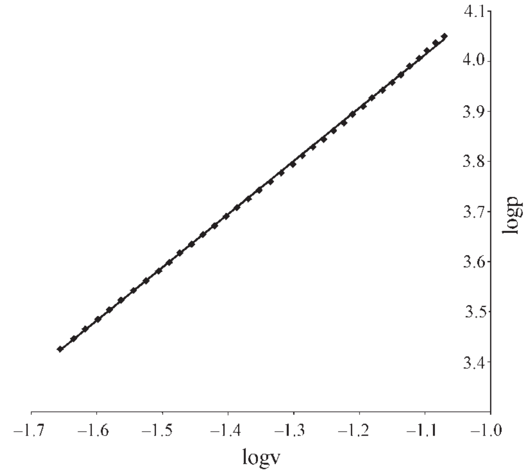

Fig. 5 Calculation for the coefficient of evaporation; plot of log$P$ *vs.* logν

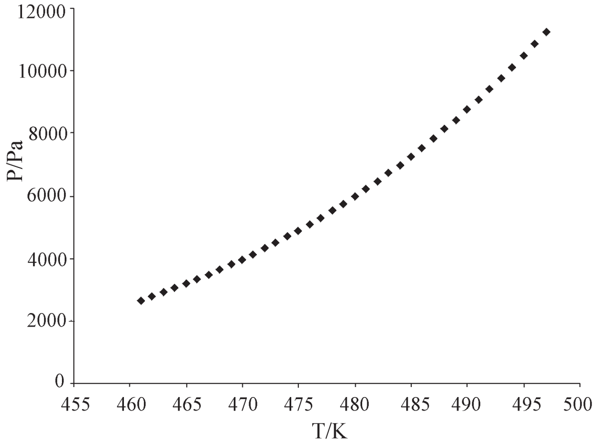

Fig. 6 Vapor pressure curve for methyl paraben

tial pressure of the material. This expectedly would alter the value for (α). However, the value of α is obtained as $5.8\cdot10^{-5}$. This extremely small quantity cannot be explained yet with the resources currently available. Further research should be performed in this direction to critically evaluate the value of (α).

Clausius–Clapeyron plots

Clausius–Clapeyron plots were generated for *ortho* and *meta* hydroxy benzoic acid. Such plots have log$P$ (logarithm of pressure) in the Y-axis and the reciprocal of absolute temperature ($1/T$) in the X-axis. An obvious anomaly was observed in the plots. The plots generated a curve rather than a straight line. If the plot is curvilinear in na-

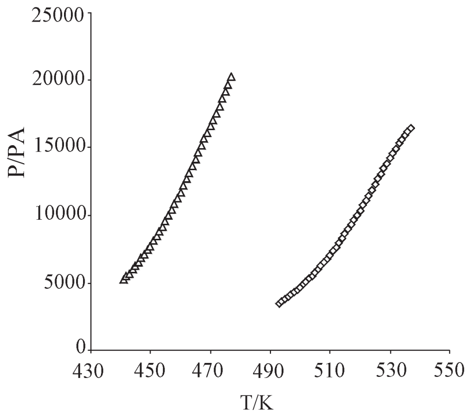

Fig. 7 Vapor pressure curves for *ortho* (◊) and *meta* (Δ) hydroxy benzoic acids

ture, fitting a straight line for regression parameters is futile. For the regression parameters and R^2-value to have any significance, the points must be perfectly scattered in nature. This suggests that the Clausius–Clapeyron equation will perhaps not be ideal in constructing vapor pressure plots, since it is not always obeying the basic assumption of any statistical operation, which presupposes the random scatter of points. It is imperative, therefore, that the Antoine equation, which has a better physical and statistical significance, be used when vapor pressure curves are to be constructed. It must be mentioned here, that if vapor pressures are actually measured directly, Classius–Clapeyron plots are unquestionable. However, in this study the vapour pressure plots were calculated indirectly and not actually measured.

Conclusions

This work demonstrates a comprehensive technique in characterizing chemical moieties by rising temperature thermogravimetric analyses. This work also suggests that thermogravimetry is an effective technique for the determination of the coefficient of vaporization, when the Antoine vapor pressure constants and the molecular masses of the substance in the vapor phase are known. Linear rising temperature conditions are very useful in obtaining a rapid means of measurement. For substances whose Antoine constants are not reported, a known substance can be effectively used to calibrate the procedure and the vapor pressure curve for that unknown substance can be plotted. There might be some disagreement regarding the value of (α), since from this study its value was determined to be extremely small. However, this method can be effectively utilized as a rapid and reliable means of estimating the vaporization characteristics of pharmaceutical and, in general, chemical ingredients.

References

1 M. E. Brown, D. Dollimore and A. K. Galwey, in: C. H. Bamford and C. F. Tipper (Eds), Comprehensive Chemical Kinetics, Reactions in the Solid State, Vol. 22, Elsevier, Amsterdam 1980, pp. 1, 12 and 115.
2 P. J. Haines, Thermal Methods of Analysis, Chapter 2, Blackie Academic and Professional, London 1995.
3 D. Dollimore, T. A. Evans, Y. F. Lee and F. W. Wilburn, Thermochim. Acta, 198 (1992) 249.
4 M. E. Brown, Introduction to Thermal Analysis, Chapman and Hall, London 1988, p. 127.
5 D. Dollimore, P. Tong and K. S. Alexander, Thermochim. Acta, 282/283 (1996) 13.
6 D. Dollimore, T. A. Evans, Y. F. Lee and F. W. Wilburn, Thermochim. Acta, 188 (1991) 77.
7 V. Majer, V. Svoboda and J. Pick, Heats of Vaporization of Fluids, Elsevier, Amsterdam 1989, p. 27.
8 R. M. Stephenson and S. Malamowski, Handbook of the Thermodynamics of Organic Compounds, Elsevier, New York 1987, p. 263.
9 Langmuir, Phenomena, Atoms and Molecules, Philosophical Library, Inc., New York 1950.
10 L. Shen and K. S. Alexander, Thermochim. Acta, 340–341 (1999) 271.
11 I. L. Finar, Organic Chemistry, 6th Edition, Longman, London 1973.
12 D. M. Price and M. Hawkins, Thermochim. Acta, 315 (1998) 19.