

A DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF THE DECOMPOSITION OF SOME LANTHANIDE NITRATES

C.A. STRYDOM * and C.P.J. VAN VUUREN

Department of Chemistry, University of Pretoria, Pretoria 0002 (South Africa)

(Received 7 November 1988)

ABSTRACT

Differential scanning calorimetric measurements at pressures of 5×10^3 kPa seem to inhibit the reversible transitions which are observed during the decomposition of the anhydrous lanthanide nitrates, $M(\text{NO}_3)_3$, where $M = \text{Nd, Eu, Gd, Ho}$ and Er . These reversible transitions seem to have a pronounced effect on the kinetic behaviour of the nitrates. In addition to these transitions, the ionic radius of the metal ion seems to be a determining factor in the stability of the lanthanide nitrates.

INTRODUCTION

Observations on the thermal decomposition kinetics of a series of lanthanum(III) nitrates, $M(\text{NO}_3)_3$, where $M = \text{La, Ce, Pr, Nd, Eu, Gd, Ho}$ and Er , have been, to some extent, previously described and discussed [1–4]. It was shown that the Arrhenius plots for the decomposition reactions of Nd through to Er in the series were discontinuous. The temperatures at which these discontinuities occur coincide with the temperatures at which the reversible transitions were observed. It was also shown that, for Nd, the observed reversible transitions were inhibited if the compound was decomposed under a nitrogen pressure of 5×10^3 kPa [2].

It was therefore thought necessary to obtain calorimetric data at a pressure of 5×10^3 kPa for the decomposition of the other nitrates of the series in an effort to give an improved interpretation of the kinetic behaviour and to quantify the thermal stability of the lanthanum(III) nitrates.

EXPERIMENTAL

The general experimental method which was followed and the apparatus used have been previously described [1,2]. Calorimetric measurements at

* Author to whom all correspondence should be addressed.

high pressures were carried out on the metal nitrates after dehydration of the hydrated species in the DSC cell in flowing nitrogen.

RESULTS AND DISCUSSION

DSC studies

Reaction enthalpy values at 5×10^3 kPa and at atmospheric pressure for the thermal decomposition of the studied lanthanide nitrates are summarized in Table 1. The DSC curves for the thermal decomposition of $\text{Eu}(\text{NO}_3)_3$, $\text{Gd}(\text{NO}_3)_3$, $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ are given in Figs. 1–3.

The DSC curves and the enthalpy values at 5×10^3 kPa for the thermal decomposition of $\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$ showed no change in shape, position or size from those at atmospheric pressure [1,3]. No reversible processes were observed during the decomposition of $\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$ [1,3].

The shoulder observed at 350°C under atmospheric pressure [3] disappeared at the pressure of 5×10^3 kPa on the DSC curve for the decomposition of $\text{Eu}(\text{NO}_3)_3$ (Fig. 1). The symmetrical DSC curve at 5×10^3 kPa indicates that the higher pressure inhibits the reversible process at 350°C and therefore a lower enthalpy value of 96.8 kJ mol^{-1} was observed (Table 1). The enthalpy value for the single reversible process at atmospheric pressure is thus approximately 22.8 kJ mol^{-1} . The peak maximum of the DSC curve for the decomposition of $\text{Eu}(\text{NO}_3)_3$ at atmospheric pressure was

TABLE 1

Comparison of the decomposition onset temperatures and reaction enthalpy values of the lanthanide nitrates

Lanthanide nitrate	Decomposition onset temperature ($^\circ\text{C}$)	Reaction enthalpy at atmospheric pressure (kJ mol^{-1})	Reaction enthalpy at 5×10^3 kPa (kJ mol^{-1})	Radii [8] (\AA)	References
$\text{La}(\text{NO}_3)_3$	375	123.4	123.4	1.14	3
$\text{Ce}(\text{NO}_3)_3$	230	111.1	111.1	1.07	1
$\text{Pr}(\text{NO}_3)_3$	365	102.6	102.6	1.06	3
$\text{Nd}(\text{NO}_3)_3$	360	109.6	89.4	1.04	2
$\text{Eu}(\text{NO}_3)_3$	320	119.6	96.8	0.98	3
$\text{Gd}(\text{NO}_3)_3$	275	138.1	95.2	0.97	4
$\text{Ho}(\text{NO}_3)_3$	250	119.9	60.6	0.91	4
$\text{Er}(\text{NO}_3)_3$	230	197.2	92.7	0.89	4

^a The decomposition onset temperatures were determined from the TG and DTA curves, using a heating rate of 5°C min^{-1} .

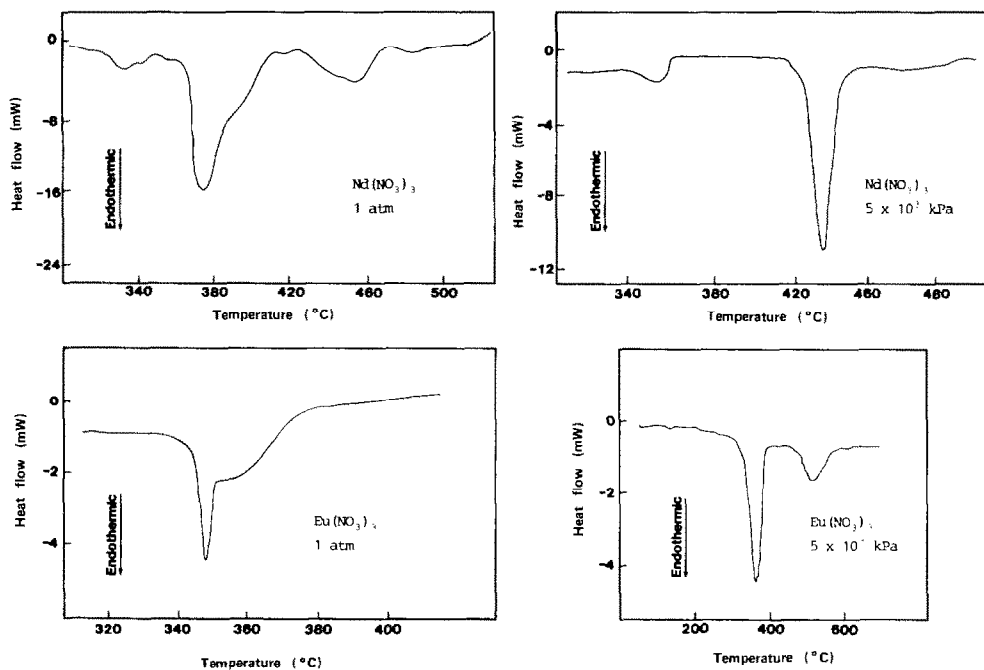


Fig. 1. DSC curves of the thermal decomposition of $\text{Nd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ at atmospheric pressure and at 5×10^3 kPa.

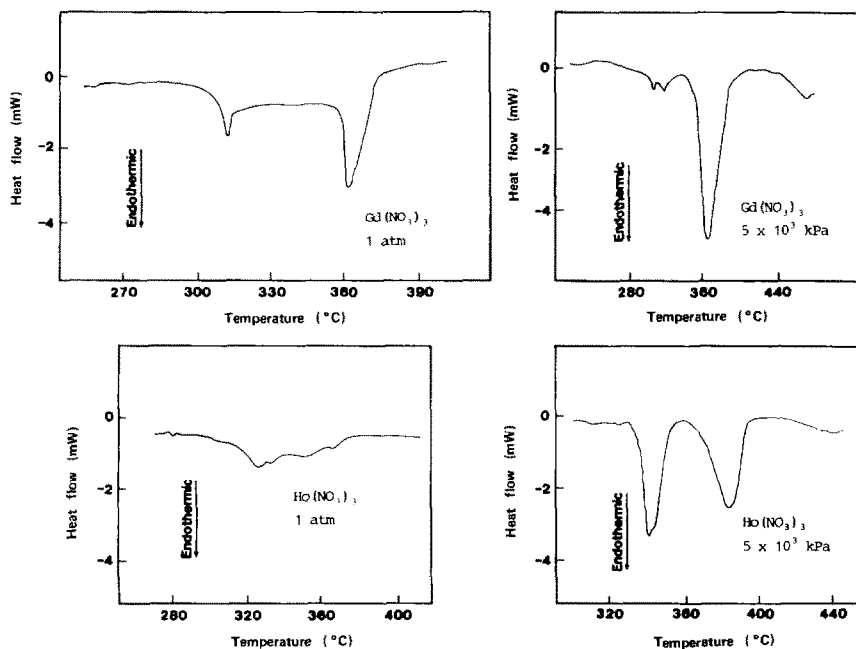


Fig. 2. DSC curves of the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ and $\text{Ho}(\text{NO}_3)_3$ at atmospheric pressure and at 5×10^3 kPa.

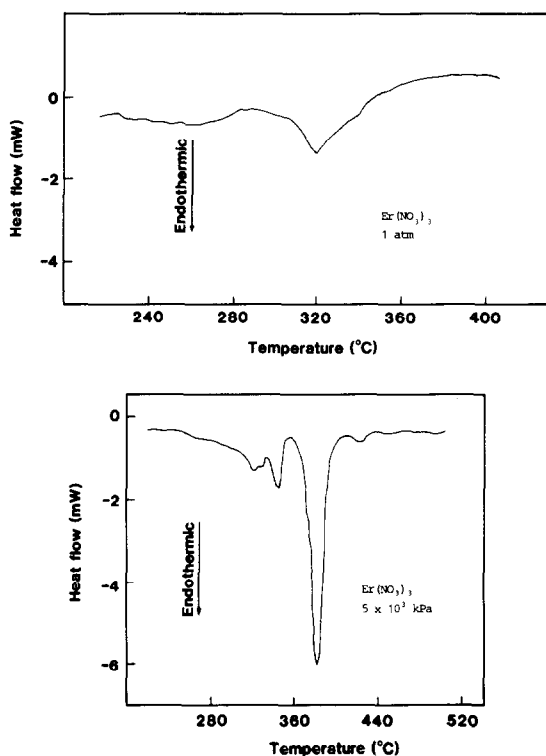


Fig. 3. DSC curves of the thermal decomposition of $\text{Er}(\text{NO}_3)_3$ at atmospheric pressure and at 5×10^3 kPa.

at 347°C and, at 5×10^3 kPa, at 352°C. Taking experimental errors into consideration, no shift of the decomposition peak occurred, implying that at both atmospheric pressure and at 5×10^3 kPa the reactant was in the same structural state at the beginning of the decomposition.

The DSC curve for the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa shows three peaks (Fig. 2). Two very small peaks ($\Delta H < 2$ kJ mol⁻¹) appeared at 308 and 322°C, and also a well-defined peak with a maximum at 365°C. The small peaks seem to be due to some reversible processes. The enthalpy of the decomposition reaction at this higher pressure was calculated to be 95.2 kJ mol⁻¹. The two reversible processes at 317 and 389°C at atmospheric pressure [4] seem to be either inhibited or shifted to higher or lower temperatures by the higher pressure. The enthalpy of the reversible process at 317°C at atmospheric pressure is reported to be 8.9 kJ mol⁻¹ [4], thus leaving a value of 34.0 kJ mol⁻¹ for the reversible process at 389°C at atmospheric pressure. The decomposition peak maximum at 368°C on the DSC curve at atmospheric pressure can be considered the same as the maximum at 365°C at a pressure of 5×10^3 kPa.

The DSC curve for the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa shows two distinct peaks with maximum values at 341 and

384°C (Fig. 2). Although under atmospheric pressure the oxynitrate starts to decompose above 400°C, it was concluded by investigations of the reaction products that the second peak is due to the oxynitrate decomposition, probably as a result of a solid state phase change of the oxynitrate that enhanced the decomposition thereof. The enthalpy of the decomposition of holmium nitrate to its oxynitrate at the pressure of 5×10^3 kPa is calculated to be 60.6 kJ mol^{-1} . The exothermic reversible process at 349°C, occurring during the decomposition of $\text{Ho}(\text{NO}_3)_3$, seems not to be inhibited by the pressure of 5×10^3 kPa.

Although the occurrence of an exothermic reversible process is unexpected, observations of such transitions during the decomposition of certain oxalates are recorded in the literature [5]. This exothermic process may indicate a low temperature form which is metastable with respect to a higher temperature form, or it may represent an "amorphous" form changing to a crystalline phase.

The peak maximum on the DSC curve for the decomposition of $\text{Ho}(\text{NO}_3)_3$ at atmospheric pressure was at 324°C [4]. This temperature is slightly lower than the peak maximum of 340°C for the reaction at 5×10^3 kPa. The reactant, $\text{Ho}(\text{NO}_3)_3$, could be in different structural states at the beginning of the reaction at the two pressures.

The DSC curve for the thermal decomposition of $\text{Er}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa shows three peaks with maxima at 318, 344 and 381°C (Fig. 3). The first two peaks are small with enthalpy values of 2.3 and 8.4 kJ mol^{-1} respectively and are due to reversible processes. The third peak is the decomposition peak of $\text{Er}(\text{NO}_3)_3$ and an enthalpy of 92.7 kJ mol^{-1} is calculated from it. The higher pressure seems to inhibit at least some of the reversible processes occurring during the decomposition reaction at atmospheric pressure. The DSC decomposition peak (Fig. 3) is sharper at this higher pressure than at atmospheric pressure [4].

The two small peaks at 318 and 344°C on the DSC curve seem to be due to some of the reversible processes, but as a result of their small size, it was difficult to obtain further data on them. On heating a sample to 360°C at a pressure of 5×10^3 kPa, cooling it to 250°C and reheating it to 360°C, these two small peaks became even smaller. This observed tendency could be due to the fact that the reversible processes are not time independent.

It proved difficult to estimate enthalpy values for the reversible processes occurring during the decomposition of $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$, as in both cases the DSC peak at atmospheric pressure consists of multiple overlapping peaks [4].

A peak-maximum shift of approximately 61°C was observed on the DSC curves for the thermal decomposition of $\text{Er}(\text{NO}_3)_3$ at atmospheric pressure and at 5×10^3 kPa. $\text{Er}(\text{NO}_3)_3$ could be in different structural states at the beginning of the reaction at the two pressures. A structural or symmetry change can influence the decomposition reaction and causes higher decom-

position onset temperatures if the reactant at this higher pressure is in a more stable structural state than at atmospheric pressure.

Thermal stability

In a study of the octahydrates of the sulphates of some lanthanides, it was found that the temperature for the removal of the first 4 or 6 water molecules increases as the cation solvation dipole interaction energy increases, that is as the cation becomes smaller [6]. Negase stated that the thermal stability of an anhydrous complex decreases as the electron affinity of the central metal ion increases [7].

The TG and DTA decomposition onset temperatures, using a heating rate of 5°C min^{-1} , were used as relative measures of the thermal stability. When comparing these temperatures, an increasing instability was found on moving down the lanthanide series (Fig. 4). The value for $\text{Ce}(\text{NO}_3)_3$ was excluded in the figure, as a different chemical reaction results on heating $\text{Ce}(\text{NO}_3)_3$ [1].

On moving down the lanthanide series, the reaction enthalpy values at a pressure of 5×10^3 kPa show a decrease in value (Table 1). The relationship between increasing ionic radii [8] and reaction enthalpy seems to be of an exponential order (Fig. 5). The enthalpy values of $\text{Ce}(\text{NO}_3)_3$ and $\text{Ho}(\text{NO}_3)_3$ were excluded from the figure. The exothermic process occurring during the decomposition of $\text{Ho}(\text{NO}_3)_3$ seems not to be inhibited by the higher pressure, thus resulting in a lower enthalpy value at the high pressure than was expected.

Reactions in which a metal–oxygen link is ruptured depend critically on the size and charge of the metal ion [9]. For the lanthanide series, the decreasing ionic radii (Table 1) give rise to greater polarization of the nitrate ion. The charge density on the lanthanide ions increases, resulting in a

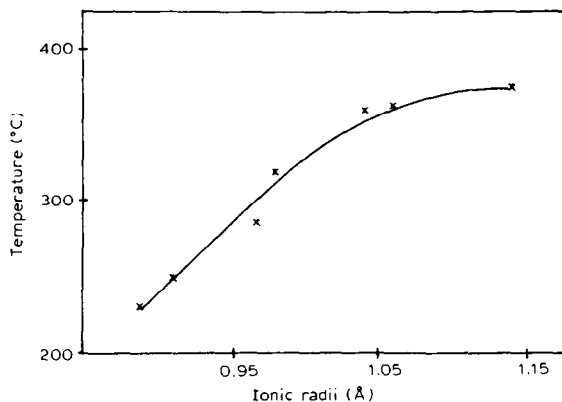


Fig. 4. Correlation between the decomposition onset temperature and ionic radii.

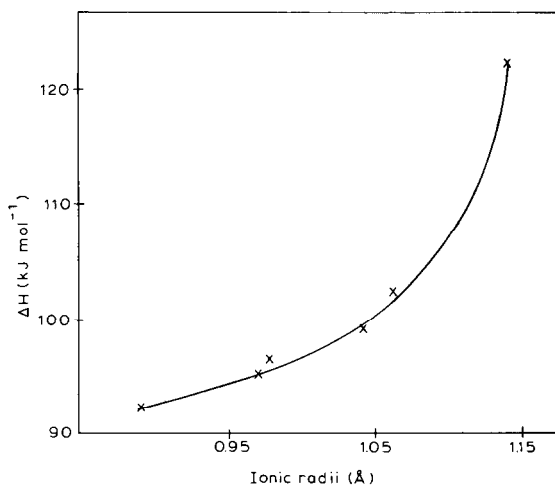


Fig. 5. Correlation between the reaction enthalpy and ionic radii.

stronger attraction of the nitrate electrons. This may increase the instability of the nitrate groups and therefore the groups are more easily decomposed.

Kinetic behaviour of the anhydrous nitrates

It was previously [2–4] suggested that the discontinuities observed in the Arrhenius plots for the decomposition reactions could be due to processes which occurred simultaneously with the decomposition reactions. Such processes could be simultaneous chemical reactions or physical transformations (phase changes) within the solid. The original shape and sizes of the particles can also have a distinct influence on the kinetic behaviour of the reaction, because they largely control the reaction interface. It was, however, not possible to control the latter since the anhydrous nitrate was prepared in situ. It was also shown that only one chemical reaction, i.e. $M(\text{NO}_3)_3(\text{s}) \rightarrow \text{MO}(\text{NO}_3)(\text{s}) + \text{gases}$, occurred in the temperature range used for data collection of the different compounds.

For $\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$, which did not show a discontinuity in the Arrhenius plot, no reversible changes seemed to occur during the decomposition reactions [1,3]. The kinetic analysis of $\text{Nd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ were found to be relatively straightforward in so far that only one kinetic expression seems to describe the reactions over the temperature ranges studied [2,3]. Although discontinuities in the Arrhenius plots were observed, no problems in the calculation of the kinetic parameters were encountered.

Analysis of the kinetic data obtained for $\text{Gd}(\text{NO}_3)_3$ [4] suggested that, judged from the linearity of the isothermal plots, $f(\alpha)$ versus t , three different kinetic equations seem to describe the reaction in the different

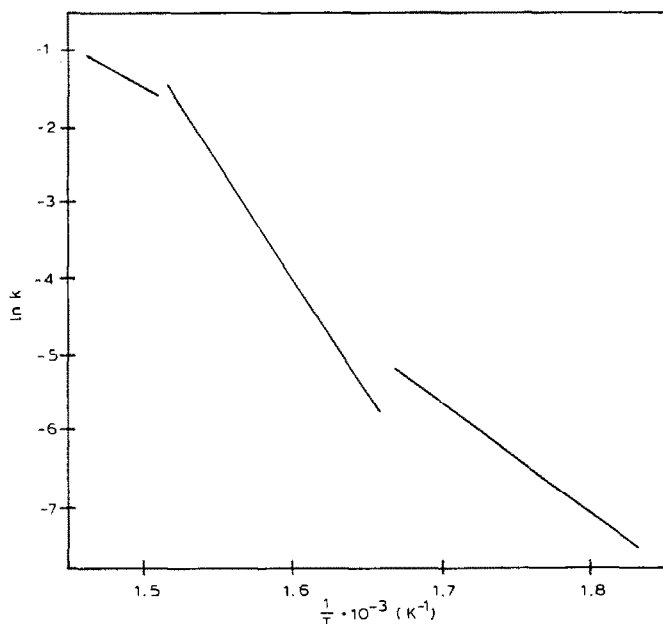


Fig. 6. Arrhenius plot for the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ with the kinetic parameters calculated from the Avrami–Erofe'ev equation ($n = 2$).

temperature ranges. A re-examination of the data seems to indicate that a nucleation and growth mechanism, Avrami–Erofe'ev with $n = 2$, might be a more appropriate mechanism to describe the reaction. However, the kinetic parameters which were calculated from the Arrhenius plot (Fig. 6) were found to be very similar to those calculated previously (Table 2). Analysis of the kinetic data obtained for $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ suggested that a nucleation and growth mechanism with variable n in the various temperature ranges, describes the decomposition reaction [4].

TABLE 2

Activation energy and frequency factors for the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$

Temperature range ($^{\circ}\text{C}$)	Kinetic model	Activation energy (kJ mol^{-1})	Frequency factor ($\ln(A \text{ min}^{-1})$)
270–315	Avrami–Erofe'ev ($n = 2$) (best fit)	82.7	10.9
320–385	Avrami–Erofe'ev ($n = \frac{3}{2}$) (best fit)	259.0	46.0
390–410	Avrami–Erofe'ev ($n = 2$)	243.2	43.2
	Prout–Tompkins (best fit)	104.2	17.3
	Avrami–Erofe'ev ($n = 2$)	99.5	17.8

It is important to note that the discontinuities in the Arrhenius plots were observed at the temperatures at which the reversible processes were observed at atmospheric pressure. It seems therefore that these transitions, which apparently occur in the nitrate and not the oxynitrate, influence the kinetic behaviour of the reactions studied. These transitions, as well as the strong possibility of a non-homogeneous particle size distribution, could be the reason for the variable n value of the Avrami–Erofe'ev equation observed for the same reaction at various temperatures.

Finally, we would like to report a correction to the data previously published for $\text{Nd}(\text{NO}_3)_3$ [2]. The correct data are; above 390°C , $E_a = 165.4$ kJ mol^{-1} and $\ln(A \text{ min}^{-1}) = 26.1$ and below 390°C , $E_a = 805.0$ kJ mol^{-1} and $\ln(A \text{ min}^{-1}) = 161.5$.

REFERENCES

- 1 C.A. Strydom and C.P.J. van Vuuren, *J. Therm. Anal.*, 32 (1987) 157.
- 2 C.P.J. van Vuuren and C.A. Strydom, *Thermochim. Acta*, 104 (1986) 293.
- 3 C.A. Strydom and C.P.J. van Vuuren, *Thermochim. Acta*, 124 (1988) 277.
- 4 C.A. Strydom and C.P.J. van Vuuren, *Thermochim. Acta*, 129 (1988) 335.
- 5 R.M. Dell and V.J. Wheeler, 5th Int. Symp., Reactivity of Solids, Munich, 1964, p. 395.
- 6 L.A. Alekseenko, A.F. Lemenkova and V.V. Serebrennikov, *Zh. Neorg. Khim.*, 4 (1959) 1382.
- 7 K. Negase, *Bull. Chem. Soc. Jpn.*, 45 (1972) 2166.
- 8 M.C. Ball and A.H. Norbury, *Physical Data for Inorganic Chemists*, Longman, London, 1974, p. 133.
- 9 D. Dollimore, *Thermochim. Acta*, 117 (1987) 331.