

THERMAL DECOMPOSITION KINETICS—PART XV. KINETICS AND MECHANISM OF THERMAL DECOMPOSITION OF TETRAMMINE COPPER(II) SULPHATE MONOHYDRATE

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ABSTRACT

The kinetics and mechanism of the thermal decomposition of tetrammine copper(II) sulphate monohydrate have been studied using non-isothermal thermogravimetry. Kinetic parameters were calculated for each step in the decomposition reaction from the TG curve using four integral methods, three “exact” and one “approximate”. The rate-controlling process for all the four stages of decomposition is random nucleation with the formation of one nucleus on each particle (Mampel equation). The stages of decomposition have been identified from X-ray diffraction and independent pyrolysis.

INTRODUCTION

The kinetics of thermal dehydration of different complexes and salts have recently been extensively studied. Both isothermal and non-isothermal methods have been used to evaluate the kinetic parameters and to elucidate the mechanism of dehydration reactions [1–4]. These studies have so far been largely confined to thermal dehydrations. A search through the literature showed that very few attempts have been made to undertake a study of the kinetics of deamination (loss of ammonia or an amine as a result of thermal treatment) [5–7]. Although transition metal ammine complexes have been known for a long time, only recently have investigations into their thermal decomposition behaviour been carried out [8]. The major objective of this investigation is to study the data obtained from non-isothermal thermogravimetric curves of tetrammine copper(II) sulphate monohydrate and to evaluate the kinetic parameters for the different stages of decomposition and to shed light on the mechanism of the thermal degradation. We have attempted to establish the mechanisms for all the four stages of the thermal decomposition of tetrammine copper(II) sulphate monohydrate.

EXPERIMENTAL

Synthesis of tetrammine copper(II) sulphate monohydrate

The tetrammine complex, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, was prepared by the method given by Brauer [9]. A stoichiometric amount of ammonia was added to copper sulphate solution with stirring and the solution was cooled in an ice bath. The complex was precipitated out by the addition of ethanol. The isolated complex was washed with ethanol and then with ether and dried in a vacuum over phosphorus(V) oxide. The resulting complex was characterized by spectral and chemical methods. The copper content in the complex was analysed gravimetrically [10].

Instruments

Simultaneous TG-DTG curves were recorded using a DuPont 990 thermal analyser in conjunction with a 951 thermogravimetric analyser. The experiment was carried out in dry nitrogen atmosphere at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The sample mass was 10 mg and the heating rate was $10^\circ \text{C min}^{-1}$. The X-ray powder diffractograms were recorded using a Philips 1710 diffractometer with a PW1729 X-ray generator using $\text{Cu } K\alpha_1$ radiation. Computational work was done with an IBM-PC using FORTRAN 77.

MATHEMATICAL TREATMENT OF DATA

Kinetic parameters were calculated from the TG curve using four non-mechanistic methods. The forms of the equations used are given below, where a term $g(\alpha)$ has been introduced for convenience and is defined as

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n}$$

The Coats-Redfern equation [11]

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\phi E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (1)$$

The MacCallum-Tanner equation [12]

$$\log_{10} g(\alpha) = \log_{10} \frac{AE}{\phi R} - 0.485E^{0.435} - \frac{(0.449 + 0.217E) \times 10^3}{T} \quad (2)$$

The Horowitz-Metzger equation [13]

$$\ln g(\alpha) = \ln \frac{ART_s^2}{\phi E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad (3)$$

The MKN equation [14]

$$\ln \left[\frac{g(\alpha)}{T^{1.9215}} \right] = \ln \left(\frac{AE}{\phi R} \right) + 3.7721 - 1.9215 \ln E - \frac{0.12039E}{T} \quad (4)$$

where α is the fractional decomposition, n is the order parameter, T is the temperature (K), A is the pre-exponential factor, ϕ is the heating rate ($^{\circ}\text{C min}^{-1}$), E is the energy of activation, R is the gas constant, T_s is the DTG peak temperature and θ is $(T - T_s)$.

Determination of order parameter n

The order parameter was evaluated for the different stages of decomposition using the Coats–Redfern equation by an iteration method. Using a computer, linear plots of $\ln[g(\alpha)/T^2]$ versus $1/T$ were drawn by the least-squares method, taking the α and the corresponding T values from the TG curve. Linear curves were drawn for different values of n ranging from 0 to 2, in increments of 0.01. The value of n which gave the best fit was chosen as the order parameter for each stage of decomposition.

The kinetic parameters were calculated from the linear plots of the L.H.S. of the kinetic equations against $1/T$ for eqns. (1), (2) and (4) and against θ for eqn. (3). The values of E and A were calculated from the slope and intercept, respectively.

The entropy of activation was calculated from the equation

$$A = \frac{kT_s}{h} \exp \left(\frac{\Delta S}{R} \right)$$

where k is the Boltzmann constant, h is Planck's constant and ΔS is the entropy of activation.

Mechanism of reaction from non-isothermal TG

Deduction of the mechanism of reactions using non-isothermal methods has been discussed by Sestak and Berggren [15] and by Satava [16]. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius-type equation

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \quad (5)$$

For a linear heating rate, $\phi = dT/dt$ and eqn. (5) becomes

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} e^{-E/RT} dT \quad (6)$$

Integration of the L.H.S. of eqn. (6) gives

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_0^T \frac{A}{\phi} e^{-E/RT} dT \quad (7)$$

TABLE 1

Mechanism-based equations

Eqn. no.	Form of $g(\alpha)$	Rate-controlling process
1.	α^2	One-dimensional diffusion
2.	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	Two-dimensional diffusion
3.	$[1 - (1 - \alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry; Jander equation
4.	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$	Three-dimensional diffusion, spherical symmetry; Ginstling–Brounshtein equation
5.	$-\ln(1 - \alpha)$	Random nucleation, one nucleus on each particle; Mampel equation
6.	$[-\ln(1 - \alpha)]^{1/2}$	Random nucleation; Avrami equation I
7.	$[-\ln(1 - \alpha)]^{1/3}$	Random nucleation; Avrami equation II
8.	$1 - (1 - \alpha)^{1/2}$	Phase boundary reaction, cylindrical symmetry
9.	$1 - (1 - \alpha)^{1/3}$	Phase boundary reaction, spherical symmetry

where $g(\alpha)$ is the integrated form of $f(\alpha)$. Mechanism-based kinetic studies depend on the assumption that the form of $f(\alpha)$ or $g(\alpha)$ depends on the reaction mechanism. The $g(\alpha)$ forms corresponding to nine probable reaction mechanisms have been proposed [16] and the mechanism is obtained from the one which gives the best representation of the experimental data. The forms of $g(\alpha)$ corresponding to the rate-controlling processes for the nine reaction mechanisms (numbered 1–9) are given in Table 1. The Coats–Redfern method was used for solving the exponential integral, as it is one of the best approaches recommended by several authors [17–19].

Linear plots of the nine forms of $g(\alpha)/T^2$ versus $1/T$ were drawn by the method of least-squares, and the corresponding correlation coefficients were also evaluated. E and A were calculated in each case from the slope and the intercept, respectively.

RESULTS AND DISCUSSION

For $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, the TG curve (Fig. 1) shows four stages of decomposition. The values of the temperature of inception of reaction T_i , the temperature of completion of reaction T_f and the DTG peak temperature T_s , for each stage of decomposition, together with the mass loss data are tabulated in Table 2. The results obtained from independent pyrolysis agrees well with the TG data.

The compound begins to lose mass at about 100°C . The first stage of mass loss corresponds to the loss of one molecule of water along with two molecules of ammonia. The second and third stages correspond to the loss of one molecule of ammonia each and the last stage represents the decom-

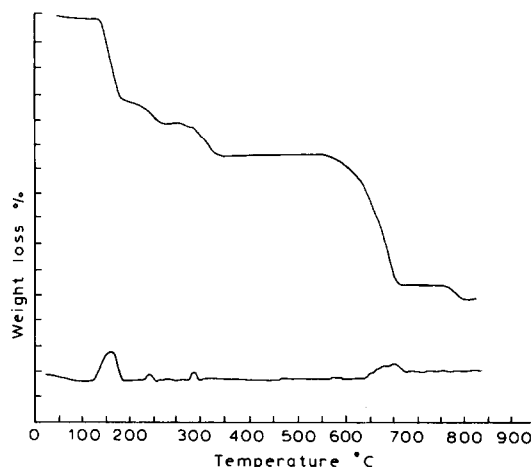


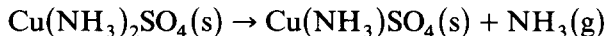
Fig. 1. TG and DTG curves of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$.

position of copper sulphate. The different stages of decomposition are given below

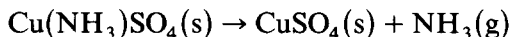
Stage I



Stage II



Stage III



Stage IV

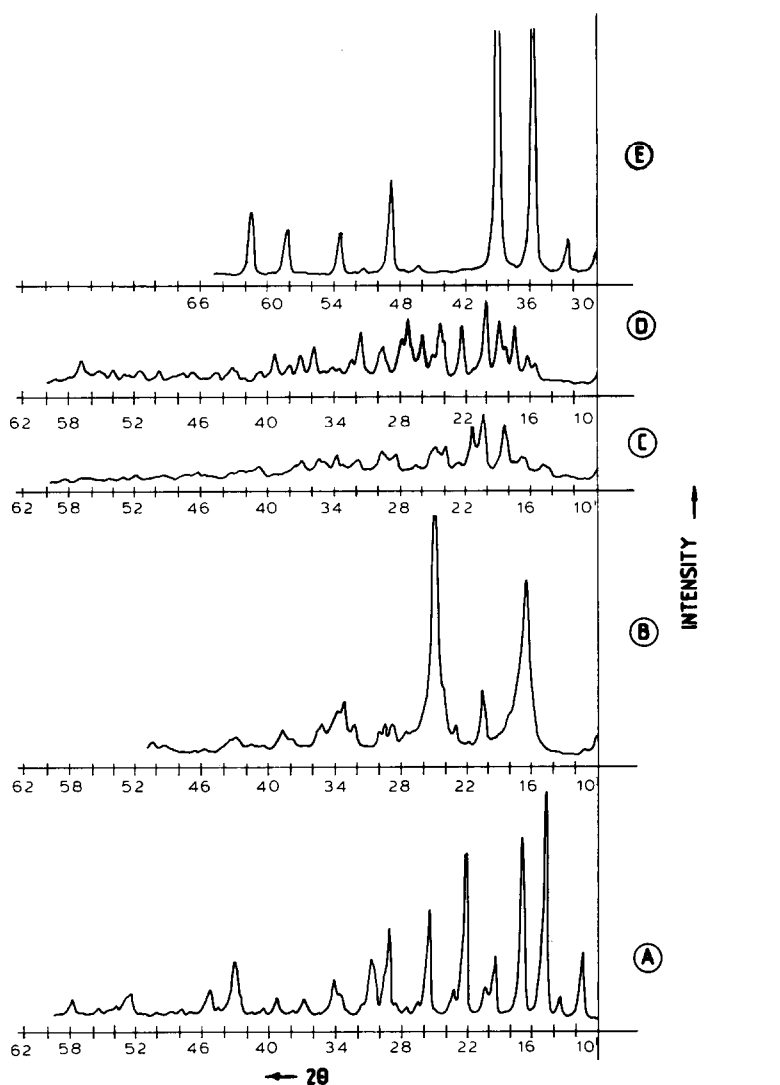


The decomposition stages observed in the case of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ are somewhat similar to those previously reported [8]. However, there are minor differences. In our investigation, the first stage of decomposition corresponds to the simultaneous elimination of two molecules of ammonia and one molecule of water. This observation is consistent with the crystal structure of the complex [20]. Single crystal studies have shown that the distance from metal ion to ligand (ammonia) and the distance from metal ion to water are almost the same, though the water molecule is usually described as “outside” the co-ordination sphere. Hence, the possibility of a distinct dehydration stage may be remote.

From its powder diffraction pattern, which has been compared with the JCPDS powder diffraction file [21], the final residue was found to be copper(II) oxide. The intermediates of the above deamination stages were obtained by keeping the complex in a muffle furnace at the appropriate temperatures. The XRD patterns of the complex and the intermediates are

TABLE 2
Phenomenological data for the thermal decomposition of tetramine copper(II) sulphate monohydrate

Stages	Decomposition	TG results				Independent pyrolysis			
		T_i (°C)		T_f (°C)	T_s (°C)	% wt. loss		Residue	
						Theoretical	Observed	Theoretical	Observed
Stage I	Loss of two NH_3 and one H_2O	105	160	135	21.18	21.25			
Stage II	Loss of one NH_3	165	285	225	6.92	6.00			
Stage III	Loss of one NH_3	300	365	355	6.92	7.13		35.02	35.55
Stage IV	Decomposition of CuSO_4	600	750	720	31.58	32.28		67.60	67.16
									CuSO_4 CuO



(A) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ (B) $\text{Cu}(\text{NH}_3)_2 \text{SO}_4$ (C) $\text{Cu}(\text{NH}_3)\text{SO}_4$ (D) CuSO_4 (E) CuO

Fig. 2. X-ray powder diffractograms.

shown in Fig. 2. The major intensities along with the d -spacings of the intermediates and residue are given in Tables 3 and 4.

The kinetic parameters evaluated for different stages of decomposition using non-mechanistic equations are listed in Table 5. The correlation coefficients (r) were in the range 0.9930–0.9977 indicating nearly perfect fits. It can be seen from Table 5 that the order parameter for different deamination stages is a decimal number. It is known from the literature

TABLE 3

X-ray powder diffraction data for the final thermolysis product of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

Experimental		JCPDS data for CuO	
d (Å)	I/I_0	d (Å)	I/I_0
2.7628	12.47	2.7510	12
2.3284	100.00	2.3200	96
1.5816	15.87	1.5810	14
1.5058	19.52	1.5050	20
1.8708	26.11	1.8660	25
2.5339	81.58	2.5200	100

[22–23] that this apparent order, n , does not have to be an integer but may also be a decimal number.

It can be observed that the energy of activation for the decomposition of each stage varies widely for the complex, from about 80 to about 310 kJ mol⁻¹. This wide variation is paralleled by a similar trend regarding the entropy of activation, which varies from about -134 to 212 J K⁻¹ mol⁻¹. From the table, it can also be seen that the kinetic parameters observed with the Horowitz–Metzger equation are higher than the values from the other three equations. This is due to the inherent error involved in the approximation method employed in the derivation of the Horowitz–Metzger equation. The highest value of activation energy is for stage III. Intermediate values are obtained for stages I and IV; the lowest value is for stage II. Similarly

TABLE 4

X-ray powder diffraction data

$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$		$\text{Cu}(\text{NH}_3)_2\text{SO}_4$		$\text{Cu}(\text{NH}_3)\text{SO}_4$		CuSO_4	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
5.9444	100.00	3.6194	100.00	4.3934	100.00	4.4197	100.00
3.9697	82.84	5.4213	65.95	4.8783	86.07	3.2566	85.86
5.1875	79.08	4.3688	29.49	4.1788	81.52	5.1104	78.72
3.4484	45.04	2.6991	23.34	4.7141	57.77	2.8272	74.34
2.0959	27.93	2.5558	17.79	3.0281	57.18	3.9795	73.22
2.8933	25.72	3.1099	16.42	3.1392	57.04	4.7603	60.95
3.0226	20.08	2.7899	15.22	2.6639	49.12	2.5024	60.95
1.9902	16.45	2.1061	13.97	2.8071	48.39	3.6766	59.19
1.5864	15.89	3.9054	13.84	2.4334	48.09	3.4332	56.82
2.4217	15.84	3.3353	13.80	5.3468	47.95	3.0150	55.44
1.7307	15.33	2.3837	13.76	2.2078	44.87	2.4223	48.56
4.4861	14.99	1.8101	12.21	2.5240	44.57	1.6196	45.57
2.6180	14.53	1.5835	10.88	3.3861	40.91	2.2854	44.80
2.2836	12.46	1.8400	10.71	6.1069	38.42	1.9009	31.54

TABLE 5

Kinetic parameters for the decomposition of tetrammine copper(II) sulphate monohydrate using non-mechanistic equations

		Stage I	Stage II	Stage III	Stage IV
n		1.37	1.17	1.75	1.14
E (kJ mol ⁻¹)	CR	123.43	78.72	277.31	251.22
	MT	122.50	78.79	280.95	260.38
	HM	131.76	90.95	306.98	291.33
	MKN	123.55	78.94	277.36	251.88
A (s ⁻¹)	CR	7.48×10^{13}	9.92×10^5	4.95×10^{21}	1.21×10^{11}
	MT	5.02×10^{13}	9.48×10^5	1.21×10^{22}	6.71×10^{11}
	HM	8.37×10^{14}	1.86×10^7	1.59×10^{24}	1.69×10^{13}
	MKN	7.76×10^{13}	1.02×10^6	5.04×10^{21}	1.26×10^{11}
ΔS (J K ⁻¹ mol ⁻¹)	CR	18.09	-134.40	164.24	-42.74
	MT	14.77	-134.77	171.73	-28.50
	HM	38.16	-109.99	212.22	-1.63
	MKN	18.39	-134.10	164.39	-42.39
r	CR	0.9973	0.9930	0.9968	0.9974
	MT	0.9976	0.9942	0.9970	0.9977
	HM	0.9967	0.9931	0.9967	0.9963
	MKN	0.9973	0.9930	0.9967	0.9975

CR, Coats-Redfern; MT, MacCallum-Tanner; HM, Horowitz-Metzger; and MKN, Madhusudanan-Krishnan-Ninan.

for the pre-exponential factor A , the highest value is for stage III, the intermediate values are for stages I and IV and the lowest value for stage II. The same trend is seen in the case of entropy of activation.

The decomposition stages with positive values of ΔS indicate that the activated complex has a less ordered structure compared to the reactant and that reaction in these cases may be described as "faster than normal" [24]. The stages having negative entropy of activation indicate that the activated complex has a more ordered structure than the reactant and the reaction is "slower than normal".

Choice of reaction mechanism

The kinetic parameters calculated for different stages of decomposition using the nine mechanistic equations are given in Table 6. From this table, it can be seen that, for all four stages of decomposition, the highest value of the correlation coefficient and, hence, the best-fit curve is obtained for the Mampel equation (eqn. (5)). We can thus infer that the rate-controlling process for the reaction is random nucleation with the formation of one nucleus on each particle. It can also be seen from the table that some more

TABLE 6

Kinetic parameters for the decomposition of tetrammine copper(II) sulphate monohydrate using mechanistic equations

Mechanistic eqn. no.		Stage I	Stage II	Stage III	Stage IV
1	<i>E</i>	161.12	116.57	371.29	397.27
	<i>A</i>	1.20×10^{18}	3.31×10^9	1.10×10^{29}	3.09×10^{18}
	<i>r</i>	0.97377	0.98313	0.97588	0.98381
2	<i>E</i>	177.34	127.72	398.74	425.40
	<i>A</i>	1.02×10^{20}	3.49×10^{10}	1.63×10^{31}	6.92×10^{19}
	<i>r</i>	0.98229	0.98779	0.98215	0.98975
3	<i>E</i>	198.98	141.84	432.67	461.31
	<i>A</i>	2.08×10^{22}	3.58×10^{11}	4.00×10^{33}	1.93×10^{21}
	<i>r</i>	0.99073	0.99167	0.98843	0.99494
4	<i>E</i>	184.40	132.37	409.93	437.16
	<i>A</i>	2.11×10^{20}	2.74×10^{10}	3.65×10^{31}	7.49×10^{19}
	<i>r</i>	0.98556	0.98938	0.98449	0.99181
5	<i>E</i>	108.08	74.48	229.43	242.29
	<i>A</i>	5.74×10^{11}	3.09×10^5	2.38×10^{17}	3.59×10^{10}
	<i>r</i>	0.99538	0.99262	0.99249	0.99720
6	<i>E</i>	50.67	33.21	109.56	113.25
	<i>A</i>	1.67×10^4	9.06×10^0	1.03×10^7	2.68×10^3
	<i>r</i>	0.99464	0.99073	0.99173	0.99675
7	<i>E</i>	31.53	19.44	69.74	70.24
	<i>A</i>	4.43×10^1	2.62×10^{-1}	3.07×10^3	9.77×10^0
	<i>r</i>	0.99372	0.98766	0.99086	0.99619
8	<i>E</i>	90.97	63.41	202.93	213.92
	<i>A</i>	1.15×10^9	7.19×10^3	4.74×10^{14}	3.74×10^8
	<i>r</i>	0.98614	0.98871	0.98496	0.99223
9	<i>E</i>	96.11	66.88	211.29	222.77
	<i>A</i>	4.22×10^9	1.25×10^4	1.81×10^{15}	8.37×10^8
	<i>r</i>	0.98998	0.99053	0.98786	0.99451

E in kJ mol^{-1} , *A* in s^{-1} .

equations give good linear curves with high values of the correlation coefficients, though not as high as eqn. (5). Therefore it may become difficult to unequivocally assign the reaction mechanisms from the linearity of the kinetic curves alone. In such cases the operating mechanism can also be chosen by comparing the kinetic parameters with those obtained from non-mechanistic equations [25]. In the present case, a comparison with the values obtained by the Coats–Redfern method is more appropriate, because the same method was used here for solving the exponential integral. The kinetic parameters calculated for the four stages of decomposition using the

Coats–Redfern equation, and the comparison with the mechanistic equation which gives the nearest values of E and A may be considered in Tables 5 and 6. It can be seen that, for different stages of decomposition, the kinetic parameters obtained from the Coats–Redfern method are in good agreement with those values obtained from the Mampel equation, which is based on random nucleation.

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REFERENCES

- 1 W.W. Wendlandt, *Thermal Methods of Analysis*, Wiley-Interscience, 2nd edn., 1974.
- 2 C.G.R. Nair and K.N. Ninan, *Thermochim. Acta*, 23 (1978) 161.
- 3 K.N. Ninan and C.G.R. Nair, *Thermochim. Acta*, 30 (1979) 25.
- 4 K.N. Ninan and C.G.R. Nair, *Thermochim. Acta*, 37 (1980) 161.
- 5 J.E. House, Jr., and John C. Bailar, *J. Am. Chem. Soc.*, 91 (1969) 67.
- 6 J.P. Smith and W.W. Wendlandt, *J. Inorg. Nucl. Chem.*, 26 (1964) 1157.
- 7 C.G.R. Nair and P.M. Madhusudanan, *Thermochim. Acta*, 14 (1976) 373.
- 8 W.W. Wendlandt and J.P. Smith, *Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam, 1967, pp. 132–143.
- 9 George Brauer, *Hand Book of Preparative Inorganic Chemistry*, Vol. 2, 2nd edn., 1965, p. 1021.
- 10 A.G. Vogel, *Text Book of Quantitative Inorganic Analysis*, Longmann, 4th edn., 1978, p. 462.
- 11 A.W. Coats and J.P. Redfern, *Nature*, 201 (1964) 68.
- 12 J.R. MacCallum and J. Tanner, *Eur. Polym. J.*, 6 (1970) 1033.
- 13 H.H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
- 14 P.M. Madhusudanan, K. Krishnan and K.N. Ninan, *Thermochim. Acta*, 97 (1986) 189.
- 15 J. Sestak and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
- 16 V. Satava, *Thermochim. Acta*, 2 (1971) 423.
- 17 M.D. Judd and M.I. Pope, *J. Therm. Anal.*, 4 (1972) 31.
- 18 J. Zsako, *J. Therm. Anal.*, 5 (1973) 239.
- 19 V.M. Gorbachev, *J. Therm. Anal.*, 8 (1975) 349.
- 20 B. Morosin, *Acta Crystallogr.*, 25 (1969) 19.
- 21 JCPDS Hannewalt Method Search Manual, International Center for Diffraction Data, p. 748.
- 22 D. Blecic and Z.D. Zivkovic, *Thermochim. Acta*, 60 (1983) 68.
- 23 A.C. Norris, M.I. Pope and M. Selwood, *Thermochim. Acta*, 41 (1980) 357.
- 24 A.A. Frost and R.G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1961, p. 101.
- 25 P.H. Fong and D.T. Chen, *Thermochim. Acta*, 18 (1977) 273.