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Molten lithium nitrate–potassium nitrate eutectic: the reactions of aluminium, gallium and thallium

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Abstract

Aluminium(III) chloride and sulphate reacted with the alkali nitrate eutectic forming alumina, with intermediate formation of two immiscible, oxide-containing layers in the case of aluminium(III) sulphate. Both chloride and sulphate anions stabilised aluminium cations by coordination. Aluminium nitride (AlN) was unreactive in pure melt, but reacted in both basic (NaOH) and acidic ($K_2S_2O_7$) melts.

Gallium(III) chloride and nitrate reacted with pure nitrate melts at temperatures which increased as chloride was added. However, additions of bromide and nitrite caused reaction at lower temperatures. In each case the product was gallium(III) oxide, but in various crystal modifications. Thallium(I) nitrate did not react in the pure melt below 500 °C, following the expected trend with increase in cation size and decrease in oxidation state. Both thallium and gallium cations were stabilised by coordination with nitrate when dissolved in the melt.

INTRODUCTION

No systematic studies of the compounds of Periodic Group IIIB metals have so far been reported. In the case of aluminium, the literature consists of brief references that aluminium(III) nitrate "evolved a brownish gas" (in $NaNO_3$–KNO_3 eutectic) at 285 °C [1], that "Al^{3+} precipitates as oxide" [2] and behaves "as a very strong acid producing nitrogen dioxide" [3] (both in $NaNO_3$–KNO_3 eutectic at 240 °C), and that hydrated aluminium(III) chloride "foams and forms a cloudy solution" (in $LiNO_3$–$NaNO_3$–KNO_3 eutectic at 160 °C) [4], although zeolites (aluminosilicates) have been used, in molten nitrates, as ion exchangers at temperatures up to 350 °C [5,6]. Aluminium metal has been anodised in various molten nitrates ($LiNO_3$–KNO_3 at 160 ° [7], $LiNO_3$–$NaNO_3$–KNO_3 at 330 °C [8], $NaNO_3$–KNO_3 at 900 °C [9] and KNO_3 at 450 °C [10]) with formation of oxide films of varying hardness.

For gallium, there is only one report, that the trichloride also "foams and forms a cloudy solution" (in $LiNO_3$–$NaNO_3$–KNO_3 at 160 °C) [4]. For thallium, there are a number of references to physical measurements on molten nitrate solutions of thallium(I) halides or nitrate, where thallium is presumably stable (the highest temperatures being solubility measurements

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in $LiNO_3$, $NaNO_3$ and KNO_3 at 311–390 °C [11] and viscosity determinations in the same nitrates at 260–420 °C [12].

To provide a more comparative study, the reactions of compounds of aluminium, gallium and thallium in lithium nitrate–potassium nitrate eutectic have been examined, as a comparison with those of indium(III) nitrate which have recently been published [13]. Aluminium nitride was chosen to provide a comparison with that of magnesium nitride, hitherto the only reported reaction of nitride in molten nitrate [14].

EXPERIMENTAL

Materials

Lithium nitrate–potassium nitrate eutectic was prepared as previously described [14]. Potassium dichromate, potassium chloride and potassium bromide, all BDH AnalaR, were dried at 110 °C for 2 h. Potassium nitrate (BDH LR) was heated at 110 °C for 24 h. Sodium hydroxide (BDH, AnalaR) and aluminium nitride, gallium(III) chromide and thallium(I) nitrate (all Alfa, Ventron) were used as received. Aluminium(III) chloride was sublimed from aluminium turnings at 200 °C (found: Al 20.2, Cl 78.9%; calc. for $AlCl_3$: Al 20.2, Cl 79.8%). Hydrated aluminium(III) sulphate was heated at 600 °C for 6 h [found: Al 15.6, SO_4 83.0%; calc. for $Al_2(SO_4)_3$: Al 15.8, SO_4 84.2%]. Gallium(III) nitrate nonahydrate (Alfa, Ventron) which, owing to hydrolysis, could not be dehydrated in nitrate melt as was indium(III) nitrate [13], was used as received [found: Ga 17.1%; calc. for $Ga(NO_3)_3 \cdot 9H_2O$, Ga 16.7%]. Potassium pyrosulphate was prepared by heating potassium persulphate (BDH AnalaR) at 250 °C for 11 h (67.9% $S_2O_7^{2-}$ by NaOH titration; calc. for $K_2S_2O_7$, 69.2%).

Procedure

Qualitative reactions, thermogravimetry and X-ray powder diffraction were carried out as previously described [14].

RESULTS AND DISCUSSION

Aluminium

Aluminium trichloride reacted in lithium nitrate–potassium nitrate eutectic above 130 °C, the initial white suspension turning yellow and rising to the top of the tube at 140 °C with visible evolution of nitrogen dioxide and a little sublimed aluminium trichloride from 160 °C. A white precipitate was formed by heating at 200 °C, which was shown to be α-alumina by X-ray powder diffraction of the unwashed solidified melt.

Thermogravimetric analysis (Fig. 1, curve A) indicated a similar reaction, with the insoluble product, after washing with water and drying, giving a confirmatory analysis (found: Al 49.9%; calc. for Al_2O_3, Al 52.9%). The weight loss was variable, between 89% and 100%, which is less than that expected for the reaction

$$2AlCl_3 + 6NO_3^- \rightarrow Al_2O_3 + 6Cl^- + 6NO_2 + \tfrac{3}{2}O_2 \qquad (1)$$

(Calc. for loss of $3N + \frac{15}{2}O$ per $AlCl_3$ 121.5%)

and is largely attributed to some protective coating of the very insoluble reaction product around unreacted aluminium trichloride. The double maximum in the thermogravimetric curve probably indicates partial stabilisation of aluminium cations by chloride anions, by formation of complexes (almost certainly $AlCl_4^-$, which has been shown to be stable in many melts).

In air, without the melt, aluminium trichloride also reacted, with a rapid loss in weight from 110 °C (Fig. 1, curve B) of 62.0%, which compares well with that for the equation

$$2AlCl_3 + \tfrac{3}{2}O_2 \rightarrow Al_2O_3 + 3Cl_2 \qquad (2)$$

(Calc. for loss of 3 Cl and gain of $\frac{3}{2}O$ per $AlCl_3$ 60.9%)

In confirmation, X-ray powder diffraction showed the product to be aluminium(III) oxide, but as a mixture of the λ, γ and δ modifications.

Aluminium(III) sulphate was incompletely soluble in nitrate eutectic at 150 °C, and 0.004–0.3 molal mixtures separated at 200 °C into an upper yellowish-white gel and a lower, more mobile, cloudy melt layer. On increasing the temperature, the layers mixed above 320 °C to give a yellowish-white suspension throughout the tube. Brown nitrogen dioxide gas was evolved from 250 °C to 450 °C. Analysis of a series of layer samples, taken from 2 to 25 minutes at 200 °C, showed all components to be present in both layers, but that the upper one contained more aluminium and sulphate with less lithium, potassium and nitrate than the lower one, the difference increasing with time (details of these analytical results are in ref. 15). These analyses indicated a deficiency of anions, which increased with time for the upper layer, thus suggesting the presence of oxide. Thermogravimetric analysis confirmed that weight loss began from 200 °C (Fig. 1, curve C) and that sulphate anions considerably stabilised the aluminium, the second weight loss maximum being at 425 °C. The total weight loss was 94.5 ± 1.2%, in accordance with the reaction

$$Al_2(SO_4)_3 + 6NO_3^- \rightarrow Al_2O_3 + 3SO_4^{2-} + 6NO_2 + \tfrac{3}{2}O_2 \qquad (3)$$

[Calc. for loss of $6N + 15O$ per $Al_2(SO_4)_3$ 95.3%]

X-ray powder diffraction showed that the white, water washed and dried, product was γ-alumina.

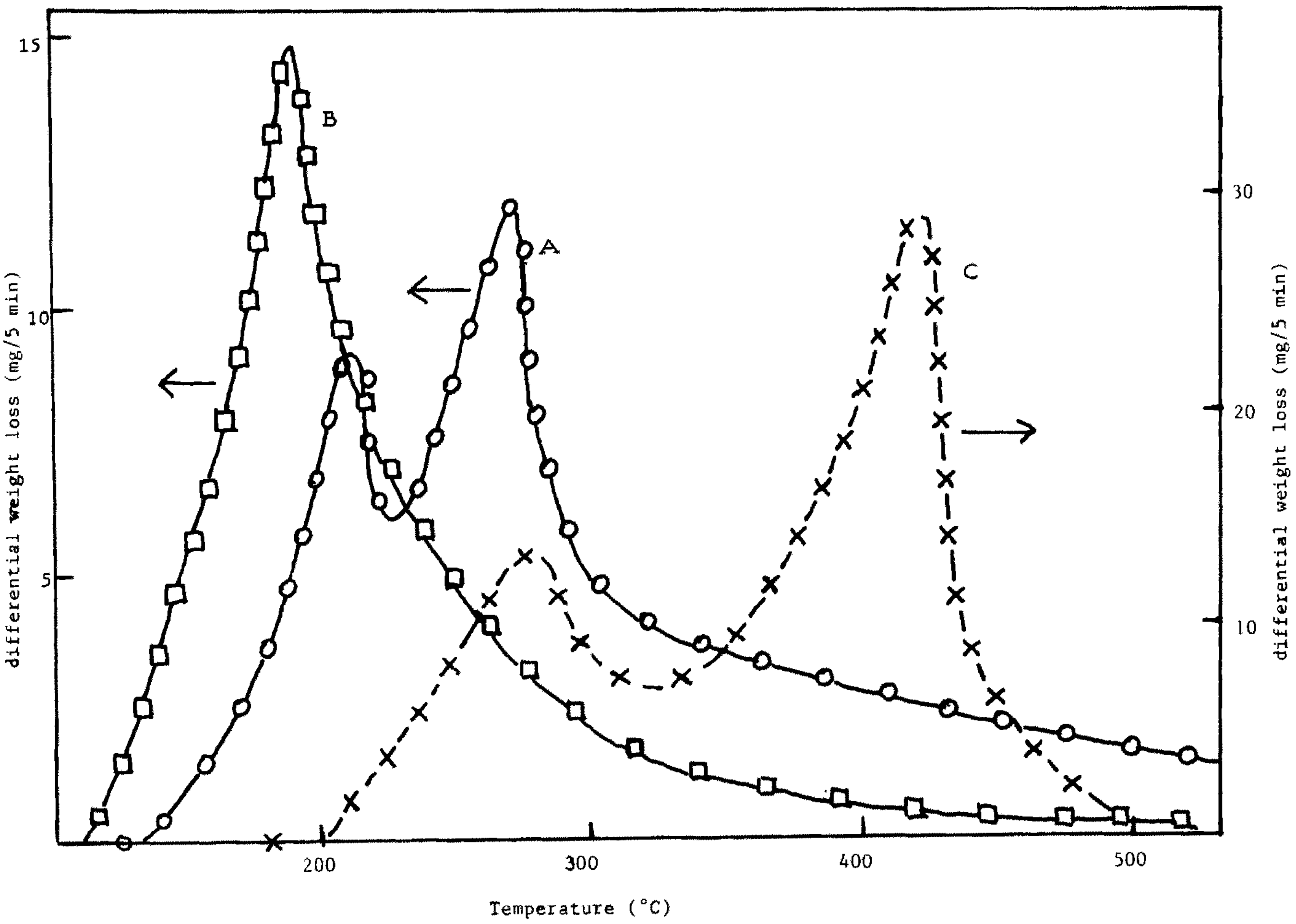

Fig. 1. Thermogravimetry of aluminium(III) chloride and sulphate. Curve A, 0.39 molal $AlCl_3$ in $LiNO_3$–KNO_3 eutectic (left-hand scale); B, 0.215 g of $AlCl_3$ in air (left-hand scale); C, 0.44 molal $Al_2(SO_4)_3$ in $LiNO_3$–KNO_3 eutectic (right-hand scale).

Aluminium nitride (AlN) did not react visibly in nitrate melts up to 500 ° C, nor did the melt contain any soluble aluminium. Thermogravimetric analysis also showed no weight loss to 500 ° C. This inertness is attributed not only to the stability of the nitride itself, but also to the protective nature of the layer of alumina that is probably formed on the outer surface of the nitride particles. The same effects are also responsible for the lack of reactivity when the nitride alone is heated in air. There was no visible change or weight loss on heating to 800 ° C.

In contrast, thermogravimetry in a nitrate melt containing added sodium hydroxide (Fig. 2, curve A) showed a slow weight loss beginning from 120 ° C, rather similar to the partial dehydration found with a melt solution of sodium hydroxide alone [16] (Fig. 2, curve B. Experimental weight loss 5.7%; calc. for loss of $H + \frac{1}{2}O$ for NaOH 22.5%). This was followed by a more rapid loss from 400 ° C with a maximum rate of weight loss at 480 ° C. The overall weight loss (85.8% with respect to AlN, or 15% with respect to NaOH) was close to that for the hydrolysis reaction

$$\mathrm{AlN + 6NaOH \rightarrow AlO(OH) + 3Na_2O + NH_3 + H_2O} \qquad (4)$$

(Calc. for loss of 5H + N + O per AlN 85.4%, or per 6NaOH 14.6%)

and analogous to that found when magnesium nitride was reacted in a nitrate melt containing high concentrations of sodium hydroxide [14].

The aluminium oxide hydroxide was no doubt combined with some sodium oxide, with the resulting sodium aluminate hydrolysing completely to aluminium hydroxide when the quenched reacted melt was washed with water (found, Al 34.0%; calc. for $Al(OH)_3$, 34.5%).

In a strongly acidic melt (containing $K_2S_2O_7$) the initial reaction began at 160 ° C (Fig. 2, curve C) with a maximum at 200 ° C. The weight loss to 330 ° C was 41.0%, similar to that for the reaction of pyrosulphate with nitrate (experimental weight loss of $K_2S_2O_7$ alone with $LiNO_3$–KNO_3 42.4%; Fig. 2, curve D).

$$\mathrm{K_2S_2O_7 + 2NO_3^- \rightarrow K_2SO_4 + SO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2} \qquad (5)$$

(Calc. for loss of 2N + 5O per $K_2S_2O_7$ 42.0%)

This reaction was followed by a further reaction (small maximum at 380 ° C, experimental weight loss 25.9% with respect to AlN), but unreacted aluminium nitride was also present, even after holding the temperature at 470 ° C for 30 min, together with soluble aluminium in the melt. It is thought that this higher temperature reaction was that of aluminium nitride with the melt, caused by the removal of the normally protective oxide layer on the surface of the aluminium nitride particles by the highly acidic pyrosulphate, and that this reaction was quenched before completion due to re-formation of the protective oxide surface.

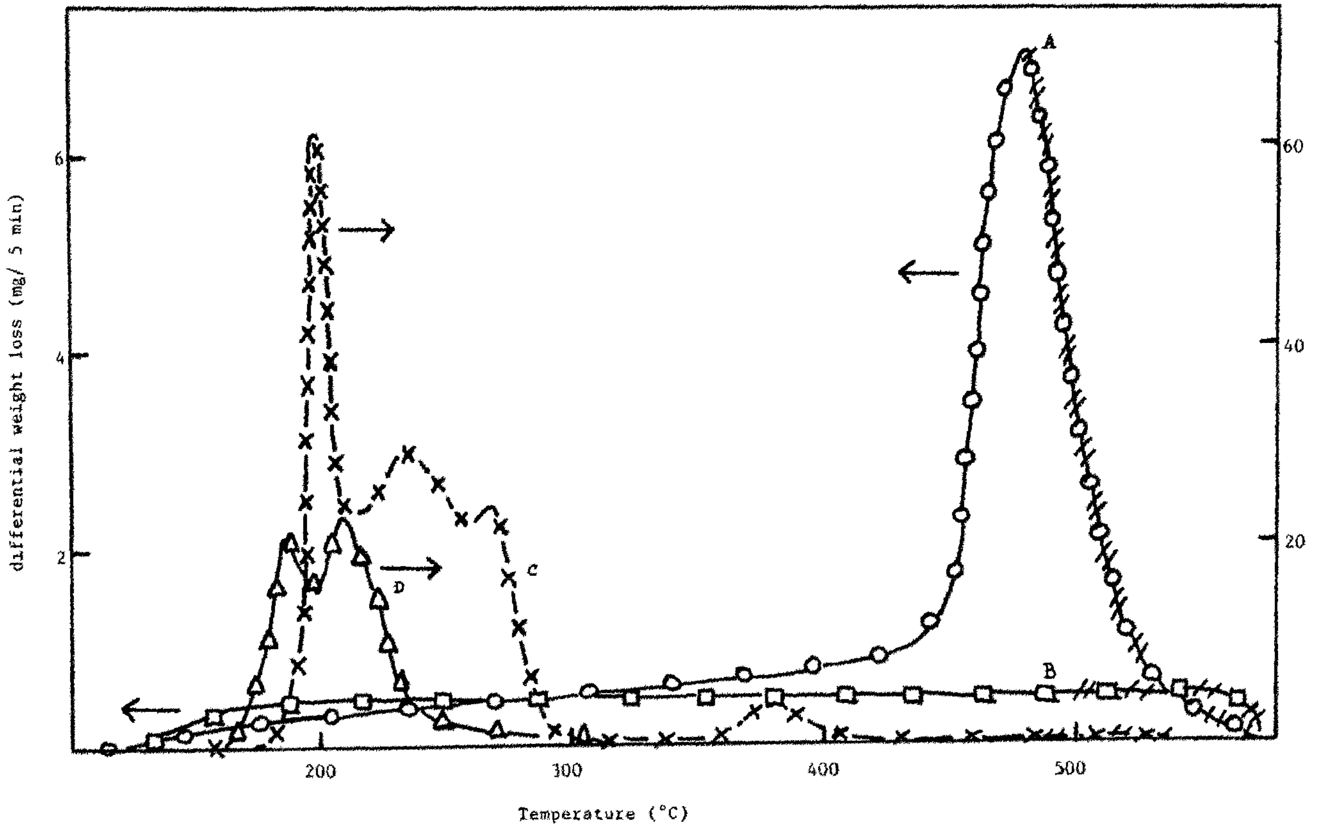

Fig. 2. Thermogravimetry of aluminium nitride in basic and acidic nitrate melts. Curve A, 0.46 molal AlN + 2.65 molal NaOH in $LiNO_3$–KNO_3 eutectic (left-hand scale); B, 2.02 molal NaOH in $LiNO_3$–KNO_3 eutectic (left-hand scale); C, 0.39 molal AlN + 0.64 molal $K_2S_2O_7$ in $LiNO_3$–KNO_3 eutectic (right-hand scale); D, 0.30 molal $K_2S_2O_7$ in $LiNO_3$–KNO_3 eutectic (right-hand scale).

Gallium

Gallium(III) nitrate [$Ga(NO_3)_3 \cdot 9H_2O$] mixed with the solid nitrate eutectic evolved water and nitric acid vapour from 70 °C. On melting, a white suspension was observed with brown nitrogen dioxide being evolved from 260 °C. Thermogravimetry showed that weight loss started at 70 °C (Fig. 3, curve A). The overall weight loss to 460 °C was 76.0 ± 0.8% in air and 77.5% in nitrogen (Fig. 3, curve B), corresponding to the stoichiometry

$$2Ga(NO_3)_3 \cdot 9H_2O \rightarrow Ga_2O_3 + 15H_2O + 6HNO_3 \qquad (6)$$

$\left[\text{Calc. for loss of } 18H + \tfrac{33}{2}O + 3N \text{ per } Ga(NO_3)_3 \cdot 9H_2O \text{ } 77.5\%\right]$

X-ray powder diffraction of the white solid remaining after water extraction of the quenched reacted melt, and drying, showed it to be the δ form of gallium(III) oxide. Thermogravimetry of the yellow hydrated nitrate alone

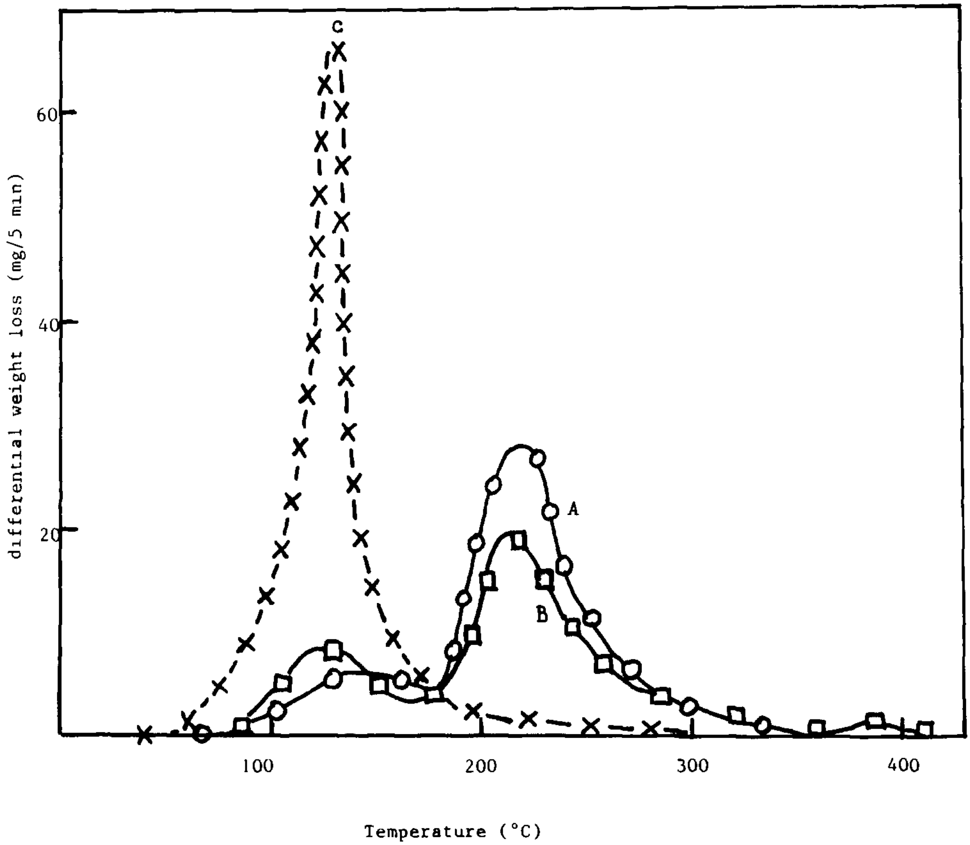

Fig. 3. Thermogravimetry of gallium(III) nitrate nonahydrate. Curve A, 0.21 molal $Ga(NO_3)_3 \cdot 9H_2O$ in $LiNO_3$–KNO_3 eutectic in air; B, 0.20 molal $Ga(NO_3)_3 \cdot 9H_2O$ in $LiNO_3$–KNO_3 eutectic under nitrogen; C, 0.295 g of $Ga(NO_3)_3 \cdot 9H_2O$ alone in air.

(Fig. 3, curve C) showed the total weight loss to be very similar (74.3 ± 1.0%) but to occur with only one maximum, which was at a lower temperature. This suggested that the presence of the nitrate melt was in fact influencing this reaction, probably by coordination of nitrate anions to gallium cations with some subsequent stabilisation. Interestingly, the gallium(III) oxide formed by heating without nitrate melt was shown by X-ray diffraction to be the α modification.

When potassium chloride was dissolved in the melt as well as gallium nitrate, the temperature of the maximum rate of weight loss increased. This was again attributed to stabilisation arising by complexation. The thermogravimetric curves (Fig. 4) showed multiple maxima, which have previously been shown to be characteristic of such stabilisation (for example in the cases of zinc [17], iron [18] and cobalt cations [19]) and here are probably due to the formation of the tetrachloro, or higher, complexes of gallium. Such stabilisation increased with chloride concentration, and with Cl/Ga ratio (Fig. 4, inset), reaching a maximum above 1.5 molal (Cl/Ga ratio 15 : 1, it is common to quote ligand/metal ratios, but in fact the concentration of the complex is proportional to the ligand concentration, or a power thereof).

By contrast, potassium bromide did not stabilise gallium nitrate but caused reaction at a lower temperature (Fig. 5, curve A). This was attributed to the known catalytic effect of bromide on the nitrate decomposition reaction

$$NO_3^- \rightarrow NO_2^- + \tfrac{1}{2}O_2 \qquad (7)$$

and the considerably greater basicity of nitrite compared with that of nitrate [20]. This received confirmation in that, when potassium nitrite was added directly to the molten nitrate eutectic, the dissolved gallium nitrate reacted at an even lower temperature (compare the maximum rate of weight loss of Fig. 5, curve B, with curve C).

Contrastingly, thermogravimetry with acidic nitrate melts showed the weight losses for the gallium nitrate reaction (the first two maxima of curves A and B of Fig. 6) to be similar to that expected for eqn. (6) being 77.0 ± 0.6% to the minimum at 380 °C for the weaker acid ($K_2Cr_2O_7$, curve A), and to the minimum at 270 °C for the rather stronger acid ($NaPO_3$, curve B). In both cases the temperature of the first maximum (largely dehydration) is little affected by the presence of the acids (cf. Fig. 3, curve A) but the temperature of the second maximum is rather higher (260 ° for $K_2Cr_2O_7$ solution, 250 ° for $NaPO_3$ compared with 220 °C in the pure melt) indicating stabilisation by these anions. With each acidic solution there was further weight loss due to the reaction of the Lux–Flood acids with the nitrate melt (at 380–480 °C with $K_2Cr_2O_7$, and 270–490 °C with $NaPO_3$), the weight losses (37.8 ± 0.1% with respect to $K_2Cr_2O_7$ and 105.5 ± 0.2%

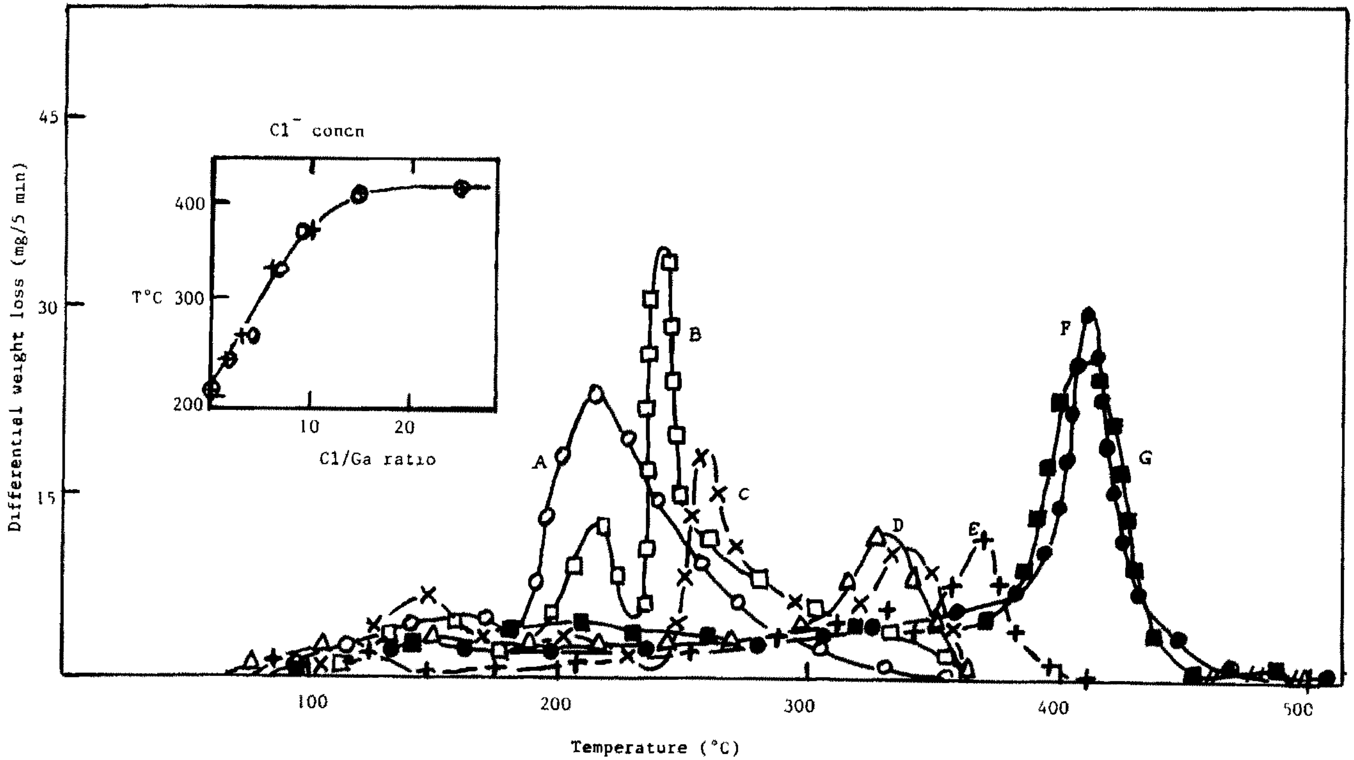

Fig. 4. Thermogravimetry of gallium(III) nitrate nonahydrate with potassium chloride in lithium nitrate–potassium nitrate eutectic. Curve A, 0.21 molal $Ga(NO_3)_3 \cdot 9H_2O$; B, 0.15 $Ga(NO_3)_3 \cdot 9H_2O + 0.23$ molal KCl; C, 0.15 molal $Ga(NO_3)_3 \cdot 9H_2O + 0.45$ molal KCl; D, 0.11 molal $Ga(NO_3)_3 \cdot 9H_2O + 0.67$ molal KCl; E, 0.08 molal $Ga(NO_3)_3 \cdot 9H_2O + 0.92$ molal KCl; F, 0.08 molal $Ga(NO_3)_3 \cdot 9H_2O + 1.20$ molal KCl; G, 0.08 molal $Ga(NO_3)_3 \cdot 9H_2O + 2.00$ molal KCl. Inset: Temperature of maximum rate of weight loss versus chloride concentration (○) and gallium : chloride ratio (+).

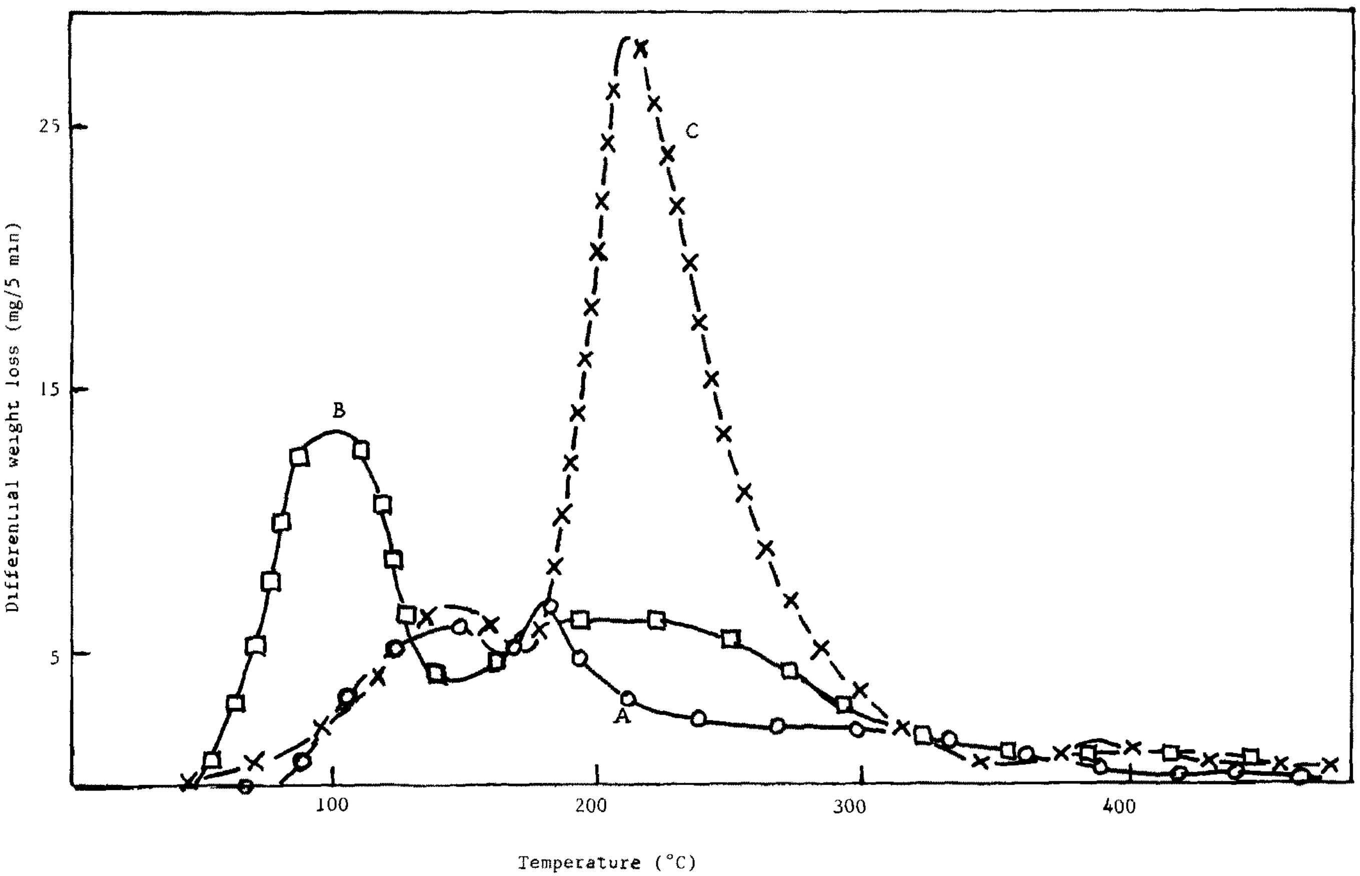

Fig. 5. Thermogravimetry of gallium(III) nitrate nonahydrate in lithium nitrate–potassium nitrate eutectic. Curve A, 0.11 molal $Ga(NO_3)_3 \cdot 9H_2O + 0.27$ molal KBr; B, 0.21 molal $Ga(NO_3)_3 \cdot 9H_2O + 0.47$ molal KNO_2; C, 0.21 molal $Ga(NO_3)_3 \cdot 9H_2O$.

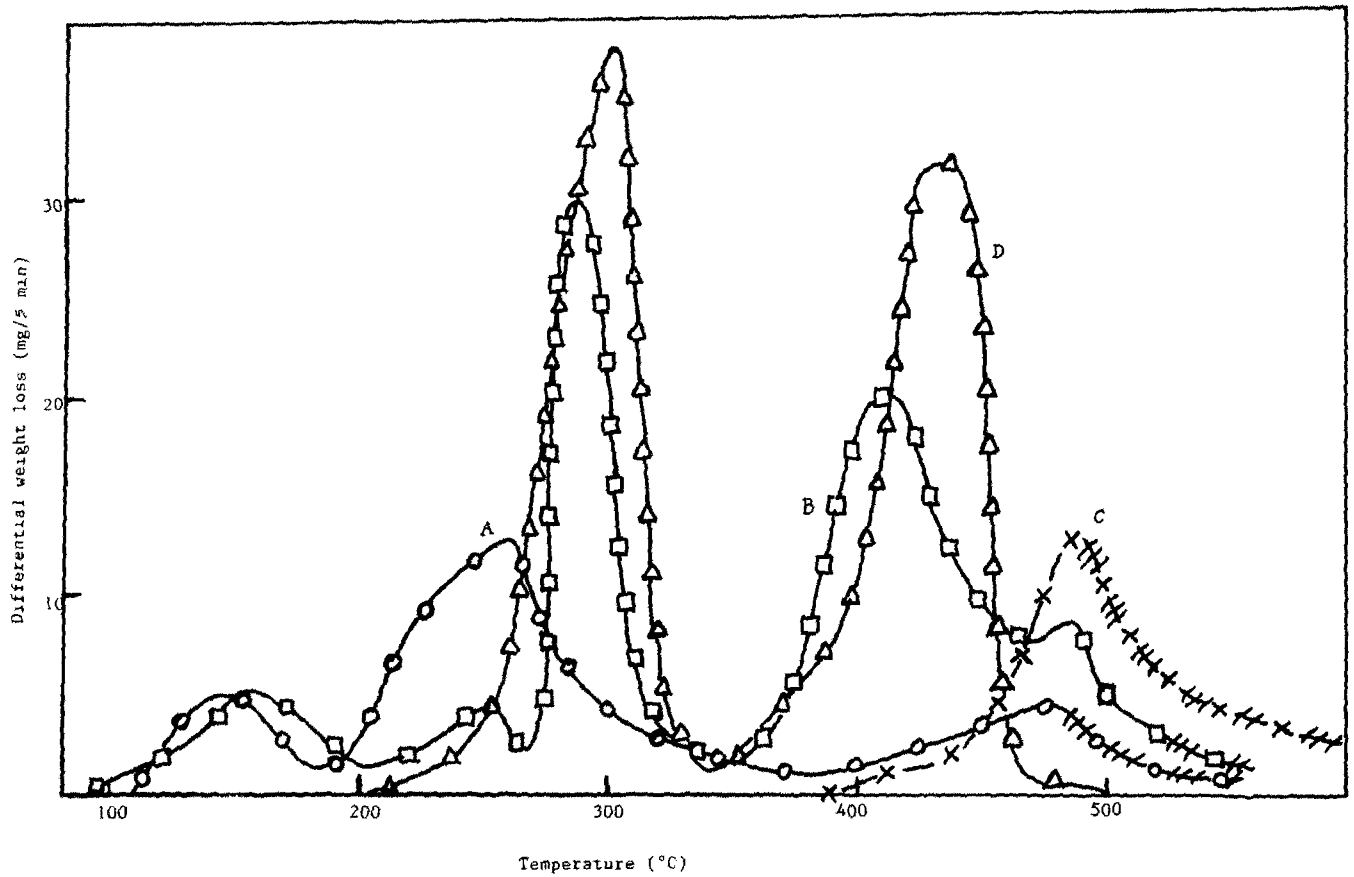

Fig. 6. Thermogravimetry of gallium(III) nitrate nonahydrate in acidic lithium nitrate–potassium nitrate melts. Curve A, 0.11 molal $Ga(NO_3)_3 \cdot 9H_2O + 0.10$ molal $K_2Cr_3O_7$; B, 0.06 molal $Ga(NO_3)_3 \cdot 9H_2O + 0.24$ molal $NaPO_3$; C, 0.27 molal $K_2Cr_2O_7$; D, 0.83 molal $NaPO_3$.

with respect to $NaPO_3$) being similar to those of these acids alone in nitrate melt [16,21], i.e.

$$K_2Cr_2O_7 + 2NO_3^- \rightarrow K_2CrO_4 + CrO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \tag{8}$$

(Calc. for loss of 2N + 5O per $K_2Cr_2O_7$ 37.0%)

and

$$NaPO_3 + 2NO_3^- \rightarrow Na^+ + PO_4^{3-} + 2NO_2 + \tfrac{1}{2}O_2 \tag{9}$$

(Calc. for loss of 2N + 5O per $NaPO_3$ 104.8%)

shown in Fig. 6, curves C and D. (The first of the higher temperature maxima with metaphosphate, at 280 °C on curve B and 300 °C on curve D, arises from the formation of pyrophosphate [16]). X-ray diffraction showed the washed and dried water-insoluble product to be the δ form of gallium(III) oxide.

Gallium(III) chloride is extremely reactive towards air, and thermogravimetry showed a weight loss in three stages (Fig. 7, curve A) with weight losses of 20.4 ± 0.8% between 110 and 200 °C, 10.6 ± 0.1% between 200 and 250 °C, and 14.5 ± 0.6% between 250 and 400 °C. The final product was shown to be the ϵ modification of gallium(III) oxide, which is customarily formed at temperatures over 500 °C. The intermediate products were evidently gallium oxide chlorides, the second intermediate product corresponding well to the simplest oxychloride (GaOCl) but the first containing more chlorine (e.g. $Ga_3O_2Cl_5$). The three stages would then be

$$3GaCl_3 + O_2 \rightarrow Ga_3O_2Cl_5 + 2Cl_2 \tag{10}$$

(Calc. for loss of $\tfrac{4}{3}$Cl and gain of $\tfrac{2}{3}$O per $GaCl_3$ 20.8%)

$$Ga_3O_2Cl_5 + \tfrac{1}{2}O_2 \rightarrow 3GaOCl + Cl_2 \tag{11}$$

(Calc. for loss of $\tfrac{2}{3}$Cl + gain of $\tfrac{1}{3}$O per $GaCl_3$ 10.4%)

$$2GaOCl + \tfrac{1}{2}O_2 \rightarrow Ga_2O_3 + Cl_2 \tag{12}$$

(Calc. for loss of Cl and gain of $\tfrac{1}{2}$O per $GaCl_3$ 15.6%)

In the nitrate eutectic, gallium(III) chloride also showed itself reactive (Fig. 7, curve B), beginning in the solid state from 50 °C, with the first maximum at 90 °C well below the eutectic melting point (132 °C). The minimum, close to 150 °C, showed that in the molten nitrate the reaction rate was reduced, probably by coordination of nitrates to the gallium, before the rate increased again to a second maximum at 350 °C, the weight losses for these two stages, below and above 150 °C, being 16.0% and 75.7%, respectively, in accord with the reactions

$$4GaCl_3 + 2NO_3^- \rightarrow Ga_4OCl_{10} + 2Cl^- + 2NO_2 + \tfrac{1}{2}O_2 \tag{13}$$

(Calc. for loss of $\tfrac{1}{2}$N + $\tfrac{5}{4}$O per $GaCl_3$ 15.3%)

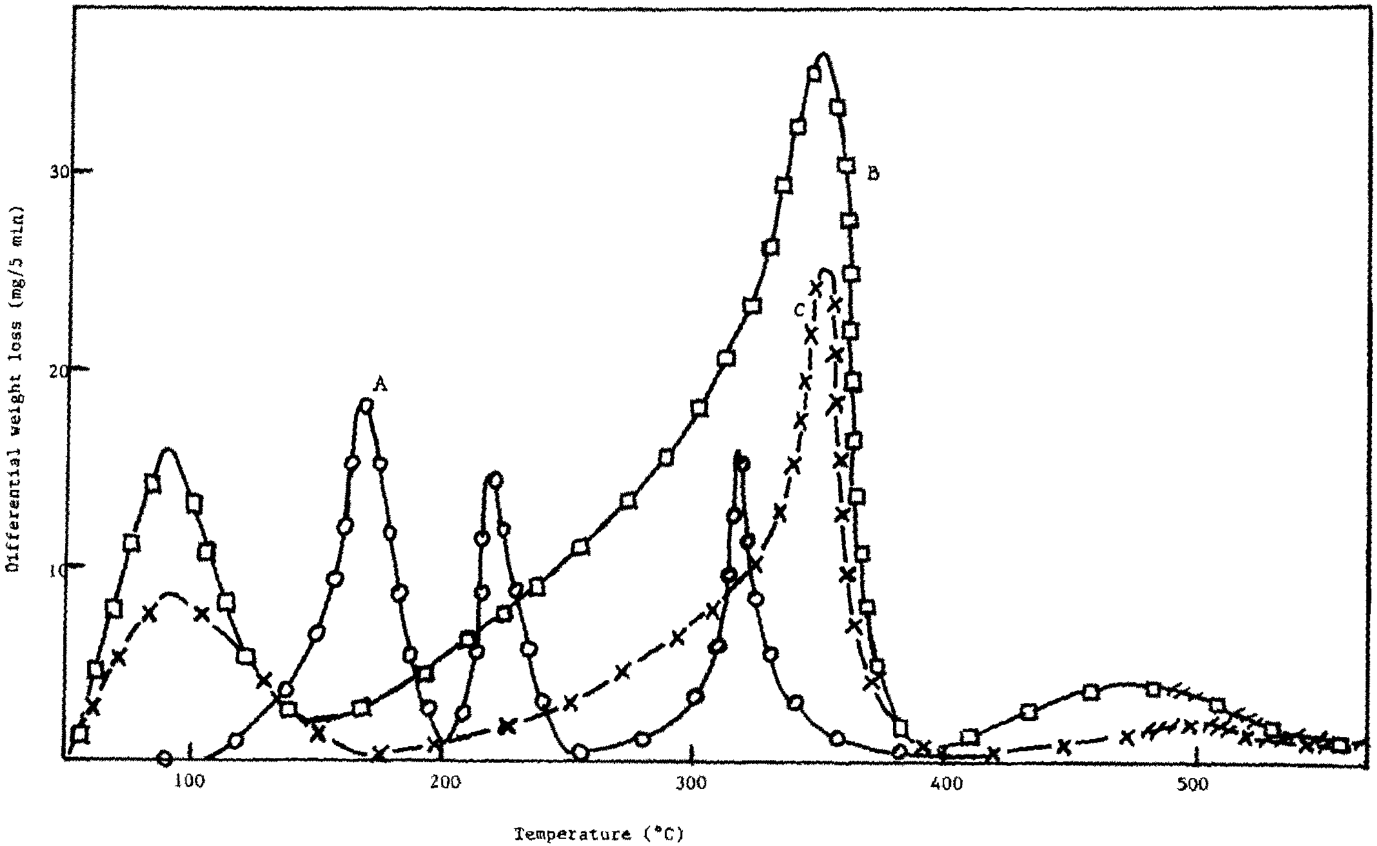

Fig. 7. Thermogravimetry of gallium(III) chloride. Curve A, 0.337 g of $GaCl_3$ alone in air; B, 0.27 molal $GaCl_3$ in $LiNO_3$–KNO_3 eutectic in air; C, 0.30 molal $GaCl_3$ in $LiNO_3$–KNO_3 eutectic under nitrogen.

and

$$Ga_4OCl_{10} + 10NO_3^- \rightarrow 2Ga_2O_3 + 10Cl^- + 10NO_2 + \tfrac{5}{2}O_2 \qquad (14)$$

(Calc. for loss of $2\frac{1}{2}N + 6\frac{1}{4}O$ per $GaCl_3$ 76.6%)

Whatever the precise stoichiometry of the intermediate oxide chloride, the overall weight loss agreed with the formation of the δ form of gallium(III) oxide that was indicated by X-ray powder diffraction and quantitative analysis (found: Ga 91.7%; calc. for Ga_2O_3: Ga 91.9%). Very similar results were obtained when the thermogravimetry was carried out under nitrogen (Fig. 7, curve C), where the first, second and overall weight losses were 21.2%, 70.6% and 91.8% respectively. The temperature of the second maxima of the reactions in the melt, around 350 °C, indicated that the gallium was being stabilised by chloride, as indicated previously by Fig. 4.

Thallium

Thallium(I) nitrate was soluble in the nitrate eutectic ($>$ 0.62 molal at 210 °C) giving colourless solutions up to 500 °C. The stability of these solutions was confirmed by thermogravimetry, no weight loss being observed up to this temperature. Once again the cations were being stabilised by coordination with several nitrate anions, since thallium(I) nitrate (m.p. 206 °C), when heated alone, gave a black precipitate at 350 °C (shown by X-ray powder diffraction to be Tl_2O_3) with some nitrogen dioxide visible from 450 °C. At 850 °C the remaining solid was yellow and dissolved completely in water when cold, indicating that it was thallium(I) oxide. Thermogravimetry (Fig. 8, curve A) showed that weight loss began at 430 °C, with a maximum at 570 °C, and a second maximum at 650 °C. The overall weight loss of 52.0% at 850 °C (37.8% at 660 °C) indicated that in addition to the Lux–Flood acid–base reaction

$$2TlNO_3 \rightarrow Tl_2O_3 + NO_2 + NO \qquad (15)$$

followed at higher temperatures by the well known decomposition

$$Tl_2O_3 \rightarrow Tl_2O + O_2 \qquad (16)$$

(Calc. for overall loss of $N + \frac{5}{2}O$ per $TlNO_3$ 26.4%)

there was also considerable volatilisation, mainly of thallium(III) oxide. This was confirmed by thermogravimetry carried out under nitrogen (Fig. 8, curve B), when the overall weight loss to 820 °C was only 25.8%. Evidently the decomposition shown in eqn. (16) would occur at a lower temperature under nitrogen and thus much less volatilisation would be possible. Certainly curve B shows no sign of the second weight loss maximum found at 650 °C in air (Fig. 8, curve A).

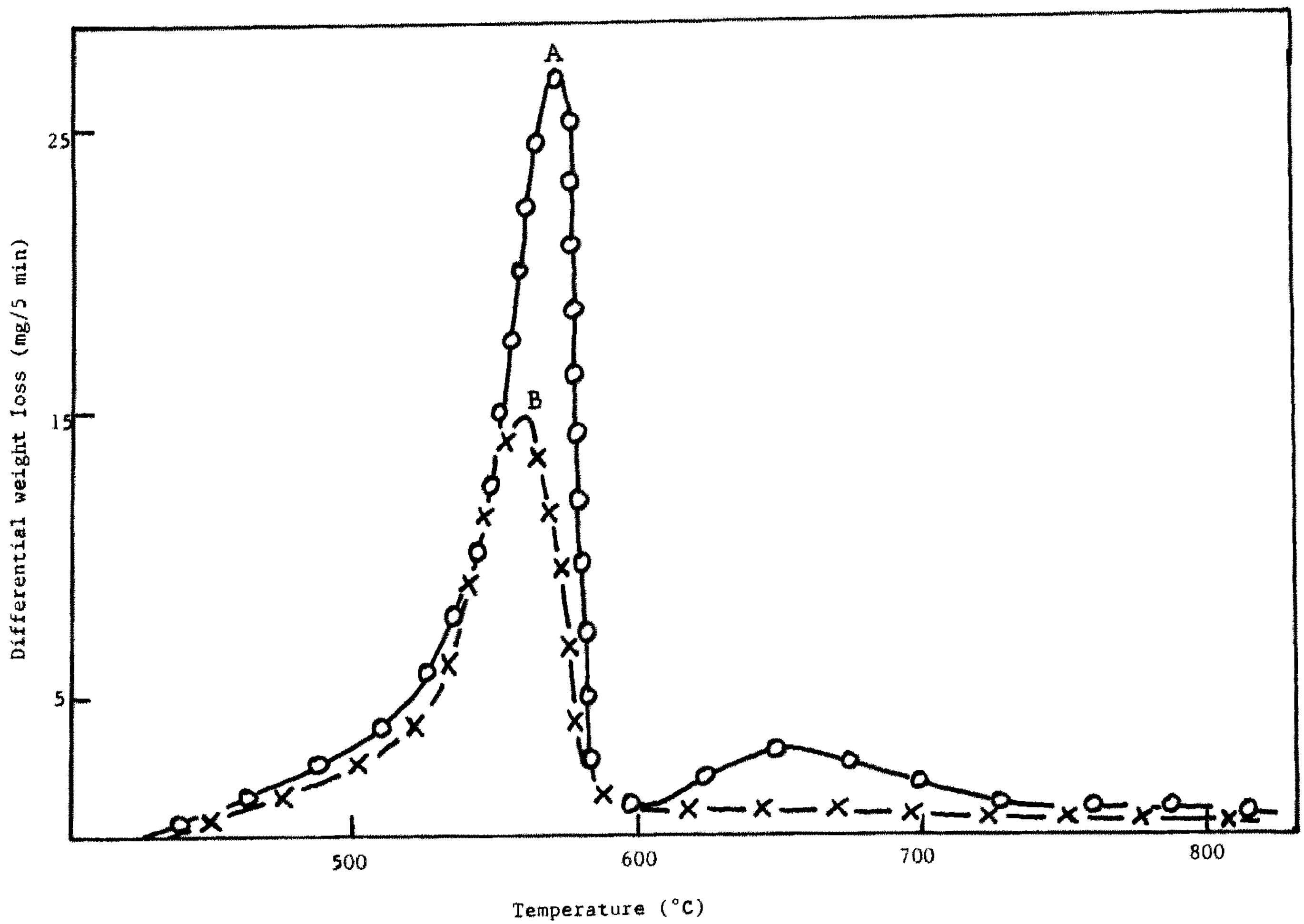

Fig. 8. Thermogravimetry of thallium(I) nitrate. Curve A, 0.219 g of $TlNO_3$ in air; B, 0.280 g of $TlNO_3$ under nitrogen.

CONCLUSION

The stability of the Group IIIB cations in nitrate melts shows the variation expected from Lux–Flood acids, reaction temperature increasing with increasing ionic radii of cations and with decreasing oxidation state. Because of complications with the dehydration reaction of hydrated gallium nitrate, perhaps the best comparison is of the temperatures of the biggest (highest temperature) maxima, being for $AlCl_3$, 280 °C (Fig. 1), $GaCl_3$ 370 °C (Fig. 7), $In(NO_3)_3 + 3KCl$ 410 °C [13] and $TlNO_3$ > 500 °C (Fig. 8).

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