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MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC: THE REACTION OF MAGNESIUM COMPOUNDS

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ABSTRACT

Anhydrous and hydrated magnesium sulphate reacted as a Lux–Flood acid in molten lithium nitrate–potassium nitrate eutectic from 400 °C with precipitation of magnesium oxide. Stabilization to above 500 °C occurred with added sulphate but a lower temperature reaction took place with added sodium hydroxide. The solubility of magnesium sulphate was determined up to 400 °C and shown to be nearly an order of magnitude less than that of potassium sulphate.

Magnesium nitride reacted only superficially with pure nitrate melt but reacted faster in melts containing added sodium hydroxide, magnesium oxide being the final product in both cases. In acidic melts ($K_2S_2O_7$ or $K_2Cr_2O_7$ added) reaction was complete with soluble magnesium being formed initially. Thermogravimetry of magnesium oxide in a hydroxide-containing melt suggested that magnesium hydroxide may have been an intermediate.

INTRODUCTION

Very little is known about the chemistry of magnesium in molten alkali metal nitrates, but magnesium cations have been used to accelerate the Lux–Flood acid–base reaction of dichromate with sodium nitrate–potassium nitrate eutectic [1]. The solubility of magnesium chromate was found to be low (5.5×10^{-3} M at 250 °C) [1] but higher than the values for magnesium oxide in this melt (1.5×10^{-7} M at 290 °C, 3.5×10^{-7} at 320 °C) which were derived from measurements with a reversible oxygen electrode [2]. These acid–base reaction results also indicated that chloride and bromide only formed, at best, weak complexes with magnesium (the measured solubility of $MgCrO_4$ first decreasing and then slightly increasing as the concentration of halide was increased [1]). Similar weak complexing with halide was also deduced from an infrared study [3] when nitrate was judged to associate preferentially with magnesium cations (at 270–310 °C in KNO_3) though Peleg found no "direct complexes" in the same solvent at 200–340 °C but nevertheless considered the magnesium occupied specific site positions around the nitrate cations [4].

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Magnesium metal was found to react in pure lithium nitrate–potassium nitrate eutectic at 420 °C, precipitating the oxide and producing nitrite, nitrogen dioxide, nitrous oxide and nitrogen, suggesting reduction by stepwise removal of oxygen from nitrate. In acidic nitrate melts, the reaction took place at lower temperatures (310 °C in 0.9 M $K_2Cr_2O_7$ and 160 °C in 0.1 M $K_2S_2O_7$ solutions) the gaseous product being only nitrogen dioxide, which indicated the increasing importance of electron transfer to the acidic nitryl cation as the concentration of this increased [5].

Although the spectroscopic measurements indicate magnesium cations to be stable to 320 °C, it was thought valuable to establish the temperature at which they reacted as Lux–Flood acids in lithium nitrate–potassium nitrate eutectics, together with the temperatures and products of reaction in basic and acidic melts. The reaction of magnesium nitride in neutral, acidic and basic nitrate melts was investigated for comparison and also because the reaction of a nitride with molten nitrates had never previously been investigated.

EXPERIMENTAL

Materials

Potassium nitrate (AnalaR, BDH) and lithium nitrate (reagent grade, BDH) were dried at 150 °C for 24 hours, mixed to eutectic composition (43 mol% $LiNO_3$), evacuated to 0.01 Torr over 10 h and filtered at 180 °C through a No. 4 grade sinter in an oven. After solidification, the eutectic was broken up and stored in a dry box.

Magnesium sulphate trihydrate (May and Baker) was used as received ($13.4 \pm 0.2\%$ Mg, corresponding to $MgSO_4 \cdot 3.28H_2O$), and dehydrated in two stages (maximum rate 110 °C, ~ 2.7 H_2O; and 330 °C, ~ 0.6 H_2O) the overall loss up to 520 °C being $32.6 \pm 0.2\%$ (calculated for loss of 3.28 H_2O from $MgSO_4 \cdot 3.28H_2O$, 32.97%). The anhydrous sulphate ($19.3 \pm 0.2\%$ Mg; calculated for $MgSO_4$, 19.98%) was white and very soluble in water. Magnesium nitride (Alfa) ($71.6 \pm 0.6\%$ Mg; calculated for Mg_3N_2, 72.26%) was used as received, as was sodium hydroxide (AnalaR, BDH). Potassium dichromate (AnalaR, BDH) was dried at 110 °C for 2 h and potassium pyrosulphate was prepared by heating potassium persulphate (AnalaR, BDH) at 250 °C for 11 h (67.9% $S_2O_7^{2-}$ by NaOH titration; calculated for $K_2S_2O_7$, 69.2%).

Procedure

Qualitative reactions were carried out in Pyrex tubes closed with a silica gel drying tube and heated in an electric furnace fitted with an Ether Transitrol (type 1291B) temperature controller.

Thermogravimetry was carried out with a Stanton TR-1 thermobalance at a heating rate of 2° min^{-1}. The well-ground reactants and eutectic (3 g) were thoroughly mixed and contained in 10 ml silica crucibles, covered with a small glass funnel if reaction was violent. Weight losses are quoted as the percentage of the reactant, the average and standard deviation being for at least three determinations, and presented graphically as differential weight loss/temperature plots (hatched lines indicate isothermal conditions when $2° \equiv 1$ min).

Solubilities were determined from the visual disappearance of all solute crystals. Reaction products were determined by conventional qualitative and quantitative methods. X-ray powder diffraction was carried out with a Philips (Eindhoven) diffractometer using nickel-filtered Cu *Kα* radiation, *d* spacings and intensities being matched with those of known compounds from the JCPDS Index.

RESULTS AND DISCUSSION

Anhydrous magnesium sulphate has a very limited solubility in lithium nitrate–potassium nitrate eutectic and commences to react at 400 °C. The reaction is relatively slow even at 500 °C, but isothermal thermogravimetric analysis at this temperature for 11 h (Fig. 1(A)) gave a total weight loss of 90.0 ± 0.1%. The reacted melt after quenching and dissolving in water gave soluble sulphate and white insoluble magnesium oxide (Mg, 57.7%; calculated for MgO, Mg, 60.0%), indicating the reaction

$$MgSO_4 + 2NO_3^- \rightarrow MgO + SO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad (1)$$

(Calculated for loss of 2 N + 5 O per $MgSO_4$, 90.0%)

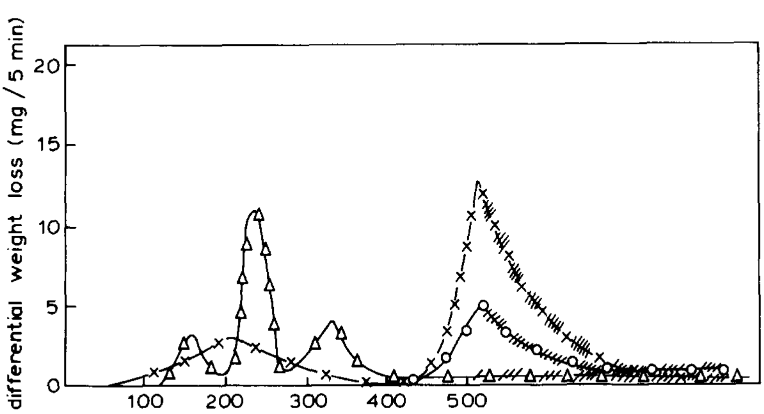

Fig. 1. Thermogravimetric analysis of magnesium sulphate in nitrate eutectic: (A), ○——○, 0.21 m $MgSO_4$; (B), ×——×, 0.27 m $MgSO_4 \cdot 3.28H_2O$; (C), △——△, 0.43 m $MgSO_4 \cdot 3.28H_2O + 1.85$ m K_2SO_4.

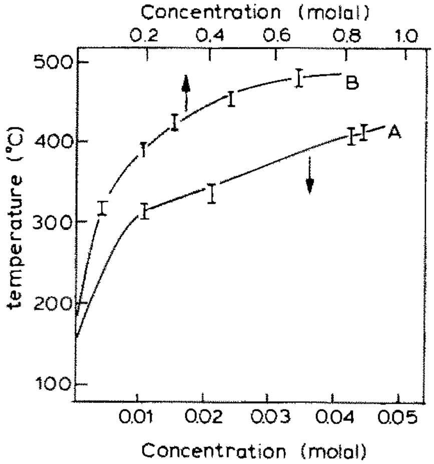

Fig. 2. Solubilities in nitrate eutectic: (A), magnesium sulphate (lower scale); (B), potassium sulphate (upper scale).

Magnesium sulphate trihydrate evolved water when dissolved in the eutectic from 70 °C, with quite a small amount of hydrolysis, the evolved water having a pH range of 1–2. The maximum rate of water loss was at 200 °C (Fig. 1, (B)), and the weight loss to the minimum at 400 °C was 33.8 ± 0.3% (calculated for loss of 3.28 H_2O per $MgSO_4 \cdot 3.28H_2O$, 32.9%), before the Lux–Flood acid–base reaction of eqn. (1) commenced at 440 °C with a weight loss of 61.4 ± 0.8% (calculated for loss of 2 N + 5 O per $MgSO_4 \cdot 3.28H_2O$, 60.3%), the water insoluble material analysing as 58.0 ± 0.7% magnesium.

The solubility of magnesium sulphate was determined at temperatures up to 400 °C, the salt initially being added as the trihydrate but dehydrating before measurement (Fig. 2(A)). The solubility is nearly an order of magnitude less than that of potassium sulphate (Fig. 2(B)), which is unexpected as the latent heat of fusion of the latter is three times that of the former while the melting points are similar, and must suggest that potassium cations enter the melt structure considerably more easily than those of the doubly charged magnesium.

Thermogravimetric analysis of hydrated magnesium sulphate with added potassium sulphate (molar ratio 1 : 4.3, Fig. 1(C)) caused the evolution of water to occur in three stages (approximately 0.5, 1.7 and 1.0 mol H_2O as temperature increased) with a total loss of 33.2%. However, no further weight loss maximum due to a Lux–Flood acid–base reaction (eqn. (1)) was observed, indicating stabilization of magnesium cations by coordination with sulphate, as has been observed for several first row transition metal cations in sulphate melts [6]. In contrast, added sodium hydroxide (ratio 1 : 6) caused more rapid precipitation of magnesium, X-ray powder diffraction of quenched melts heated to 450 °C indicating the presence of mag-

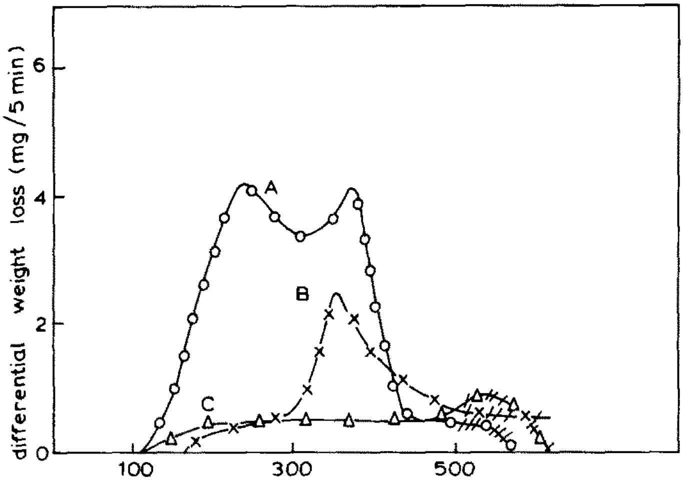

Fig. 3. Thermogravimetric analysis in basic nitrate eutectics: (A), o——o, 0.26 m $MgSO_4$ $3.28H_2O + 1.59$ m NaOH; (B), ×——×, 0.67 m $MgO + 3.10$ m NaOH; (C), △——△, 2.02 m NaOH.

nesium oxide with possibly a very small amount of magnesium hydroxide. Thermogravimetric analysis (Fig. 3(A)) showed weight loss over a broad range (120–500 ° C) with two incompletely separated maximum rates of loss at 260 ° and 375 ° C. The overall weight loss (43.0 ± 0.1%) corresponded well to the reaction

$$MgSO_4 \cdot 3.28H_2O + 2NaOH \rightarrow MgO + Na_2SO_4 + 4.28H_2O \qquad (2)$$

(calculated for loss of 4.28 H_2O per $MgSO_4 \cdot 3.28H_2O$, 43.0%)

The water of hydration probably began to be lost first, because the culminative weight loss to the minimum in the rate of loss at 320 ° C is very close to that calculated for the loss of 3.28 water molecules (33.0%), followed by acid–base reaction and precipitation of magnesium oxide (loss of H_2O per $MgSO_4 \cdot 3.28H_2O$, 10.0%), but for much of the temperature range both processes would be occurring together as the individual weight loss curves were not separated.

It is possible that magnesium hydroxide was the first product because thermogravimetric analysis showed that magnesium oxide in sodium hydroxide-containing melt (mole ratio 1 : 4.6) lost weight with a clear maximum in the rate of loss also at 375 ° C (Fig. 3(B)) whereas sodium hydroxide alone in the melt (Fig. 3(C)) showed no such maximum, which suggests interaction with the magnesium oxide (and possibly formation of magnesium hydroxide). The overall weight loss (20.5% of original NaOH; calculated for loss of $\frac{1}{2}$ H_2O per NaOH, 22.5%) indicated almost complete dehydration, but not of course, the intermediate stages. The final form of the white insoluble

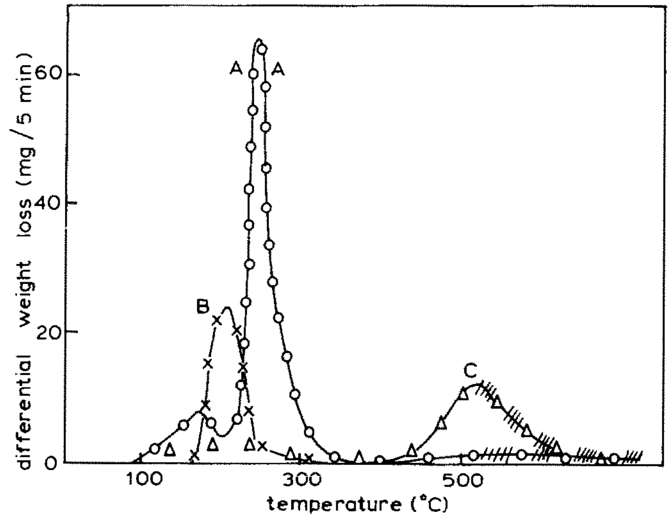

Fig. 4. Thermogravimetric analysis of magnesium sulphate in acidic nitrate melts: (A), o——o, 0.24 m $MgSO_4 \cdot 3.28\ H_2O + 0.63$ m $K_2S_2O_7$; (B), ×——×, 0.30 m $K_2S_2O_7$; (C), △——△, 0.27 m $MgSO_4 \cdot 3.28H_2O$.

magnesium product after water extraction and drying, was magnesium hydroxide ($41.3 \pm 0.2\%$ and $40.9 \pm 0.2\%$ Mg, respectively, from the above thermograms (calculated for $Mg(OH)_2$, 41.4% Mg), whereas magnesium oxide itself was not hydrolysed in water even after 1 h ($59.3 \pm 0.6\%$ Mg, calculated for MgO, 60.0% Mg). This again suggests some intermediate reaction.

Reaction of hydrated magnesium sulphate in melt containing added potassium pyrosulphate (ratio 1 : 0.4) showed three stages of weight loss (Fig. 4(A)), the first up to 200 °C (maximum at 170 °C, weight loss $30.6 \pm 0.4\%$) attributed largely to the evolution of water. The second, which overlaps the first but with a large maximum at 240 °C, is attributed to the loss of nitrogen dioxide and oxygen (weight loss from 200 ° to a minimum at 360 °C being $44.2 \pm 0.6\%$ of original $K_2S_2O_7$) due to the Lux–Flood acid–base reaction (see Fig. 4(B))

$$K_2S_2O_7 + 2NO_3^- \rightarrow 2SO_4^{2-} + 2K^+ + 2NO_2 + \tfrac{1}{2}O_2 \quad (3)$$

(calculated for loss of 2 N and 5 O per $K_2S_2O_7$, 42.0%)

The third weight loss from 400–500 °C ($13.6 \pm 3\%$) is considered to be the acid–base reaction of magnesium cations (eqn. (1)), although it is only about 15% complete because of the stabilizing effect of the sulphate ions produced (eqn. (3)), the concentration of sulphate and the extent of the reaction both being intermediate between those of (A) and (C) of Fig. 1.

Magnesium nitride was insoluble in the nitrate eutectic from 200–450 °C in that no soluble magnesium could be detected over this range. This is in

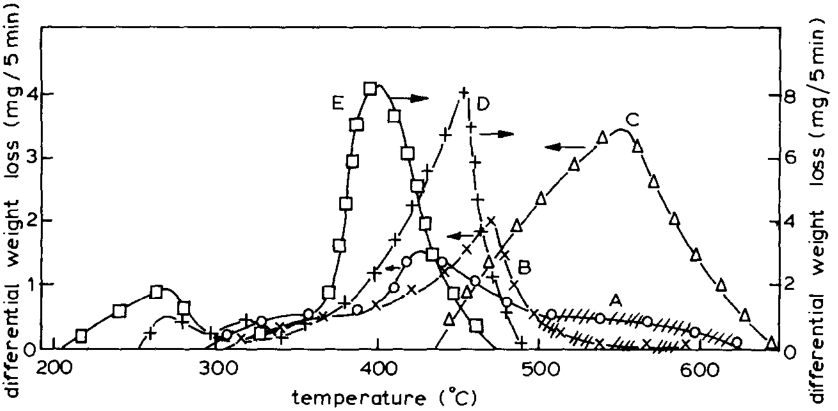

Fig. 5. Thermogravimetric analysis of magnesium nitride in neutral and basic nitrate eutectic: (A), ○———○, 0.45 m Mg_3N_2 (left hand side); (B), ×———×, 0.20 m Mg_3N_2 (left hand side); (C), △———△, 0.14 m Mg_3N_2 alone (no nitrate melt) (left hand side); (D), +———+, 0.28 m Mg_3N_2 + 1.23 m NaOH (right hand side); (E), □———□, 0.31 m Mg_3N_2 + 1.85 M NaOH (right hand side).

contrast to the ready solubility of nitrides (Li_3N and Ca_3N_2) in alkali metal chloride melts [7,8], where the nitrides were more soluble than the corresponding metal chlorides and where molten lithium salts were found to be the best solvents. The absence of apparent solubility in the nitrate eutectic may very well be due to surface reaction and formation of insoluble magnesium oxide, for thermogravimetry has shown a small and variable weight loss from about 300 °C (two examples are shown as (A) and (B) of Fig. 5). This rate of loss was in fact too small to give visual evidence of gas formation but the total weight loss varied between 15 and 25% in up to 10 h. X-ray powder diffraction of pale green quenched melts after this time showed the presence of magnesium oxide as well as magnesium nitride suggesting the reaction

$$Mg_3N_2 + 6NO_3^- \rightarrow 3MgO + 3O^{2-} + 6NO_2 + N_2 \qquad (4)$$

(calculated for loss of 8 N and 12 O per Mg_3N_2, 30.1%)

though evidently only a small proportion of the magnesium nitride reacted, a surface layer of magnesium oxide product probably protecting it to a considerable extent. Magnesium nitride oxidized in air, without nitrate melt (Fig. 5(C)), also to form the oxide (59.0% Mg), the reaction proceeding at a higher temperature but essentially completely (overall loss 19.7 ± 0.2%)

$$2Mg_3N_2 + 3O_2 \rightarrow 6MgO + 2N_2 \qquad (5)$$

(calculated for loss of 2 N and gain of 3 O per Mg_3N_2, 20.0%)

Thus the oxide layer is protecting over a limited temperature range only.

In basic melts containing added sodium hydroxide, magnesium nitride reacted considerably more readily but the temperatures of reaction and of maximum rates were still variable (Fig. 5(D) and (E) show typical results). Small amounts of magnesium were found in solution at 250 °C, increasing to 300 °C but decreasing to zero at 350 °C and probably attributable to magnesium hydroxide complex anions ($Mg(OH)_n^{(n-2)-}$). The final product of at least the soluble magnesium, however, was small amounts of magnesium oxide, as shown by X-ray diffraction of quenched samples, together with melt components and unreacted magnesium nitride. The overall weight losses (20.7 ± 0.7%) were close to complete dehydration of sodium hydroxide (calculated 22.5%) and gave no indication of the much larger weight losses expected if significant proportions of magnesium nitride had reacted, for example, by eqn. (6) followed by oxidation of the nitride anions as in eqn. (4)

$$Mg_3N_2 + 6NaOH \rightarrow 3MgO + 6Na^+ + 2N^{3-} + 3H_2O \qquad (6)$$

(calculated for loss of 3 H_2O per 6 NaOH, 22.5%)

or even if the magnesium nitride had reacted entirely as in eqn. (4).

In a strongly acidic melt (with added $K_2S_2O_7$), magnesium nitride reacted more completely, with a considerable amount of the soluble magnesium in the reacting melt from 160 °C, the soluble magnesium reaching a maximum at 200 °C, but still amounting to 38.3 ± 0.2% of the original magnesium nitride after thermogravimetric analysis (including 2 h at 505 °C), and 34.7 ± 0.3% of the original magnesium nitride added after 12 h at 400 °C. Thermogravimetry (Fig. 6(A)) showed that the very vigorous weight loss began at 160 °C (maximum rate 180 °C) which was very similar to the reaction of pyrosulphate alone in the melt (beginning at 150 °C, maximum rate at 200 °C, Fig. 6(B)) where the overall weight loss can be easily explained as a combination of the two reactions [9]

$$K_2S_2O_7 + NO_3^- \rightarrow 2SO_4^{2-} + 2K^+ + NO_2^+ \qquad (7)$$

$$NO_2^+ + NO_3^- \rightarrow [N_2O_5] \rightarrow 2NO_2 + \tfrac{1}{2}O_2 \qquad (8)$$

However, the nitryl cations produced by reaction (7) are considered to react with nitride

$$3NO_2^+ + N^{3-} \rightarrow 3NO_2 + \tfrac{1}{2}N_2 \qquad (9)$$

and the remaining excess magnesium nitride (over the $Mg_3N_2:6K_2S_2O_7$ ratio) reacting as in eqn. (4). (In the specific example of Fig. 6(A) 0.076 g Mg_3N_2 reacted with 1.140 g $K_2S_2O_7$ via eqn. (9) with a weight loss of 0.229 g, the remaining 0.050 g Mg_3N_2 reacting as eqn. (4) with a loss of 0.150 g. The overall calculated loss of 0.379 g compared to a 0.350 g weight loss found experimentally and eqn. (4) suggests 79% of the total magnesium will be precipitated as the oxide whereas 38.3 ± 0.2% soluble magnesium was found experimentally.)

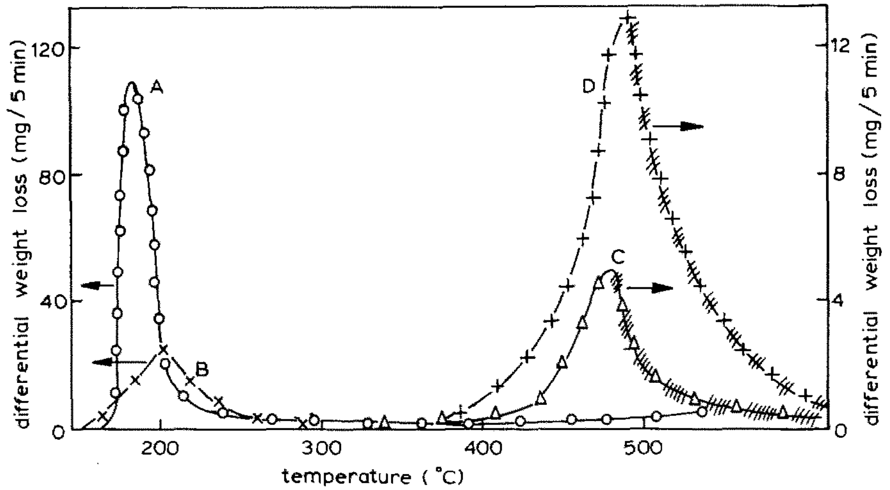

Fig. 6. Thermogravimetric analysis of magnesium nitride in acidic nitrate eutectic: (A), o——o, 0.35 m $MgN_2 + 1.24$ m $K_2S_2O_7$ (left hand side); (B), ×——×, 0.30 m $K_2S_2O_7$ (left hand side); (C), △——△, 0.23 m $Mg_3N_2 + 1.10$ m $K_2Cr_2O_7$ (right hand side); (D), +——+, 0.27 m $K_2Cr_2O_7$ (right hand side).

A similar sequence of reactions was thought to occur in weakly acidic melts, to which potassium dichromate had been added (Fig. 6(C) and (D)). In this specific example in which 0.106 g Mg_3N_2 reacted in nitrate melt containing 1.480 g $K_2Cr_2O_7$, 0.083 g Mg_3N_2 reacted as eqn. (9) with loss of 0.276 g of gas, and the remaining 0.023 g Mg_3N_2 reacted via eqn. (4) with loss of 0.069 g, indicating precipitation of 44% of original magnesium as MgO. The slightly higher experimental weight loss, 0.373 g, and lower soluble magnesium, 43.3 ± 0.5%, could both be attributed to some thermal decomposition of the nitrate melt

$$NO_3^- \rightarrow NO_2^- + \tfrac{1}{2}O_2 \qquad (10)$$

and the known higher basicity, and hence reactivity toward magnesium cations, of nitrite-containing melts. Subsequent Lux–Flood acid–base reaction of magnesium cations in the more acidic pyrosulphate solutions would be reduced by the cation complexation and stabilizing effects of the sulphate anions [6] produced in reaction (7), and possibly by the similar stabilizing effect of the chromate anions produced when the dichromate reacts.

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