

## **MOLTEN LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC. THE REACTION OF IRON(II) OXALATE AND BASIC NICKEL(II) CARBONATES**

N.A. CARTHEY, D.H. KERRIDGE and S.A. TARIQ \*

*Department of Chemistry, The University, Southampton SO9 5NH (Gt. Britain)*

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### **ABSTRACT**

Iron(II) oxalate reacted very differently when heated in the ternary carbonate eutectic than when heated alone. At the eutectic melting point free oxalate was found in solution which was considered to be formed by a partial anion exchange. The solid product initially formed was mainly magnetite ( $\text{Fe}_3\text{O}_4$ ) which was reduced to iron(II) oxide by  $590^\circ\text{C}$ , probably by reaction with oxalate, the excess of which also thermally decomposed. The final reaction up to  $800^\circ\text{C}$  resulted in the formation of insoluble lithium ferrate(III).

Three basic nickel(II) carbonates were found to lose carbon dioxide and water in carbonate eutectic at very much the same temperatures as when heated alone. The solid product (NiO) did, however, partially dissolve in the melt at  $420\text{--}500^\circ\text{C}$  on longer heating, to give stable yellow-orange solutions.

### **INTRODUCTION**

The chemistry of molten carbonate is becoming more systematised; a number of reactions of transition metal oxides and oxyanions have now been reported [1] as have those of several transition metal cations [2]. However, the latter have been combined with stable anions such as chloride and sulphate, which are known to act as ligands in other oxyanion melts (e.g.  $\text{Cl}^-$  with  $\text{Co}^{2+}$  [3] and  $\text{SO}_4^{2-}$  with  $\text{In}^{3+}$  [4], both in  $\text{LiNO}_3/\text{KNO}_3$  eutectic) with resulting stabilisation of the reacting cations. Thus it seemed desirable to study transition metal compounds where the anions would not act in this way. Ideally, transition metal carbonates would be considered, but since most of these are not readily obtainable in the pure state, anions thermally decomposing to carbonate could be used.

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\* Present address: Department of Inorganic and Analytical Chemistry, La Trobe University, Melbourne, Victoria, Australia.

As an initial investigation, the basic form of nickel(II) carbonate along with the more stoichiometric and easily available iron(II) oxalate were chosen for study, as representatives of these two possibilities. A great number of basic nickel(II) carbonates are known, many of which are hydrated, though the water is usually combined in at least two different ways [5]. In this study a commercially available form was chosen as well as one prepared by precipitation, which it has been suggested gave some evidence of being present as the orthocarbonate anion ( $\text{CO}_4^{4-}$ ) [6].

The thermal behaviour of these compounds is complex, basic nickel(II) carbonates losing carbon dioxide as well as water, sequentially and simultaneously, [5,7] while that of iron(II) oxalate has been the subject of a large number of studies, the most complete of which are at some points mutually conflicting [8–12]. Thus it seemed most desirable to establish the behaviour of these particular compounds on being heated alone under an atmosphere of carbon dioxide, as a preliminary for their study in lithium carbonate–sodium carbonate–potassium carbonate eutectic.

## EXPERIMENTAL

The ternary eutectic was prepared as described previously [1], as were the X-ray diffractometry and the thermogravimetric analyses, the weight losses being reported as a percentage of the original weight of transition metal reactant, all being carried out under flowing carbon dioxide ( $250 \text{ ml min}^{-1}$ ).

Iron(II) oxalate (BDH reagent grade) was heated at  $180^\circ\text{C}$  under nitrogen to constant weight, the loss being equivalent to that for  $2.04 \text{ H}_2\text{O}$ . Iron was analysed volumetrically with EDTA and both iron and oxalate by titration with permanganate. (Found: Fe, 37.1%;  $\text{C}_2\text{O}_4^{2-}$ , 56.4%. Calcd. for  $\text{FeC}_2\text{O}_4$ : Fe, 38.8%;  $\text{C}_2\text{O}_4^{2-}$ , 61.2%). Confirmation of the loss of water was given by the X-ray diffraction pattern [ $d$  values: 5.15(70), 3.95(100), 3.68(75), 2.87(15) and 2.40(50)] which were close to those given by Brown and Bevan [9] for the anhydrous oxalate [5.20(90), 3.95(100), 3.69(80), 2.85(40) and 2.40(90)] but unlike those for the dihydrate [4.95(100), 3.90(40), 3.10(70), 2.61(70), 2.11(50) and 1.88(40)]. Basic nickel(II) carbonate (Hopkins and Williams, quoted as  $\text{NiCO}_3 \cdot 2 \text{ Ni}(\text{OH})_2 \cdot 4 \text{ H}_2\text{O}$ ) was heated at  $105^\circ\text{C}$  to constant weight (losing the equivalent of  $1.99 \text{ H}_2\text{O}$ , i.e. 9.5%). Nickel was analysed by titration with EDTA. (Found: Ni, 51.2%. Calcd. for  $\text{NiCO}_3 \cdot 2 \text{ Ni}(\text{OH})_2 \cdot 2 \text{ H}_2\text{O}$ : Ni, 51.2%). A basic carbonate with different stoichiometry was made by the method of Gibbs [13] (adding  $\text{NiSO}_4$  to boiling  $\text{Na}_2\text{CO}_3$  solution). The product, which contained no sulphate, was analysed by EDTA titration, and by back titration with sodium hydroxide after solution in excess standard hydrochloric acid. [Found: Ni, 51.7%;  $\text{O}^{2-}$ , 14.3%. Calcd. for  $\text{NiCO}_3 \cdot \text{NiO} \cdot 2 \text{ H}_2\text{O}$ : Ni, 51.3%;  $\text{O}^{2-}$ , 14.0%. Calcd. for  $\text{NiCO}_3 \cdot \text{NiO}$  (the stoichiometry claimed): Ni, 60.7%;  $\text{O}^{2-}$ , 16.6%].

## RESULTS AND DISCUSSION

When heated alone on the thermobalance under a carbon dioxide atmosphere, the iron(II) oxalate (previously heated to constant weight at 180°C) lost weight slowly up to 280°C when the yellow powder changed to black. The total weight lost was slightly variable (2.0–3.3%) and was attributed to a slow decomposition reaction rather than to loss of tenaciously retained water. The main weight loss (see Fig. 1, curve A) was, however, from 280–470°C with a maximum rate of loss at 410°C. The total weight loss of 44.1% was close to that expected for the equation



By 470°C the colour of the solid product was still black, or a very dark brown, but on cooling under carbon dioxide it became a distinct red-brown. The X-ray diffraction  $d$  values of this product were 2.95(35), 2.51(100), 2.08(20), 1.60(25) and 1.47(40) [ASTM Index for  $\gamma$ - $\text{Fe}_2\text{O}_3$ ; 2.95(34), 2.51(100), 2.08(24), 1.61(33) and 1.48(53)], the change in colour on cooling probably being due to a narrowing or shift in the absorption band. This was not the product reported in previous studies, as both Brown and Bevan [9] and Macklen [10] found a mixture of magnetite and metallic iron which were considered to be the disproportionation products of the iron(II) oxide initially formed. However, formation of this oxide would have given rise to a

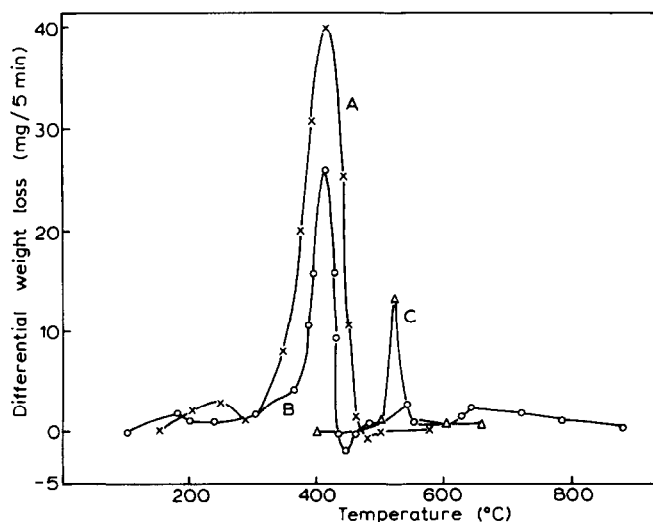


Fig. 1. Thermogravimetric analysis of iron(II) oxalate. Curve A,  $\times$ , 0.68 g  $\text{FeC}_2\text{O}_4$  alone; curve B, O, 0.45 m  $\text{FeC}_2\text{O}_4$  in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  eutectic; curve C,  $\Delta$ , 0.20 m  $\text{Na}_2\text{C}_2\text{O}_4$  in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  eutectic.

larger weight loss, that is a calculated value of 50% for the equation



(whether or not followed by the disproportionation  $4 \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$ ) and not the 60.07% incorrectly quoted by Macklen [10], who reported an experimental weight loss of 59–59.2% on heating this oxalate which is close to that expected for the dihydrate. Complete formation of magnetite ( $\text{Fe}_3\text{O}_4$ ) would have given a weight loss of 46.3%.



However, some iron may have been present, as its oxidation (or less likely that of FeO) would be the most obvious explanation of the small weight gain, at 470–500°C, of 1.5%.

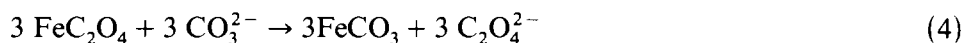
When comparing these findings with those of previously published work, it is interesting to note that Macklen [10] did report a slow weight loss from 200°C similar to that found here, followed by a more rapid loss from 300 to 430°C, with a maximum around 390°, both of which were attributed to thermal decomposition as dehydration had been found to occur at 140–200°C. Similarly, Ugai [8] found two exothermic peaks by DTA (that from 200 to 214°C being considered due to dehydration and that from 371 to 379°C to thermal decomposition) as did Brown and Bevan [9], though the latter only found one thermogravimetric peak (at 120–220°C) which they were compelled to attribute to both dehydration and decomposition occurring simultaneously, and accounted for the second exotherm by assuming a phase change in the magnetite.

Despite the complexities in fully understanding the thermal behaviour of iron(II) oxalate alone, and re-interpreting the numerous and somewhat conflicting studies reported, the main aim of the present investigation was to observe the differences when the oxalate was heated in the carbonate eutectic. A weight loss again began slowly (see Fig. 1, curve B), the solid mixture changing to a grey colour by 250°C. The rate of weight loss then increased considerably, reaching a maximum rate at 400°C, but then dropping abruptly to zero near the melting point of the eutectic when the surface became black. When the oxalate was heated alone, it was still showing a significant rate of weight loss at temperatures near the melting point of the eutectic. Qualitative analysis of reaction mixtures quenched at this stage showed the presence of oxalate anion and of soluble iron(II), while X-ray diffraction of the insoluble black magnetic material which also contained iron(II) [2.96(40), 2.55(100), 2.54(75), 2.52(85), 2.09(20), 1.61(40), 1.48(40)] indicated the presence of magnetite [ASTM Index for  $\text{Fe}_3\text{O}_4$ : 2.97(30), 2.53(100), 2.10(20), 1.61(85) and 1.48(85)] with a small amount of  $\gamma$ -iron(III) oxide.

However when heating was continued, further bubbling and formation of froth occurred from 450 to 550°C but at 590°C, the melt was again quiet.

The black insoluble material was now no longer magnetic and was shown to be largely iron(II) oxide by X-ray diffraction [2.53(30), 2.44(50), 2.12(100), and 1.50(40). ASTM Index for FeO; 2.48(80), 2.15(100), 1.56(60)]. Further increase in temperature caused a further reaction and the  $d$  values indicated the black, non-magnetic solid formed at 890°C was lithium ferrate (III) [2.40(30), 2.08(100), 1.47(40). ASTM Index for  $\alpha$ LiFeO<sub>2</sub>; 2.39(50), 2.07(100), 1.47(80)].

Thermogravimetric analysis showed that the weight loss associated with the initial slow reaction and the more rapid loss up to the melting point was, in total, an average of 39.4%, somewhat less than that expected from eqn. (1). This strengthened the conclusion that the thermal decomposition of iron(II) oxalate was different in the presence of carbonate eutectic. This had been suggested by the finding of oxalate anions and soluble iron(II), and of magnetite as the major solid product [which cannot have been formed directly as the experimental weight loss is even further from that expected for eqn. (3)]. The difference is considered to be caused by partial anion exchange and the subsequent decomposition of the postulated iron(II) carbonate in the manner previously found by Berg and Buzdov [14], i.e.



and

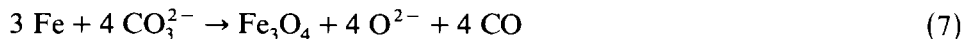


(Calcd. weight loss per FeC<sub>2</sub>O<sub>4</sub>, 26.4%) while the rest of the iron(II) oxalate thermally decomposes initially as eqn. (2) (gaseous oxidation is less rapid in a melt) but with immediate disproportionation (FeO is only stable above 570°C [15]).



(Calcd. weight loss per FeC<sub>2</sub>O<sub>4</sub>, 50.1%).

The small weight gain (Fig. 1, curve B) around 430°C, an average of 1.6%, is then attributed to oxidation of the metallic iron thus formed, i.e.



followed by an acid-base reaction at the melt surface, most likely with the carbon dioxide bubbles still trapped in the recently melted and still viscous eutectic, i.e.



This gives an overall calculated weight gain for eqns. (7) and (8) of 3.7% per FeC<sub>2</sub>O<sub>4</sub>. The lower temperature of this weight gain, by 40°C over curve A, suggests again that the course of the reactions is changed when eutectic is present.

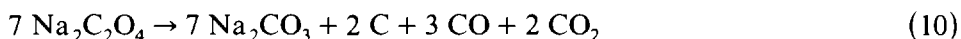
On heating to 500°C a further small weight loss occurred which caused the formation of black froth. It is considered that the gas evolved is formed

by reduction of magnetite with the oxalate anions in the melt solution, producing the iron(II) oxide found at 590°C, i.e.



(Calcd. weight loss per  $\text{FeC}_2\text{O}_4$ , for  $\text{Fe}_3\text{O}_4$  initially produced, via eqns. (4) and (5), or via eqns. (6) and (7), is 10.2%)

A separate investigation of the behaviour of sodium oxalate showed a darkening of the initially yellow solution as the temperature was raised above 425°C, the solution becoming black at 480°C. A vigorous release of gas produced a black froth at 515°C, which the thermogravimetric curve (Fig. 1, curve C) showed was the temperature of maximum rate of weight loss. The overall weight loss was 17.5% which supported the equation suggested by Scott [16].

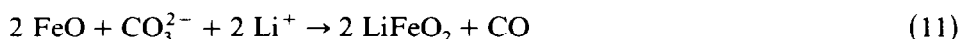


(Calcd. weight loss 18.3%)

Further support was given by the finding that heating magnetite (finely divided, and previously prepared from the reaction of  $\text{FeC}_2\text{O}_4$  with carbonate eutectic) with a solution of sodium oxalate in carbonate melt did produce some iron(II) oxide. However, it was once again found that of the  $d$  values not attributable to magnetite [i.e. 3.63(25), 3.28(25), 2.70(40), 2.45(25), and 2.10(50)], the latter two were somewhat intermediate between those of iron(II) oxide and those of  $\alpha$ -lithium ferrate(III), suggesting that at these temperatures some lithium and oxide ions may be entering the iron(II) oxide lattice. This reaction was carried out using a 0.2 m sodium oxalate solution with a 4:1 mole ratio (of  $\text{Na}_2\text{C}_2\text{O}_4$ : $\text{Fe}_3\text{O}_4$ ) at 600°C but when the same solution was held at 500°C for one hour, only the lines of magnetite were obtained.

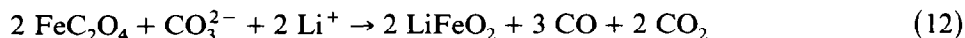
The average overall weight loss of iron(II) oxalate in carbonate melt heated to 570°C, where all the original iron was present as iron(II) oxide and the excess oxalate [over that needed for eqn. (9)] had decomposed as eqn. (10), was 49.8%. It would be expected to be close to, but slightly less than that for eqn. (2). Assuming the hypothesis of partial anion exchange is correct, it is possible to calculate from the first weight loss that, on average, 45% of the iron(II) oxalate reacts via eqns. (4) and (5) and 55% via eqns. (6)–(8), giving a calculated weight gain of 2.0% for the oxidation of metallic iron [eqn. (7)] as compared to the average experimental value of 1.6%, and an overall weight loss of 49.3%. In view of the many assumptions and inaccuracies, this agreement seems to offer reasonable support to the hypothesis.

By contrast the last weight loss, fairly slow from 570 to 880°C without a well marked maximum, seems clearly to be an oxidation plus a Lux–Flood acid-base reaction, i.e.



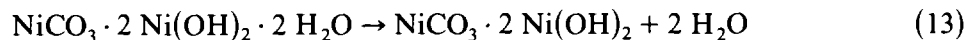
(Calcd. weight loss per  $\text{FeC}_2\text{O}_4$ , 9.7%)

as indicated by the solid product. In addition, the temperature range of reaction is close to those previously found (630 to 900°C) for the reaction of iron(II) and iron(III) chlorides with this carbonate melt, which also gave lithium ferrate(III). The experimental weight loss for this stage (average 12.0%) is higher than that calculated from eqn. (10) as was also found in the earlier work [2] when it was attributed to an accelerated melt decomposition. The overall weight loss, from room temperature, averages 65.0% and again, for the same reason, was somewhat above that expected for the overall reaction.



(Calcd. weight loss 59.7%)

Basic nickel(II) carbonate [BDH, after heating to constant weight at 105°C, was close to  $\text{NiCO}_3 \cdot 2 \text{Ni(OH)}_2 \cdot 2 \text{H}_2\text{O}$ ] lost weight from 100°C with a maximum rate near 220°C (Fig. 2, curve A). At the minimum near 290°C the weight loss was 10.8%, which is close to that expected for the loss of the two remaining water molecules.



(Calcd. weight loss 10.6%)

The green powder turned grey on increase of temperature and the weight loss became much more rapid up to a maximum at 380°C when it decreased even more rapidly to 450°C when the cumulative weight loss was 32.0%. A further slow loss occurred up to 800°C with a total loss of 35.8%, near to

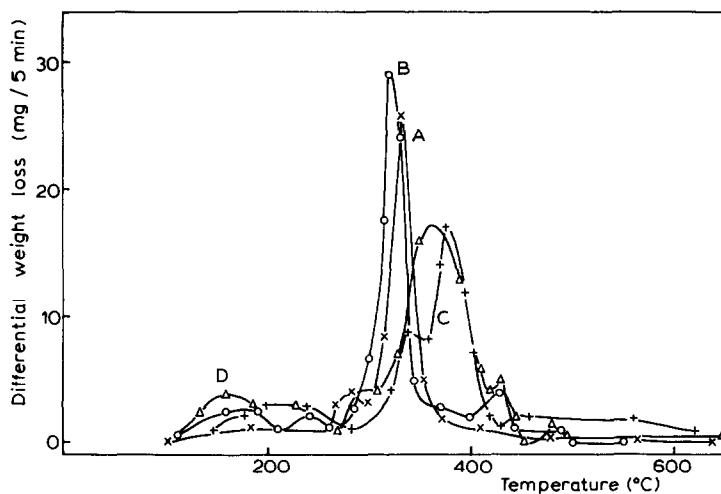
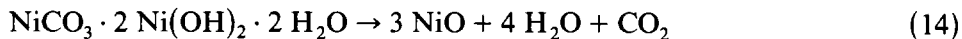


Fig. 2. Thermogravimetric analysis of basic nickel(II) carbonates. Curve A,  $\times$ , 0.37 g  $\text{NiCO}_3 \cdot 2 \text{Ni(OH)}_2 \cdot 2 \text{H}_2\text{O}$  alone; curve B,  $\circ$ , 0.39 m  $\text{NiCO}_3 \cdot 2 \text{Ni(OH)}_2 \cdot 2 \text{H}_2\text{O}$  in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  eutectic; curve C,  $+$ , 0.38 g  $\text{NiCO}_3 \cdot \text{NiO} \cdot 2 \text{H}_2\text{O}$  alone; curve D,  $\Delta$ , 0.78 m  $\text{NiCO}_3 \cdot \text{NiO} \cdot 2 \text{H}_2\text{O}$  in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$  eutectic.

that for the reaction



(Calcd. weight loss 34.1%)

During this loss the colour of the solid had become black, which slowly changed from 600°C onwards to green at 800°C, the black colour being due to non-stoichiometry (deficiency of Ni). Recrystallisation then slowly occurred establishing the stoichiometric ratio and forming the better known green oxide.

On heating in carbonate eutectic very little difference was detectable (Fig. 2, curve B), the weight losses being very similar (9.1% to the minimum at 270°C, 33.3% at 450°C and a total loss of 35.8% at 815°C) and the temperatures matching closely. Only the maximum at 480°C, which though small was very reproducible, indicated that some interaction with the melt was taking place. At this temperature the melt was black but at higher temperatures the oxide settled out and became more green in colour.

Very similar thermogravimetric curves were obtained with basic carbonate which had not been previously heated to constant weight, except that the experimental weight losses were proportionally larger. The temperatures of maxima and minima were also very similar except that the first minimum was not found when heating alone. (There was a smooth increase in the rate of loss up to the maximum at 375°C). However, when melt was present there was a clear minimum at 280°C [loss 20%; calcd. for loss of 4 H<sub>2</sub>O per NiCO<sub>3</sub> · 2 Ni(OH)<sub>2</sub> · 4 H<sub>2</sub>O, 19.2%].

Use of the other basic nickel(II) carbonate showed generally similar curves, (Fig. 2, curves C and D) except that the temperature of maximum rate of loss was lower, at 320–330°C. No support was found for the existence of NiCO<sub>3</sub> · NiO (or Ni<sub>2</sub>CO<sub>4</sub> as suggested by Duval [6]) as not only was this stoichiometry not the product of the preparation, it was not indicated by any change of slope in the thermogravimetric curve, the small minimum before the much faster rate of loss corresponding to a loss of 8.1% at 300°C when heated alone and 5.4% at 280°C in melt (calcd. for loss of 2 H<sub>2</sub>O per NiCO<sub>3</sub> · NiO · 2 H<sub>2</sub>O, 15.7%). As would be expected here, at temperatures well below the melting point of the eutectic, the curve was little altered by the presence of carbonate. However, a small maximum was observed at 430°C when the solution was black. The total weight losses, 28.4% at 640°C when heated alone and 27.9% at 550°C when heated with carbonate, were somewhat below that calculated (34.9% for loss of 2 H<sub>2</sub>O + CO<sub>2</sub> from NiCO<sub>3</sub> · NiO · 2 H<sub>2</sub>O). Clear evidence of interaction with the melt was a further reaction revealed by visual observation. When heated in glass, melts ten times more dilute in basic nickel(II) carbonate (e.g. ~ 0.04 m as compared to the ~ 0.4 m used in TGA) initially gave grey-black suspensions as loss of water and carbon dioxide occurred at 420°C but after 20 min took on an orange tinge becoming cloudy yellow after one hour, and at 500°C an



orange solution was formed, presumably more concentrated. These solutions did not change further with time, nor did it prove possible to persuade all the solid to dissolve. Addition of potassium chloride produced no visible colour change.

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