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Molten sodium nitrite–sodium nitrate–potassium nitrate eutectic: The reactions and spectra of iron(III), cobalt(II), nickel(II) and copper(II) compounds

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Abstract

In the sodium nitrite–sodium nitrate–potassium nitrate ternary eutectic, iron(III), cobalt(II) and nickel(II) chlorides were found to undergo Lux–Flood acid–base reactions to form their most stable oxides, which were insoluble, while copper(II) sulphate reacted to form a basic nitrate. The stoichiometry of the reactions in the presence of the competing basic anions was much more similar to those found in pure nitrite than in pure nitrate melts, but the oxidation of nitrite to nitrate, possibly via nitric oxide and nitrogen dioxide, was shown to be important.

The green solution of nickel(II) chloride had a spectrum which was much more similar to that in pure nitrite than in pure nitrate melts. Octahedral coordination by nitro, nitrito and nitrato ligands is suggested, in the ratio 2:1:3.

Keywords: Reactions; Spectra transition metal corrosion; Molten nitrite; Nitrate eutectic

1. Introduction

The academic study of molten salts has hitherto been directed very largely towards melts made of one anion, though frequently the melting point of the single salt has been lowered to a more acceptable value by forming a eutectic, using the salt of another cation with the same anion. Nevertheless, as eutectics formed from salts of more than one anion can have useful thermal properties and chemical applications, the question arises as to the chemical behaviour of such melts towards reactive solutes and how far their behaviour and reaction pathways follow those of melts containing only one of the component anions.

This question is also of importance for nominally pure melts containing impurities, and in the particular case of pure nitrate melts, when the impurity, consisting of nitrite, is inevitably generated by the thermal equilibrium

$$NO_3^- \Rightarrow NO_2^- + 1/2O_2 \qquad (1)$$

and is therefore always present, unless the nitrite impurity has been recently removed by a preferential reaction, e.g. Ref. [1], or more deliberately by treatment with nitrogen dioxide [2]. The importance of reaction (1) is further emphasised because evidence is steadily accummulating that the oxida-

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tion and basic reactions of nitrate melts are in fact to be attributed to the nitrite impurity, e.g. Ref. [1,3].

A more usual situation concerns melts where two, or more, anions have been deliberately mixed. For example, a recent paper concerning a eutectic, containing both nitrate and nitrite anions in approximately equal proportions [1], has shown that chromium compounds react largely with the nitrite and that the reaction temperatures are much closer to those found in pure nitrite melts than those for pure nitrate melts. Unexpectedly, the reverse of the thermal decomposition (Eq. (1)) was shown to be important in interpreting the reaction of the chromium(III) cation.

Strangely, this eutectic (sodium nitrite–sodium nitrate–potassium nitrate, containing 48.9, 6.9, and 44.2 mol% respectively, melting point 142°C), named Heat Transfer Salt (HTS) because it has been used for more than 40 years for both small-scale and large-scale industrial purposes, e.g. the cooling circuit of a catalytic oxidiser may contain 200 tonnes of HTS, has not hitherto been used systematically as a reactive solvent. The present paper extends the investigation of chromium compounds [1] to four other first-row transition metal compounds. Their reactions will be compared with those in melts made entirely from alkali metal nitrates and from alkali metal nitrites, the chemistry of which is comparitively well known and has been reviewed [4,5].

2. Experimental

2.1. Materials

The ternary sodium nitrite–sodium nitrate–potassium nitrate eutectic was prepared by taking appropriate quantities of the previously dried salts ($NaNO_2$ (BDH Technical) dried at 130°C for 30 h, $NaNO_3$ and KNO_3 (both BDH Analar) dried at 180°C for 24 h), mixing, melting and holding at 180°C for 4 h. The melt was then filtered through sintered glass (No. 4 grade) in an oven at 180°C. After solidification and storage in a desiccator, the melt was dehydrated, in batches, by evacuation on a rotary pump, the pressure being reduced gradually, using a needle valve to minimise bumping, then held at 10^{-2} torr for 10 h at 250°C.

Hydrated cobalt(II) and nickel(II) chlorides (BDH, Analar) were dehydrated by refluxing with thionyl chloride at 70°C for 4 h [6], decanted and then pumped to remove excess thionyl chloride, finally being heated to 200°C under a stream of dry oxygen-free nitrogen. (Found: Co, 45.12; Cl, 54.96; Calc. for $CoCl_2$: Co, 45.39; Cl, 54.61%. Found: Ni, 44.70; Cl, 54.29; Calc. for $NiCl_2$: Ni, 46.29; Cl, 54.71%). Hydrated copper(II) sulphate (BDH Analar) was heated under vacuum at 200°C for 4 h. (Found: Cu, 39.51; SO_4, 59.80; Calc. for $CuSO_4$: Cu, 39.82; SO_4, 60.18%). Iron(III) chloride (BDH, Analar) was used as received.

2.2. Methods

Reactions were carried out in Pyrex tubes under an air atmosphere, but closed with silica gel guard tubes, and heated in an electric furnace controlled with an RS CAL 9000 temperature controller and a step-down transformer.

Thermogravimetric analyses were carried out using a Stanton TR-1 thermobalance with 10-ml silica crucibles and a heating rate of 2°C min^{-1}. The results are reported as a percentage weight loss, calculated on the weight of the specified reactant, and graphically represented as the differential weight loss (mg per 5 min) against temperature (hatched lines indicate isothermal conditions, when 2°C equals 1 min).

Electronic absorption spectra were obtained with a Unicam SP-700 spectrophotometer modified with reversed optics from 4000–13000 cm^{-1} and with RF-heated cells.

3. Results and discussion

Iron(III) chloride was only slightly soluble in the eutectic at 160°C forming a faintly reddish-brown solution which slowly evolved brown nitrogen dioxide gas. Thermogravimetry showed weight loss occurred from 75°C (Fig. 1, curve A) with a maximum rate at 125°C which ceased at 275°C. A red-brown solid was formed in the melt, which after washing and drying, analysed as iron(III) oxide. (Found: Fe, 69.40%; calc, for Fe_2O_3, 69.9%). This material was amorphous to XRD, but after heating to 1000°C for two hours gave the diffraction lines for haematite: d_n values 3.697(30), 2.706(100), 2.524(71), 2.211(22), 1.844(31); JCPDS Index: 3.684(30), 2.700(100), 2.519(69), 2.292(3), 2.207(20), 1.840(39). The overall weight loss was 60.5 ± 1.6% and supports the suggested stoichiometry

$$2FeCl_3 + 8NO_2^- \rightarrow Fe_2O_3 + 6Cl^- + 2NO_3^- + 5NO + NO_2 \quad (2)$$

(Calc. for loss of $6N + 7O$ per $FeCl_3$, 60.4%.)

The temperature at which this reaction began, 45°C below the melting point of the eutectic, is typical of the higher Lux–Flood acidity of the oxidation state(III) cation, as compared to the oxidation state(II) cations whose reactions with melt are described below, and was also observed when iron(III) chloride reacted in a all-nitrate eutectic [7], although in the latter case two weight loss maxima were observed. The higher temperature one, at 175°C, was considered to be the result of the stabilisation of iron(III) cations by complexation with chloride anions. In the case of the ternary eutectic, nitrite anions may well be expected to be more effective ligands than either chloride, or the comparitively poorly coordinating nitrate, and may thus be responsible for the single weight loss maximum observed.

In an all-nitrite melt [8], reaction also began below the melting point, in fact at 130°C, some 90°C below the melting point of the sodium nitrite–potassium nitrite eutectic (m.p. 220°C), although the single maximum was in this case slightly above the melting point. Evidently there is a balance between ligand strength and concentration, together with the basicity of the melt. With both the all-nitrate and all-nitrite melts the solid product was iron(III) oxide as it was with the ternary eutectic.

Dark blue cobalt(II) chloride dissolved very quickly in the ternary melt at 150°C giving an opaque solution which became darker with increase in temperature, evolved brown nitrogen dioxide and formed insoluble black particles. Thermogravimetry (Fig. 1 curve B) showed weight loss to begin at 145°C, reaching a maximum rate at 230°C and decreasing to zero rate at 260°C. A small weight gain occurred from 280 to 490°C, while a second weight loss ensued above 580°C. The weight loss to 260°C was 41.8 ± 0.2%. The black precipitate formed in this reaction, after washing and drying, gave the X-ray diffraction lines of tricobalt tetroxide, the most stable oxide of cobalt: *d*-values, 2.84(42), 2.43(100), 2.02(37), 1.43(42); JCPDS Index, 2.86(40), 2.44(100), 2.02(25), 1.43(45). These observations suggest the stoichiometry

$$3CoCl_2 + 8NO_2^- \rightarrow Co_3O_4 + 6Cl^- + 2NO_3^- + 6NO \quad (3)$$

(Calc. for loss of $2N + 2O$ per $CoCl_2$, 46.2%.)

The somewhat lower experimental weight loss than that calculated is thought to result from oxidation of nitrite

$$NO_2^- + 1/2O_2 \rightarrow NO_3^- \quad (4)$$

This well-known thermal oxidation reaction has been shown to be an equilibrium, with the equilibrium composition, at these temperatures, being very much lower than the nitrite content of the ternary eutectic. This gain of oxygen reduces the size of the weight loss actually observed. No doubt it also occurs in the reaction with the all-nitrite melt [8] but in that case the experimental weight loss was adjusted for the formation of nitrate, whose amount was determined by analysis. No such analysis, or adjustment of weight loss, was possible in the present series of thermograms since the large nitrate concentration inherent in this ternary melt completely concealed any small increase in nitrate concentration due to reaction (3). Such nitrite oxidation may also have occurred in the iron(III) chloride reaction, for example if two nitrogen dioxide molecules had been produced in Eq. (2) then the calculated weight loss would have been 65.3%.

It should be pointed out that the increase in nitrate concentration in the pure nitrite melt was attributed to a different reaction

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \quad (5)$$

and it may well be that the presence of nitric oxide, and its ready oxidation by atmospheric oxygen to nitrogen dioxide, together with reaction (5), does facilitate ("catalyse") the attainment of reaction (4). This evidence for the importance of reaction (4) in nitrite-containing melts was unfortunately ob-

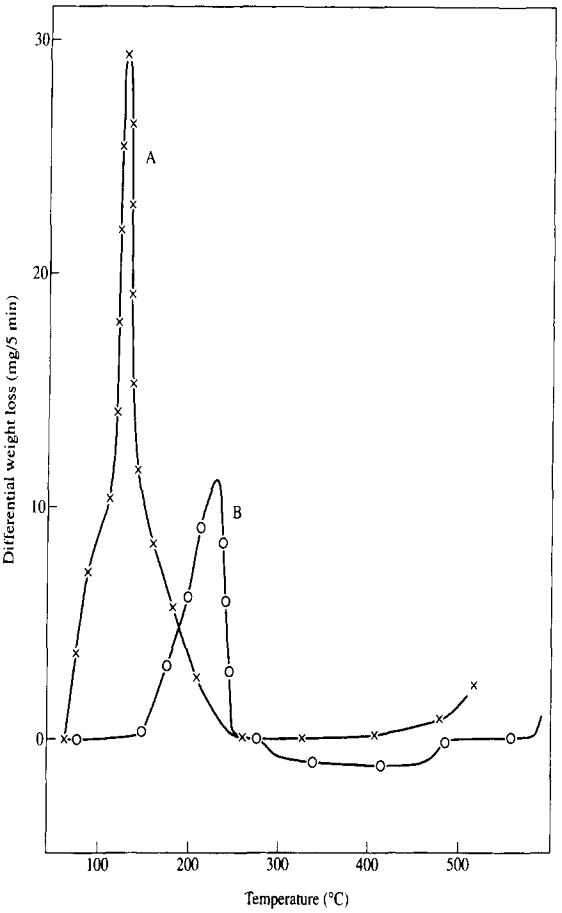

Fig. 1. Thermogravimetric analysis in sodium nitrite–sodium nitrate–potassium nitrate eutectic. Curve A, -x-x-x-, 0.60 m iron(III) chloride. Curve B, -o-o-o-, 0.27 m cobalt(II) chloride.

scured in the earlier work by the decision to correct for the formation of nitrate.

Again the temperature of this cobalt(II) chloride reaction is considerably more like that in an all-nitrite melt, i.e. beginning at 130°C, maximum at 275°C, [5] than that in an all-nitrate melt, i.e. beginning at 230°C, maximum at 380°C [9]. In all three melts the same tricobalt tetroxide was the solid reaction product.

Yellow nickel(II) chloride dissolved quickly in the ternary eutectic at 155°C to form a clear green solution which was stable for more than seven days. This solution had an absorption spectrum with three maxima, 9600 cm^{-1} (5 $M^{-1}cm^{-1}$), 16000 (8 $M^{-1}cm^{-1}$), and 23500 (40 $M^{-1}cm^{-1}$), which indicate octahedral coordination, and were thus attributed to the usual spin-allowed transitions: ν_1, $^3T_{2g} \leftarrow {}^3A_{2g}$; ν_2, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$; and ν_3, $^3T_{1g}(P) \leftarrow {}^3A_{2g}$. However, the band positions are much closer to those found in an all-nitrite melt, 10800 cm^{-1} (13 $M^{-1}cm^{-1}$), 17000 (14 $M^{-1}cm^{-1}$) and 22800 (23 $M^{-1}cm^{-1}$) [10], than those found in nitrate melt [11,12]. The coordination in nitrite melt had previously been suggested to be by both nitro ($-NO_2^-$) and nitrito ($-ONO^-$) ligands, in fact by equal numbers of nitrogen and oxygen ligands, i.e. $[Ni(NO_2)_3(ONO)_3]^{4-}$ [10].

In the case of nickel(II) in the ternary eutectic, the absorption bands agree most closely with coordination by all three potential ligands, nitro, nitrito and nitrato. Using Jorgensen's Rule of Average Environment [13], the v_1 band is matched most closely by coordination of two nitro, one nitrito and three nitrato ligands. Such mixed coordination would also explain the rather higher extinction coefficients found. The v_3 band was rather asymmetric, with less absorption on the higher energy side, as was found previously with nickel(II) [10] and also with chromate(VI) [14]. As in these cases this is attributed here to some limitation of the spectrometer on the high energy side by almost complete absorption in both sample and reference beams by the nitrite anion absorption at 27000 cm^{-1} [14].

On raising the temperature to 180°C, a slow reaction began which evolved brown fumes of nitrogen dioxide. Thermogravimetry (Fig. 2, curve A) showed that the maximum rate of gas evolution was reached at 240°C, while reaction ceased at 300°C, the total weight loss being 45.3 ± 2.0%. A dark grey precipitate formed in this reaction, which after washing with water and drying, gave the X-ray diffraction lines of nickel(II) oxide: *d*-values 2.09(100), 2.41(92), 1.48(52); JCPDS Index 2.09(100), 2.41(91), 1.48(57). The reaction stoichiometry suggested by this data is

$$\begin{aligned} NiCl_2 + 3NO_2^- &\rightarrow NiO + 2Cl^- \\ &+ NO_3^- + 2NO \qquad (6) \end{aligned}$$

(Calc. for loss of 2N + 2O per $NiCl_2$, 46.3%.)

Again the experimental weight loss was possibly less than the minimum calculated and is also considered to be due to oxidation of nitrite (Eq. (4))

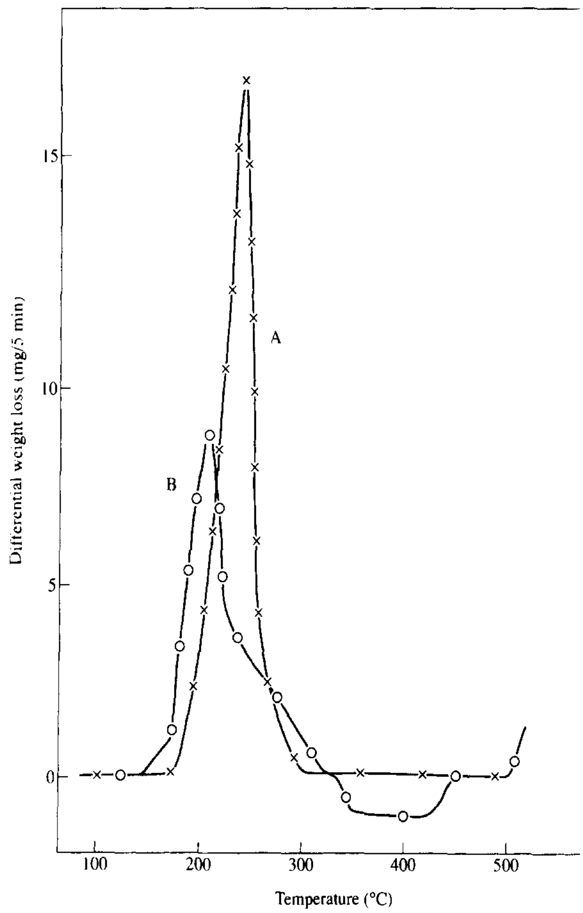

Fig. 2. Thermogravimetric analysis in sodium nitrite–sodium nitrate–potassium nitrate eutectic. Curve A, -x-x-x-, 0.26 m nickel(II) chloride. Curve B, -o-o-o-, 0.21 m copper(II) sulphate.

above. Once more the reaction temperature in the ternary melt is more similar to that in an all-nitrite melt (beginning at 280°C, maximum at 450°C [15]).

Copper(II) sulphate was very soluble in the ternary eutectic at 150°C forming a brownish-green solution; a small extent of reaction was also indicated by some black particles in suspension. The latter increased in quantity when the temperature was raised to 160°C and then also brown nitrogen dioxide was seen to be evolved. Thermogravimetry showed weight loss to begin at 150°C (Fig. 2, curve B) which reached a maximum rate at 200°C. The weight loss changed to a weight gain at 325°C until 450°C when a second weight loss became evident. The overall weight loss to 520°C was 28.9 ± 1.6%. The black precipitate was washed with distilled water until the filtrate gave no positive brown ring test for nitrate, then dried, dissolved in dilute hydrochloric acid and analysed, when a positive test was given for nitrate and the copper content suggested the black precipitate was a basic copper nitrate. Found: Cu, 50.75%; calc. for $\mathrm{CuO_{0.58}(NO_3)_{0.84}}$: Cu, 50.75%, or for $\mathrm{11CuO.8Cu(NO_3)_2}$: Cu, 50.8%. The stoichiometry suggested by these results is

$$\begin{aligned}&\mathrm{CuSO_4 + 1.16NO_2^- + 0.84NO_3^-}\\&\quad\mathrm{\rightarrow CuO_{0.58}(NO_3)_{0.84} + SO_4^{2-}}\\&\quad\mathrm{+\,0.58NO_2 + 0.58NO}\end{aligned}\qquad(7)$$

(Calc. for loss of 1.16N + 1.74O, 27.62%.)

It is evident that these results provide more evidence for the importance of the nitrite oxidation (reaction (4)). With this reactant, as with cobalt(II) chloride, thermogravimetry actually indicates a weight gain, in this case extending over a 100°C rise, while the experimental weight loss was smaller than the smallest that can be calculated on the basis of a Lux–Flood acid–base reaction. This again, as with each of the transition metal reactants studied here, illustrates the dominant nature of the nitrite oxidation (Eq. (4)). The temperature of the weight gain is also significant, for with copper(II) sulphate, as with cobalt(II) chloride, the thermograms show clearly that the weight gain occurs over a much lower temperature range than that found for the ternary melt without a transition metal solute. In the latter case, the gain is also over a 100°C range, but from 600 to 700°C, before again being reversed by the weight loss due to thermal decomposition of nitrate (Eq. (1)) and possibly also of nitrite.

The oxidation (weight gain) in the presence of transition metal solute is therefore evidently being catalysed, presumably or so by the surface of the transition metal oxide species being formed. Thus the cobalt and copper oxides (or copper oxide nitrate) appear to have the most effective surfaces for bringing about reaction (4). However, the lower than calculated weight losses also found with iron(III) and nickel(II) chloride solutes are probably also due to catalysis by their oxides, even though they are of sufficiently low activity that an actual gain was not observed. However all these catalytic reactions could be of economic significance in the industrial use of Heat Transfer Salt, e.g. as a coolant, when contained in steel, which could corrode to insoluble transition metal oxides on its surface.

In conclusion, it may also be said that with each of the reactants in the ternary eutectic, nitrite appears to be the source of the oxide ions, in preference to nitrate. The higher basicity of nitrite has, of course, been known quantitatively since the work of Kust and Burke [16], but the present results show that the preferential reaction of nitrite persists at least down to the almost 1:1 proportion of anions in the ternary eutectic. Such a preferential reaction may well also persist with lower proportions of nitrite and indicate at least part of the reason why so many molten nitrate reactions seem to be dependant on the impurity nitrite concentration, e.g. of iodate [17], and of chromium(III) chloride [15], this nitrite being always present from the thermal decomposition reaction (reverse of Eq. (4)).

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