# Investigation of some transition metal compounds in molten nitrate and nitrite eutectics

by

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# ABSTRACT

## FACULTY OF SCIENCE
## DEPARTMENT OF CHEMISTRY

## MASTER OF PHILOSOPHY

## Investigation of some transition metal compounds in molten nitrate and nitrite eutectics

**By**

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Investigations of reactions of various first and second-row transition metal compounds (of copper, cobalt, nickel, iron and zirconium) in molten nitrate (pure and basic) and molten nitrite eutectics were carried out and interpreted in terms of oxidation-reduction or acid-base behaviour.

In pure nitrate eutectic, (lithium nitrate-potassium nitrate) compounds of copper(II), cobalt(II), nickel(II) and iron(II) were found to give insoluble copper(II) oxide, cobalt(II & III) oxide, nickel(II) oxide and iron(III) oxide. However, in basic molten nitrate new compounds (probably with anionic species) with higher oxidation states have been formed. These basic solutions of melts tend to stabilise the higher oxidation states.

X-ray diffraction and quantitative chemical and thermogravimetric analysis proved the formation of these new compounds with higher oxidation states which contained cuprate(III), cobaltate(III), nickelate(III) and ferrate(III).

In the case of second-row transition metal zirconium(IV) compounds, in both molten nitrate (pure and basic) and molten nitrite, an insoluble gelatinous oxide was formed but with no change in the oxidation state (+4) despite the oxidising nature of molten nitrate and the strong basicity of molten nitrite. Oxidation beyond the (+4) state is extremely unlikely as this is the group valency of zirconium.

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# CHAPTER ONE

# INTRODUCTION

## 1.1 General

The chemistry of molten salts as non-aqueous solvent systems is one that has blossomed in recent years, due to the needs of high-temperature technologies, primarily those related to extractive metallurgy, molten salt breeder reactor development and reactor fuel reprocessing. The most obvious differences when compared with the chemistry of aqueous solutions are the strongly bonded and stable nature of the solvent, a concomitant resistance to destruction of the solvent by vigorous reactions and higher concentrations of various species, particularly coordinating anions, than can be obtained in saturated solutions in water. In addition to the high thermal stability, other attractive properties are the low vapour pressure, low viscosity, high electrical conductivity, wide usable temperature range and the high temperature which can usually be reached.

A brief survey of the past and present industrial applications of molten salts will be given. Thousands of years ago molten salts were used in the arts of glass making and pottery glazing, but the first scientific use was due to Sir Humphry Davy[1] who found that perfectly dried potassium hydroxide was a non-conductor, but could be rendered conductive if it was slightly moistened. On passing high current the hydroxide fused, and electrolysis of the melt resulted in the first production of metallic potassium. The early systematic scientific studies were carried out by Faraday[2], who established the fundamental laws of electrolysis and obtained the comparative electrochemical force series of the elements in molten salts. Since then, electrolytic processes have been developed for the production of large amounts of electropositive metals from their molten salts. An example is the extraction of aluminium from its bauxite ore[3], purified alumina ($Al_2O_3$) is electrolysed in molten cryolite ($Na_3AlF_6$) as solvent. Similarly sodium, magnesium, etc., are extracted from their fused salts by electrolysis.

The application of molten salts to nuclear technology was begun in the early 1940's in the United States to develop nuclear power initially for military and later for commercial use. Molten fluorides appeared particularly appropriate in this respect due to their high solubility for uranium, plutonium, cerium and many other radioactive rare earth metals[4,5,6], good heat transfer, low corrosive nature and stabilities as liquids at high but not impossible temperatures. In 1945, the first molten salt reactor of the Aircraft Reactor Experiment was operated successfully at temperatures up to 800°C using a fuel salt mixture of NaF, $ZrF_4$ and $UF_4$[7]. More recently the Molten Salt Reactor Experiment (M.S.R.E.) has successfully shown that a molten salt nuclear reactor can be operated for a number of years for the generation of electrical power using a fluid fuel of uranium fluoride, lithium fluoride, beryllium fluoride and zirconium fluoride at a temperature greater than 625°C.

Molten salts, due to their electrochemical properties, have been used as the electrolytes in fuel cells for the production of electric power. For example, one much studied type of high temperature fuel cell utilizes as the electrolyte a mixture of lithium, sodium and potassium carbonates[8].

In 1971 Angell[9] reviewed a number of developing areas for molten salts which include use of computer simulation to predict physico-chemical properties of organic melts, hydrate and solvate melts, particularly aquated salts, unusual oxidation states and polynuclear ions such as $Bi_9^{5+}$, and relaxation time and correlation time studies. The area of applications is also rich in possibilities, varying from the topical recovery of metals from nodule ores on the ocean floor (Kane, 1975)[10], to the gasification of domestic waste using molten sodium carbonate (Yosim, 1976)[11] and the low temperature decomposition of water using molten lithium nitrate and nitrite (Abraham, 1973)[12] for the production of hydrogen as a general fuel or "energy carrier".

## 1.2 Nature and Structure of Molten Salts

Bloom and Bockris (1959)[13] showed that the following information is necessary in order to define the structure of a molten salt:-

a. the type of entities present, i.e. ions, molecules, complex ions, etc.

b. the nature and effect of holes or vacancies present.

c. the type and distribution functions relating to the relative positions of structural entities and holes.

d. the nature of the bonds or interionic forces between the various entities in the melt.

The availability of the above information would suffice to define the structure of both simple salts as well as salt mixtures and a discussion of the nature of molten salts may profitably be considered in such terms, e.g. the distribution of holes or other forms of free volume is of fundamental importance to transport properties since without any free space in the liquid, transport processes would be difficult. Also, if distribution functions were available, it would be possible to calculate thermodynamic properties of the melt.

On fusion of the solid lattice, there is often a substantial increase in volume[14-16], the liquid state being characterised therefore by large voids. Thus some description of the structures of molten salts have been based on the free spaces between ions (sometimes described as holes) while others are based on the lattice properties of the clusters[17] (where clusters mean small close groups).

In an attempt to solve structural problems numerically rather than analytically, computers with large capacities have been used in conjunction with the Monte Carlo or molecular dynamics methods[18-20]. Some success in the reproduction of at least some of the equilibrium properties of ionic liquids by these approaches has been achieved. According to another approach, the structure of molten salts can be regarded as quasi-lattices, in which random distribution is possible only within the anionic or cationic partial lattice. Despite the high freezing points of molten salts, they have a wide temperature range in the molten state. The electrical conductivity of molten salts is often high due to the presence of large numbers of monatomic or polyatomic ions, which are able to move within the liquid structure. In consequence of this it would be expected that with increasing temperature, the conductances of molten salts and consequently ionic mobilities, would be raised due to increase in volume, while increasing pressure should cause a decrease in conductance, due to reduction in free volume with the consequent decrease in ionic mobilities. This has been found to be true as long as the composition and degree of ionization remains the same. Thus the conductance of liquid potassium iodide at 780°C falls from about 1.7 $\Omega^{-1}$ $cm^{-1}$ at 100 bar to only 1.1 $\Omega$ $cm^{-1}$ at 1000 bar[21]. However, the feebly ionized molten salt, mercuric iodide, becomes markedly more ionic with increasing pressure, because the equilibrium

$$2HgI_2 \rightleftharpoons HgI^+ + HgI_3^- \qquad \dots (1)$$

is increasingly displaced to the right hand side as the result of the contraction in volume attending the ionization reactions[22].

## 1.3 Acid-Base Theories

The concept of acids and bases has undergone numerous revisions and is still the subject of considerable controversy. Of several definitions which have been proposed for acids and bases, the following will be briefly discussed:

### 1.3.1. The Arrhenius Theory

Arrhenius[23] defined an acid as a hydrogen compound which ionizes in water to produce hydrogen ions, whereas a base is a hydroxyl compound which yields hydroxide ions in aqueous solution. The neutralization reaction between an acid and a base produces a salt and water only.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{BOH} \rightleftharpoons \underset{\text{salt}}{BA} + \underset{\text{water}}{H_2O} \qquad \dots (2)$$

The Arrhenius Theory of electrolytic dissociation placed the major emphasis on the role of water as an ionizing solvent. It was soon realised that much of the chemistry of non-aqueous solutions could be interpreted as acid-base phenomena but a broader definition was required to explain the chemistry of such solutions.

### 1.3.2. The Bronsted-Lowry Theory

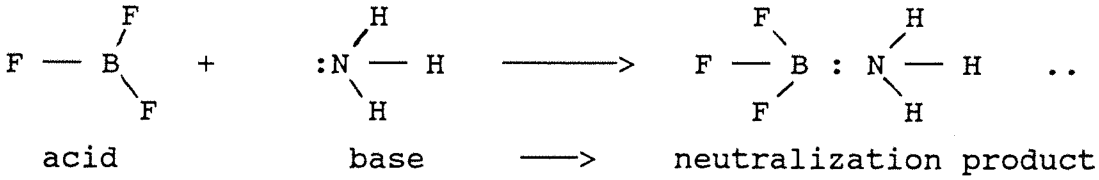
Bronsted[24] and Lowry[25] simultaneously proposed a more general theory of acids and bases which incorporates all protonic solvents, not just water. They defined an acid as a species which has a tendency to yield a proton and a base as a substance which can accept a proton.

$$\begin{array}{ccccccc} NH_3 & + & HCl & \rightleftharpoons & NH_4^+ & + & Cl^- \\ \text{base} & & \text{acid} & & \text{conj. acid} & & \text{conj. base} \end{array} \qquad \ldots (3)$$

Critics of the Bronsted-Lowry concept pointed out that only protonic substances were capable of losing protons and could thus be designated as acids and this explains why the theory was inapplicable to most molten salts.

### 1.3.3. The Lewis Theory

Lewis defined an acid as an electron pair acceptor and a base as the electron pair donor. Neutralization then is the formation of a coordinate covalent bond between the acid and the base.



.. (4)

This theory has been successfully applied to molten halides which, due to simplicity of their ionic structures, were amongst the first classes of ionic liquids studied, but it is not usually applied to molten nitrates, nitrites, sulphates, carbonates or phosphates.

### 1.3.4. The Lux-Flood Theory

Lux[26] and Flood[27], separately, but virtually simultaneously, defined acids as oxide acceptors and bases as oxide donors, i.e.

$$\text{Acid} + O^{2-} \rightleftharpoons \text{Base} \qquad \ldots (5)$$

For example:

$$Ca^{2+} + O^{2-} \longrightarrow CaO \qquad \ldots (6)$$

$$SO_3 + O^{2-} \longrightarrow SO_4^{2-} \qquad \ldots (7)$$

On the above basis, in the reaction between sodium metaphosphate and sodium carbonate observed in halide melts[28],

$$NaPO_3 + Na_2CO_3 \longrightarrow Na_3PO_4 + CO_2 \qquad \ldots (8)$$

metaphosphate is the acid and carbonate is the base.

In reaction with Lux-Flood acids, such as pyrosulphate or dichromate[29], nitrate ions act as Lux-Flood bases.

$$2NO_3^- + S_2O_7^{2-} \longrightarrow 2SO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots (9)$$

$$2NO_3^- + Cr_2O_7^{2-} \longrightarrow 2CrO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots (10)$$

However, the mechanism of reaction involved in acid-base dissociation of the nitrate ion has created a number of controversies. The main features of these and the actual acidic and basic species in molten nitrates are reviewed in the next two sections.

## 1.4 The Nature of the Acidic Species in Molten Nitrate

As a result of a series of kinetic[30-33] and e.m.f. studies[34-35], Duke <u>et al</u>. suggested the self-ionization scheme

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \qquad \ldots (11)$$

where K was $2.7 \times 10^{-26}$ at 250°C and $5.7 \times 10^{-24}$ at 300°C in equimolar $NaNO_3/KNO_3$ eutectic. The nitronium cation ($NO_2^+$) is thermally unstable, even though it is probably stabilized by ion-pair formation with nitrate ion:

$$NO_2^+ + NO_3^- \rightleftharpoons [NO_2^+ . NO_3^-] \longrightarrow 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots (12)$$

The concentration of nitryl or nitronium ion was markedly increased by the addition of Lux-Flood acids, such as potassium pyrosulphate, i.e.

$$S_2O_7^{2-} + NO_3^- \longrightarrow NO_2^+ + 2SO_4^{2-} \qquad \ldots (13)$$

where K was 7.2 x $10^{-3}$ at 250°C and 5.08 x $10^{-2}$ at 300°C. In support of this mechanism, addition of bromide to molten nitrate containing dichromate solution produced[30] gaseous nitrogen dioxide and bromine.

$$NO_2^+ + Br^- \longrightarrow [NO_2Br] \longrightarrow NO_2 + \tfrac{1}{2}Br_2 \qquad \ldots (14)$$

The above self ionization (eqn. 11) was, however, contested by Topol _et al_.[36] who, on the basis of their voltammetric and chronopotentiometric studies on solutions of acids and bases in $NaNO_3/KNO_3$ eutectic between 280°C and 350°C, did not find evidence for the existence of nitronium ion. They suggested instead that nitrogen dioxide was the actual acidic species in these solutions, and the non-reversible decomposition of the nitrate ion was:

$$2NO_3^- \longrightarrow 2NO_2 + \tfrac{1}{2}O_2 + O^{2-} \qquad \ldots (15)$$

or in presence of acids, such as pyrosulphate

$$S_2O_7^{2-} + 2NO_3^- \longrightarrow 2NO_2 + \tfrac{1}{2}O_2 + 2SO_4^{2-} \qquad \ldots (16)$$

However, Topol's proposal did not provide any explanation of the pathway by which the nitrogen dioxide was formed. This mechanism has been criticised[37] and subsequently became less popular.

In addition to the above proposals, Kerridge[38] has suggested that nitrogen dioxide can dimerise and the dimer further ionize (e.g. as it does in low temperature solvents of high dielectric constants) both unsymmetrically,

$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO^+ + NO_3^-$ ... (17)

and less readily, symmetrically,

$2NO_2 \rightleftharpoons N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$ ... (18)

though the concentration of the dimers at the melt temperature would be extremely small (and K of eqn. 11 is very small). If this idea is applicable to molten salts, the distinction between the Duke and the Topol hypotheses is not clear cut. However, Duke's hypothesis appears to be more helpful at the present time, because all acid-base reaction pathways can be more easily explained by postulating a nitryl ion ($NO_2^+$) than using nitrogen dioxide alone.

## 1.5 The Nature of the Basic Species in Molten Nitrate

Initially some workers, including Topol _et al_. and Duke _et al_., accepted the oxide ion ($O^{2-}$) as the Lux-Flood basic species in molten nitrates, but later Zambonin and Jordan[39-46] suggested that oxide was incapable of existence at appreciable concentration in fused nitrates. They have proposed that there was virtually complete oxidation of the oxide ion by nitrate, i.e.

$O^{2-} + NO_3^- \rightleftharpoons NO_2^- + O_2^{2-} \quad K \simeq 3$ ... (19)

and

$O_2^{2-} + 2NO_3^- \rightleftharpoons 2NO_2^- + 2O_2^- \quad K \simeq 6.5 \times 10^{-11}$ ... (20)

or by gaseous oxygen

$O_2 + O_2^{2-} \rightleftharpoons 2O_2^- \quad K \simeq 3.5 \times 10^5$ ... (21)

to peroxide ($O_2^{2-}$) and superoxide ($O_2^-$). They also suggested that peroxide and superoxide were the important oxyanionic species, interrelated by electron transfer and disproportionation equilibria,

$$O_2 \overset{e^-}{\rightleftharpoons} O_2^- \overset{e^-}{\rightleftharpoons} O_2^{2-} \qquad \ldots (22)$$

$$2O_2^- \rightleftharpoons O_2^{2-} + O_2 \qquad \ldots (23)$$

and pointed out that it was essential to remove water and perform reactions in silica-free melts since failure to do this would result in the existence of oxide species. For example, the above reactions suggest that in the presence of oxygen, superoxide would be produced which would oxidise nitrite to nitrate. In the presence of water, however, hydroxide would be produced.

$$O^{2-} + H_2O \rightleftharpoons 2OH^- \qquad \ldots (24)$$

$$O_2^{2-} + H_2O \rightleftharpoons 2OH^- + \tfrac{1}{2}O_2 \qquad \ldots (25)$$

$$2O_2^- + H_2O \rightleftharpoons 2OH^- + 3/2O_2 \qquad \ldots (26)$$

Many electrochemists who had used glass or silica vessels found the oxygen electrode to involve a two electron reaction and K for eqn. 24 to be small (e.g. $2 \times 10^{-2}$, Fredericks <u>et al.</u>[47]), but Zambonin and co-workers who used platinum containers found the oxygen electrode to involve one electron reaction and the value of K for eqn. 24 to be large (e.g. $10^{18}$).

In agreement with Zambonin, Schlegel[48] found that added oxide was oxidised at 229°C in molten equimolar $NaNO_3/KNO_3$ to a mixture of peroxide and superoxide, though predominantly to peroxide, and in oxygen the peroxide was converted almost exclusively to superoxide. However, the mechanism in $LiNO_3/KNO_3$ melt did not seem to be the same. It was also found that sodium peroxide ($Na_2O_2$) decomposed to give stable oxide ($O^{2-}$) between 250°C-370°C[49] which seemed to support Topol's and Duke's conclusions.

The situation becomes more complicated because of other claims that the basic species are in fact oxide combined with one or two nitrate ions. Kohlmuller[50], who studied molten alkali metal nitrates, claimed that orthonitrate ($NO_4^{3-}$) was formed, for example on the addition of sodium monoxide ($Na_2O$)

to molten sodium nitrate. Cryoscopic measurements could not distinguish compound formation[51] but more recently the hitherto unknown sodium orthonitrate ($Na_3NO_4$) has been claimed and studied by X-ray diffraction and Raman spectroscopy. It has been found to be chemically unstable[52-53]. Later, Shams El-Din and El-Hosary[54-55] claimed a further compound, oxide ion solvated with two nitrate ions. A stabilisation of the latter types can be represented by the general Lux-Flood acid-base equation (A is an oxide acceptor)

$$A + O^{2-} \rightleftharpoons AO^{2-} \qquad \ldots (27)$$

In a review, Burke and Kerridge[56] developed an evaluation of the way that the stabilisation of oxide ion by nitrate and other species can affect the concentration of the various anionic oxygen species ($O^{2-}$, $O_2^{2-}$ and $O_2^-$) in nitrate melts. They reported that the main species were the superoxide and the stabilised oxide, $AO^{2-}$, while the free oxide ion could only be in concentration of less than 0.001 per cent of the initial value. For this reason they suggested that the electrode reactions might be better written as

$$AO^{2-} \rightleftharpoons A + \tfrac{1}{2}O_2 + 2e^- \qquad \ldots (28)$$

Several workers explained the difference as due to the type of container used. The one electron slope behaviour is observed if platinum[57] or teflon[58] are used whereas the two electron behaviour is observed only if glass or silica containers are used. Therefore the latter reactions (27) and (28) can be represented as follows:

$$xSiO_2 + O^{2-} \rightleftharpoons (SiO_2)_x.O^{2-} \qquad \ldots (29)$$
$$(SiO_2)_x.O^{2-} \rightleftharpoons xSiO_2 + \tfrac{1}{2}O_2 + 2e^- \qquad \ldots (30)$$

Reaction with Y, a Lux-Flood acid, gives

$$Y + (SiO_2)_x.O^{2-} \rightleftharpoons YO^{2-} + xSiO_2 \qquad \ldots (31)$$

instead of eqn. 28, which would have been applicable if silica free vessels had been used.

In conclusion, it may be said that in both acidic and basic situations it is very difficult to draw absolute and firm conclusions as to the actual ions existing in nitrate melts, partly because of the lack of data from other kinds of evidence.

## 1.6 The Nature of the Acidic and Basic Species in Molten Nitrite

The species characteristic of, and actually present in, nitrite melts have been the subject of very little curiosity and no controversy comparable to that recorded earlier for nitrate melts.

It has been found that compounds which functioned as Lux-Flood acids (i.e. metal ions and condensed anions) in molten nitrates behaved in a very similar fashion in molten nitrites, and it had therefore been assumed by several authors that an ionization similar to that of equation (11) did exist in molten nitrites, and that possibly the concentrations of the acidic and basic species were rather larger than in molten nitrate.

However, the first quantitative work on the equilibrium

$$NO_2^- \rightleftharpoons NO^+ + O^{2-} \qquad \ldots(32)$$

has only been quoted very recently[130], the value of the equilibrium constant ($K_{32}$) being given as $1.3 \times 10^{-9}$ at 300°C, though so far no experimental details of this investigation have been published[83]. It has been assumed that the nitrosyl ion has a similarly short-lived existence (again probably as an ion-pair with a melt anion) as has the nitryl ion in nitrate melts, and would therefore decompose to form nitrogen dioxide and nitric oxide,

$$NO^+ + NO_2^- \rightleftharpoons [N_2O_3] \rightarrow NO_2 + NO \qquad \ldots(33)$$

The latter product has been frequently identified from melts held under vacuum or inert gas, though of course for melts in contact with oxygen the former product is the only one that can be isolated.

Although the authors quoted above, and many others, have made the simple assumption that oxide ions were the basic species in nitrite melts, Kohlmuller[50] has claimed the existence of the compounds $Na_3NO_3$ and $K_3NO_3$ (i.e. an oxide ion in combination with nitrite) though the evidence was only stronger than in the case of the corresponding nitrate compounds because the cryoscopic values (four ions per molecule in lithium nitrate solvent) did seem to rule out the possibility that the oxide ions were merely solvated.

## 1.7 Oxidation-Reduction Reactions

Oxidation-reduction (redox) reactions occur in many melts, and can be described in terms of the increase and decrease in the oxidation states of the relevant species. Nitrate melts are generally considered to be oxidising in nature, thus chromium (III) is oxidised to dichromate[59] and uranium (IV) to uranium (VI)[60] in molten nitrate systems. Conversely, thiocyanate melts are effective reducing agents, dichromate and iron (III) are reduced to chromium (III) and iron (II)[61] respectively, while copper (II) is reduced to copper (I) (this is the most stable oxidation state of copper in most melts,[62,63] although not in nitrate melts) with the production of parathiocyanogen.

Spink[59], Gruen[64] and co-workers have reported that a number of salts initially dissolve in nitrate melts, subsequently being oxidised either to anion species or to oxides. For example, Nb(IV), Cr(III) and Pu(III), after dissolving in nitrate melts are oxidised to anionic species, while Mn(II), Th(IV) and Ce(IV) have been found to be converted to insoluble oxides.

More research has been carried out on molten nitrates by several workers, often from the University of Southampton, to study oxidation-reduction reactions in basic melts and acid melts. It has been found that basic solutions tend to stabilise higher oxidation states (details and examples will be discussed in section 4.1), but in contrast the stability of low oxidation states is much improved in acidic molten salts, e.g. $MnO_2 \rightarrow Mn^{2+}$ in lithium nitrate-potassium nitrate + acid[37] (e.g. $K_2S_2O_7$).

Molten nitrite chemistry has shown both oxidising and reducing power. Acting as an oxidising agent, nitrite melt oxidised iron(II) to iron(III), chromium(III) to chromium(VI) and cobalt(II) to cobalt(III)[132,133]. On the other hand, nitrite ion has been found to act as a reducing agent, in the reaction between vanadium pentoxide and nitrite eutectic, here vanadium(IV) dioxide was produced[141].

Due to the basic nature of nitrite melts, examples of the stabilisation of high oxidation states are found, such as Mn(V) in sodium nitrite-potassium nitrite in the presence of sodium peroxide at 300°C and Fe(V) in sodium nitrite in the presence of sodium peroxide at 300°C[134].

## 1.8 Aims of the Present Investigation

Molten salts are a promising lower temperature route for precipitation of oxides, and are just beginning to be explored for the production of the precursor particles for conventional ceramics (e.g. of zirconia, by reaction in molten chlorides[65], fluorides[66], hydroxides[65] and nitrates[67]). In the present investigation the melt used is molten alkali metal nitrate (as the lower melting eutectic lithium nitrate-potassium nitrate, m.p. 132°C) because its chemistry is relatively well understood[38]. Metal oxides can be readily precipitated from oxyanion melts by oxide anions, either produced by dissociation of the melt itself which increases with increasing temperature,

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \qquad \ldots(34)$$

or by additions of melt solutions of alkali metal oxide, peroxide, hydroxide, carbonate, oxalate etc. Such solutions can also stabilise higher oxidation states of transition metals (e.g. Bi(V) in $LiNO_3/KNO_3 + Na_2O_2$ at 450°C).

Copper (III) is one of the components of superconducting ceramics (e.g. $YBa_2Cu_3O_{7-x}$, where $x = 0 - 0.5$), but problems have arisen in the production of pure submicron particles since surface impurities (aluminate or silicate) have been detected. These impurities have been considered to arise from regrinding using ball milling and resintering the ceramic in the course of homogenisation, and in the final sintering in oxygen to partially oxidise the copper from oxidation state (II) to (III).

Thus, the first aim of the present investigation was to study the conditions for the formation of copper (III) in the basic nitrate melts, since use of copper (III) oxide, or less desirably a copper (III) oxyanion, could reduce the sintering time/temperature by avoiding the present necessity of introducing additional oxygen into the ceramic during the final annealing to oxidise some Cu(II) to Cu(III). This may well be advantageous in minimising the formation of an impurity surface layer by avoiding the final sintering. In addition, if all the components of the superconducting ceramic could be precipitated from a single molten nitrate solution, as seems potentially possible, then ball milling and much sintering would be avoided.

The second aim was to study the oxidation-reduction reactions of some first-row transition metal compounds of iron, cobalt and nickel in basic nitrate melts, again with a view to investigating whether the additional stability of high oxidation states caused the formation of unusual products in basic nitrate melts.

The third aim was to investigate the reaction of compounds of the second-row transition metal zirconium in basic nitrate and pure nitrite melts.

# CHAPTER TWO

# EXPERIMENTAL

## 2.1 Introduction

Alkali metal nitrates are the most thoroughly investigated class of molten salts. This is due to the fact that they are available in a pure form at low cost, are stable over a reasonable temperature range with desirable physical properties, (i.e. they are colourless, have low volatility, and have a viscosity and surface tension similar to aqueous solutions) and above all, have conveniently low melting points (e.g. $LiNO_3$ 255°C, $NaNO_3$ 307°C and $KNO_3$ 334°C). Their binary eutectics have even lower melting points, e.g., $NaNO_3/KNO_3$ (50:50 mole %) 220°C, $LiNO_3/NaNO_3$ (54:46 mole %) 193°C and $LiNO_3/KNO_3$ (43:57 mole %) 132°C. These binary eutectics behave as oxidising agents as well as solvents with a long stable liquid range.

The use of alkali metal nitrates introduces a great variety of possible chemical reactions because they contain polyatomic anions. These include coordination, oxidation-reduction and sometimes acid-base reactions.

## 2.2 Preparation and Purification of the Melts

### 2.2.1. Lithium Nitrate-Potassium Nitrate Eutectic (m.p. 132°C)

Lithium nitrate trihydrate (B.D.H. General Purpose Reagent) and potassium nitrate (B.D.H. Analar) were heated separately in an oven at 180°C for 24 hours to dehydrate. Great care had to be taken with the low melting lithium nitrate trihydrate which tended to froth and run down the sides of the dish. The nitrates were allowed to cool in a desiccator, and were then weighed out to give a eutectic mixture of 43 mole % lithium nitrate (34.0 wt. %). 200-600 g batches of the melt were normally prepared. The mixture of the nitrates was melted at 180°C over the course of a few hours with occasional stirring. The melt was filtered to remove solid matter in a forced convection oven at approximately 180°C (Fig. 1) using a No. 4 porosity sintered filter with attached B24 drip cone in the top of a conical flask of appropriate size. A side arm of this flask terminated in a B7 cone which mated with a socket through an outlet in the oven roof. This technique achieved a rapid, very effective filtration while the temperature was held to within ± 5°C. After filtration, the melt was poured into a porcelain dish and allowed to cool in a desiccator. The frozen salt was broken into convenient lumps and stored in a dry box or desiccator.

### 2.2.2. Sodium Nitrite-Potassium Nitrite Eutectic (m.p. 220°C)

AnalaR sodium nitrite (BDH) and potassium nitrite (Hopkins and Williams GPR) were fired at 150°C for 30 hours in order to obtain both nitrites in an anhydrous condition.

The compounds were then mixed in the proper proportions to produce a eutectic of 35 mol % $KNO_2$. The crystalline mixture was melted over the course of a few hours in a forced convection oven at 270°C with occasional stirring and the small amount of solid matter in the melt was filtered off at ~270°C using the same technique mentioned above in the preparation of the nitrate melt.

## 2.3 Furnaces and Temperature Control

The furnaces used in all experiments consisted of an 8 cm deep steel pot with an inner diameter of 4 cm, wound with nichrome resistance wire, threaded with insulating refractory beads and embedded in alumina cement. The pot was held vertically in a square asbestos box, and the free space filled with "Micafil" as thermal insulation (Fig. 2). Such a furnace had a rating of about 1500watts and a temperature range of up to 800°C, depending upon the resistance wire and the number of windings.

The power supplied to the furnace was regulated by a "Variac" variable transformer, while the temperature was controlled and measured using an "Ether Electro Thermal Transitrol" or "RS 9000" fitted with a chromel-alumel thermocouple, which was located between the furnace and the test tube.

Figure 1. Apparatus for filtration of the melts

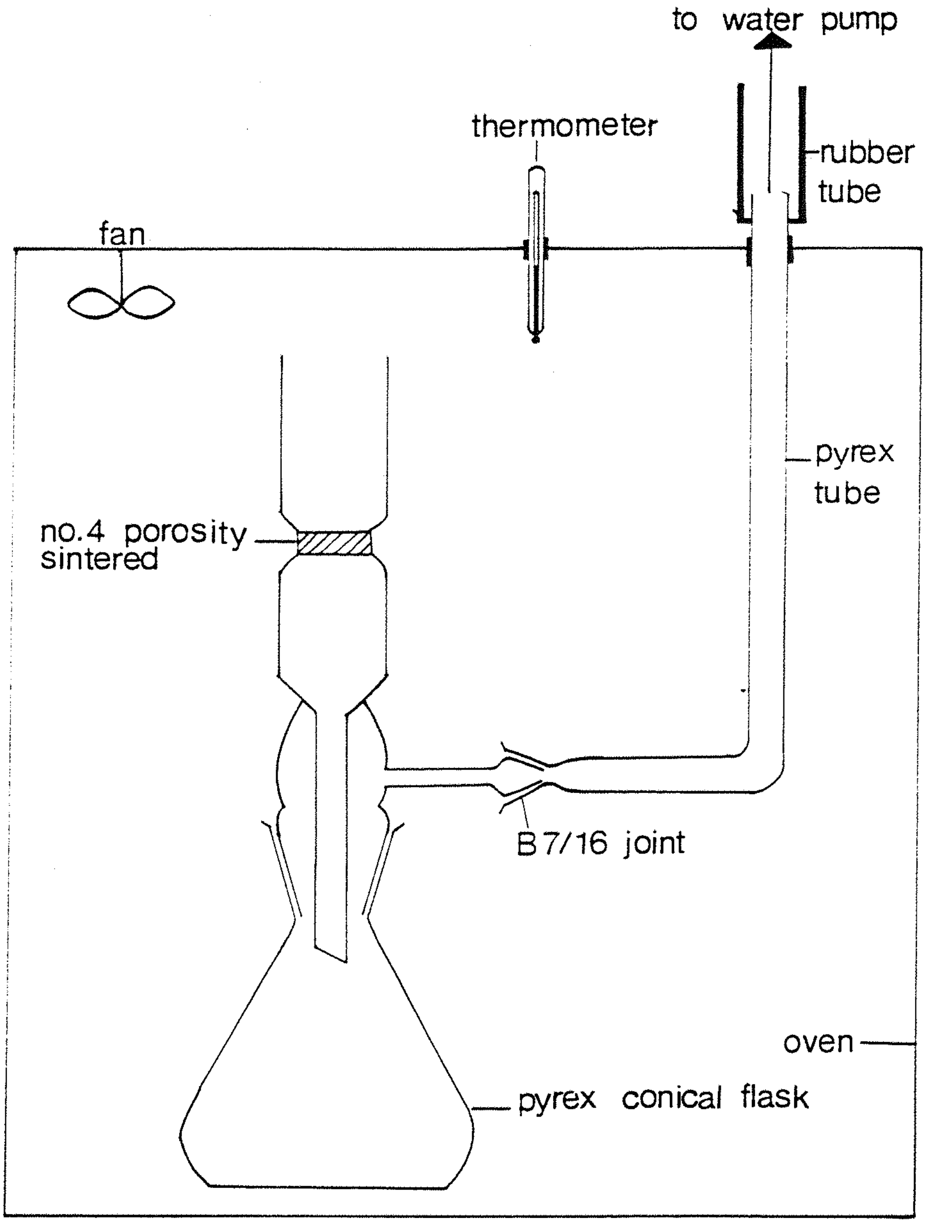
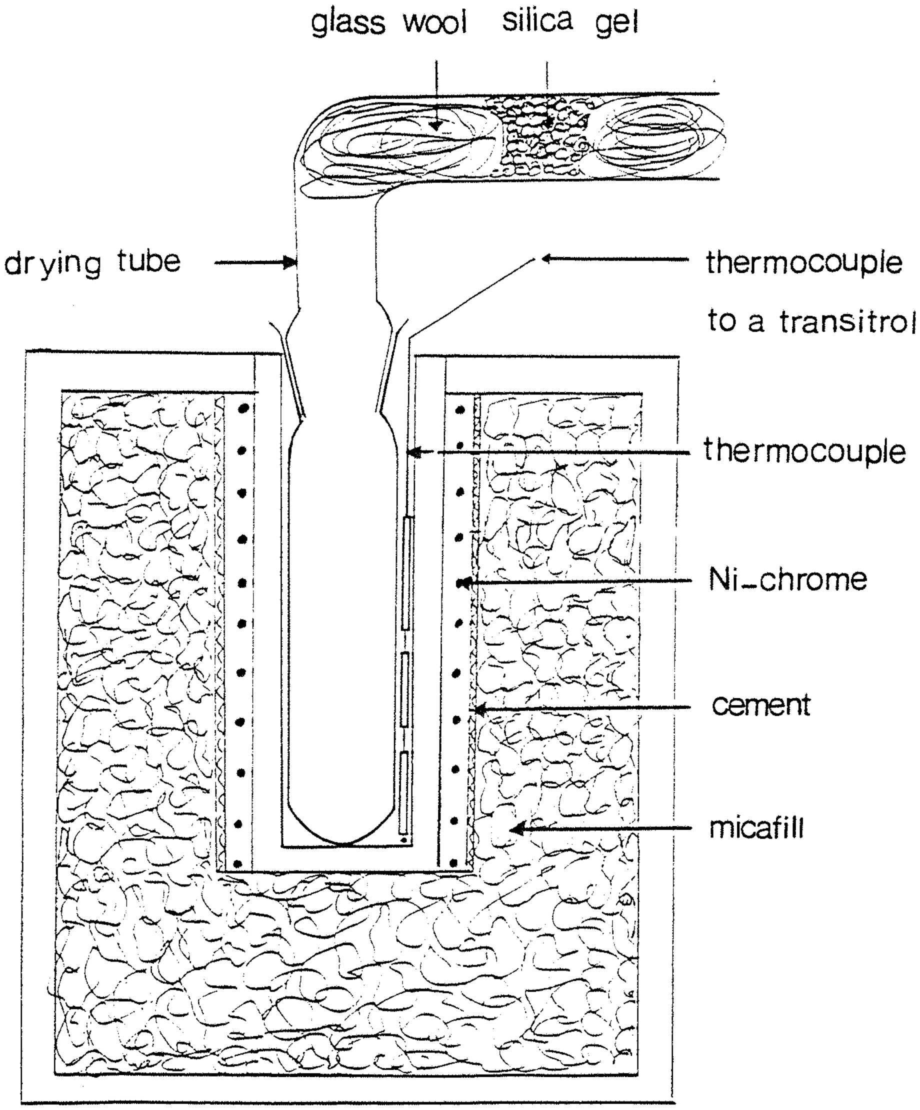


**Figure 2. Reaction apparatus**



## 2.4 Technique for Qualitative Study of Reactions

A B24 pyrex test tube was generally used as a reaction vessel. The contents were protected from humid air with a silica gel drying tube with glass wool plugs at both ends (Fig. 2). The soluble product(s) formed were identified by qualitative tests on small samples obtained by inserting a cool glass rod into the reaction melt, withdrawing the rod and sliding off the solidified melt. The amount of eutectic used for reaction was ~15g.

When the reaction was completed, or at an earlier suitable stage, the melt was quenched, ground, then dissolved either in water or in lithium hydroxide solution (3 wt. %). Any insoluble residue was dried either in an oven for ~15 mins. or washed with diethyl ether. The precipitate was analysed qualitatively and quantitatively while the filtrate was tested qualitatively.

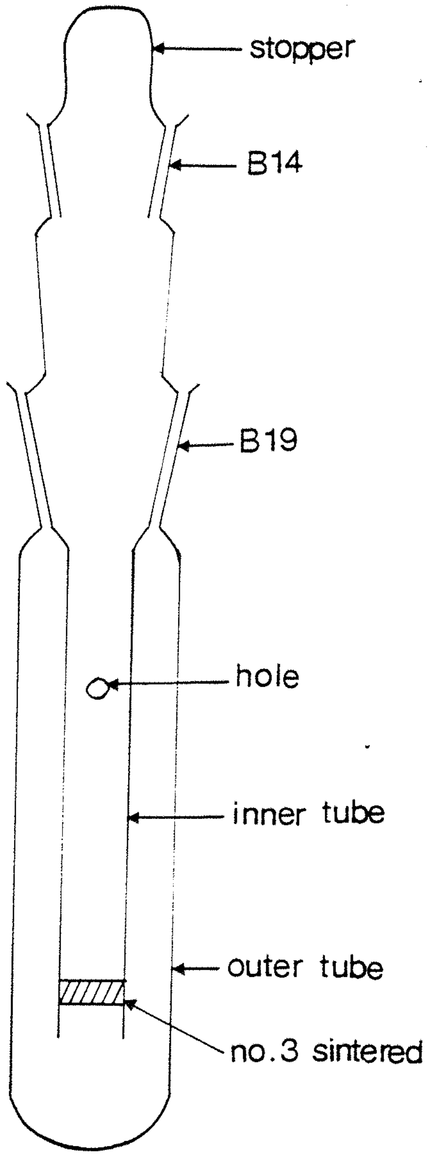
Two techniques were used for separating any precipitate present in the melt before freezing. The first was to filter off the precipitate in an oven using the apparatus shown in (Fig. 1). The second was to centrifuge off the precipitate in a specially adapted electric centrifuge MSE 10 with a maximum speed of 6000 r.p.m. used with the apparatus shown in (Fig. 3).

The furnace used in the centrifuge has similar specification, connections and temperature control as described in (2.3) except the depth was 12 cm and the inner diameter 2.5 cm.

## 2.5 X-Ray Diffraction

A Philips X-ray powder diffractometer was used to identify the reaction products. It consisted of a goniometer for measuring the diffraction angles and an X-ray counter with a system of electronic circuits for determination of the intensity of the diffracted beam at any angle ($\theta$). The apparatus recorded automatically the relative intensities of the peaks for the various values of $2\theta$. It was thus possible to calculate the d-spacings using Bragg relationship:

Figure 3. Apparatus for separation of the precipitate from the melt in the centrifuge



$\lambda = 2d \sin\theta$

The d-spacing and intensity values for the peaks were compared with those found in the American Society for Testing of Material[68] (A.S.T.M.) index whose title has recently been changed to the Joint Committee on Powder Diffraction Standards[69] (J.C.P.D.S.).

### 2.6 Analysis

### 2.6.1. Qualitative

Species formed in the melt solution, precipitates or filtrates were identified as follows:

1. Nitrate

(a) About 10 drops of Nitron reagent[70] were added to the aqueous solution (normally 3 ml). Appearance of a white crystalline precipitate indicated the presence of nitrate.

(b) 3 ml of the aqueous solution were carefully poured down the side of a test-tube containing 3 ml of diphenylamine reagent[71], so that the former was a layer above the solution of the reagent. A blue ring formed at the zone of contact of the two liquids and indicated the presence of nitrate.

(c) 3 ml of a freshly prepared saturated solution of ferrous sulphate were added to 2 ml of the aqueous solution, then 3-5 ml of concentrated sulphuric acid was slowly poured down the side of the test-tube so that the acid formed a layer beneath the mixture. A brown ring[72] formed where the liquids met, indicating the presence of nitrate.

To measure the sensitivity of these tests a 2.3548 M standard stock aqueous solution of lithium nitrate-potassium nitrate was prepared. Five more solutions were made by successive ten-fold dilution of the standard solution. At each stage these six solutions were tested qualitatively. The results of these tests are shown in (Table -1); the blue ring

test was the most specific and sensitive.
Sensitivity: 0.06 mg Concentration limit: 1 in 50,000.

2. Oxidising Agents

1 ml of concentrated hydrochloric acid and 2 ml of manganous chloride reagent[73] (consists of saturated solution of manganous chloride, $MnCl_2.4H_2O$ in concentrated hydrochloric acid) were added to 2 ml of the prepared solution. A dark brown or black colouration indicated the presence of a strong oxidising agent (e.g. nitrate, nitrite, ferricyanide, chlorate, bromate, iodate, chromate or permanganate) and a greenish-brown colouration by a mild oxidising agent. In this work, it has been found that 0.05 g or less of nitrate gives a negative result with manganous chloride reagent.

3. Peroxide

Approximately 3-5 ml of titanic sulphate solution ($Ti(SO_4)_2$)[74] was added to 3 ml of the solution to be tested, and made slightly acidic. The presence of peroxide ion is indicated by an orange-red colouration (yellow if very dilute).

4. Oxide

Phenolphthalein reagent was used to detect oxide. The prepared oxide ion solution gave a purple colouration with phenolphthalein reagent.

5. Lithium

Approximately 0.5 g of the substance was placed on a watchglass and was moistened with 2 ml concentrated hydrochloric acid. 10 mg of this mixture was placed on a clean nichrome or platinum wire into the base of a non-luminous Bunsen flame. A carmine-red flame indicated the presence of lithium.

Table 1: Qualitative tests for nitrate in aqueous solution

| Solution No | Molarity of $LiNO_3/KNO_3$ aqueous soln | $g.NO_3^-/3$ ml | white ppt ↓ Nitron Reagent | Blue ring test diphenylamine Reagent | Brown ring test ferrous sulphate + Conc. sulphuric acid |
|---|---|---|---|---|---|
| 1 | 2.3548 | 0.6162 | + | + | + |
| 2 | 0.23548 | 0.06162 | + | + | + |
| 3 | 0.023548 | 0.006162 | + | + | + |
| 4 | 0.0023548 | 0.0006162 | - | + | - |
| 5 | 0.00023548 | 0.00006162 | - | + | - |
| 6 | 0.000023548 | 0.000006162 | - | - | - |

6. Cobalt II

When excess of sodium hydroxide solution was added to the prepared solution a blue coloured precipitate indicated the presence of cobalt II. Upon warming with excess of sodium hydroxide solution the precipitate dissolved to give a pink solution (cobalt II hydroxide) confirming the presence of cobalt II. The cobalt II hydroxide initially formed was oxidised to brownish-black cobalt III hydroxide on exposure to the air, or by prolonged boiling of the aqueous suspension[75].

7. Copper (II)

When 3 drops of concentrated ammonium hydroxide were added to the prepared solution, a characteristic dark-blue coloured[76] solution was formed, indicating the presence of copper (II).

### 2.6.2. Quantitative

1. Dehydration of Copper II sulphate pentahydrate

Among the several published studies, Duval[77] showed that hydrated copper sulphate gradually lost 4 molecules of water from 67°C to 153°C (these molecules coordinated to the copper cation). The residual monohydrated salt then commenced losing the remaining water molecule at around 250°C. However, other workers[78] have reported that the transition from five to three molecules of water occurs at 30°C to 38°C, from $3H_2O$ to $1H_2O$ between 68°C and 74°C and from monohydrate to the anhydrous salt at 200°C to 220°C[80].

The dehydration of B.D.H. Analar $CuSO_4.5H_2O$ was carried out in an oven (230°C - 240°C) for three hours obtaining a grey coloured anhydrous copper sulphate ($CuSO_4$), the latter dissolved completely in water to a clear blue solution.

Thermogravimetric analysis was carried out on copper sulphate pentahydrate, and showed no further weight loss after 303°C (Fig. 4).

Wt. loss found = 35.81%

Wt. loss calculated for loss of $5H_2O$ per $CuSO_4.5H_2O$ = 36.05%.

2. Determination of Copper using 0.05 M ethylenediaminetetra-acetic acid (EDTA) and Fast Sulphon Black F (FSBF) as an indicator.

25.0 ml of copper solution (cupric sulphate pentahydrate[79]) was diluted with an equal volume of water, 5 ml of concentrated ammonia solution and 5 drops of FSBF indicator solution were added and the whole titrated with 0.05 M EDTA until the colour changed from blue to dark green.

Calculation: 1 ml of 0.05 M EDTA = 3.177 mg Cu.

Quantitative analysis of copper sulphate penta-hydrate gave 25.70% Cu, (Calculated percentage for $CuSO_4.5H_2O$ = 25.46%).

3. Determination of copper using 0.1 M sodium thiosulphate.

25.0 ml of copper solution (cupric sulphate pentahydrate[80]) was adjusted to a pH of 4-5.5 by adding a few drops of dilute sodium carbonate until a faint permanent precipitate remained, which was removed by means of a drop or two of acetic acid. 10 ml of a 10% potassium iodide solution was added and the librated iodine titrated with standard 0.1 M sodium thiosulphate until the brown colour of the iodine faded, when 2 ml of starch solution was added and the addition of the thiosulphate solution continued until the blue colour commenced to fade. 1 g of ammonium thiocyanate was then added to intensify the blue colour, and the titration was completed as quickly as possible. A pale flesh-coloured precipitate indicated the endpoint.

The reaction written in molecular form is:

$$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4 \qquad \ldots (35)$$

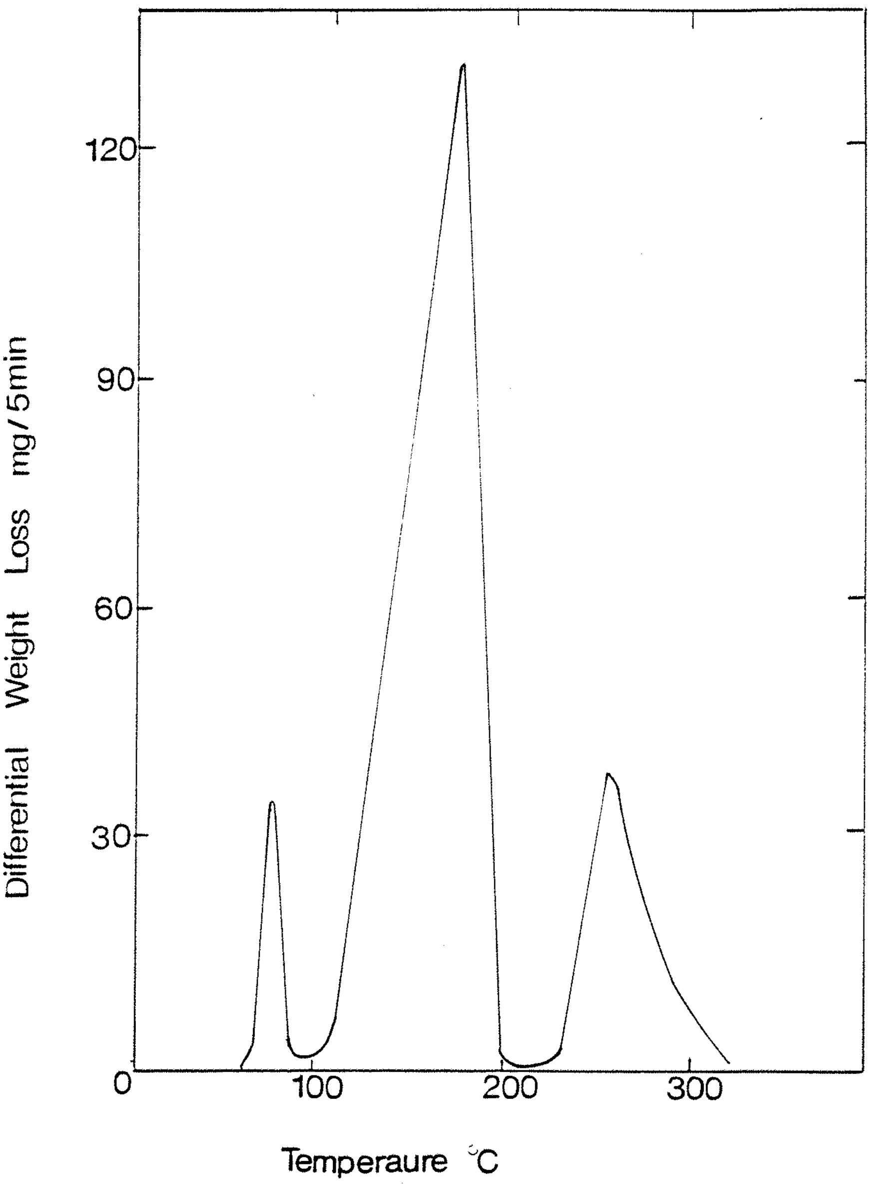
from which it follows that:

$$2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3$$

Calculation: 1 ml of 0.1 M $Na_2S_2O_3$ = 0.006354 g Cu.

Quantitative analysis of copper sulphate pentahydrate gave 25.85% (Calculated percentage for $CuSO_4.5H_2O$ = 25.46%).

Figure 4. Thermogravimetric analysis of $CuSo_4.5H_2O$



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## 4. Colorimetric determination of copper with ammonia.

The determination of copper, which depends upon the production of the intense blue colour of the cupric ammonia complex when ammonia is added to a solution of a cupric salt, is one of the oldest colorimetric methods[81].

A standard stock solution of cupric sulphate pentahydrate, each millilitre of which contained 4 mg of copper, was made by dissolving 15.7160 grams of cupric sulphate pentahydrate in distilled water, adding 1 ml of concentrated sulphuric acid, and accurately diluting to 1 litre.

To produce the colour, 5 ml of the standard copper solution in a 100 ml volumetric flask were just neutralised (pH ~6) with 15 M ammonium hydroxide, then diluted to the mark with 3 M ammonium hydroxide[82], and thoroughly shaken.

Spectral transmission curves were determined for a solution thickness of 1 cm and a spectral band width of 10 $m\mu$. Compensation for the absorption of the glass cell and solvent was obtained by placing in the reference beam of light a similar cell filled with 3 M ammonium hydroxide.

The absorbancies at 620 $m\mu$ for five solutions, containing 40, 80, 120, 400 and 600 p.p.m. of copper in 3 M ammonium hydroxide were measured with a Shimadzu double-beam spectrophotometer UV-190, and were plotted against the respective concentrations. A straight line was obtained (Fig. 5), showing that Beer's law was obeyed. This calibration curve was used to determine the percentage of copper in other samples.

## 5. Zirconium sulphate

Although the literature contains several methods[135,136,137] for the preparation of anhydrous zirconium sulphate, the method proposed by Bear[137] was chosen because of the good results obtained. The method consisted of heating zirconium sulphate tetrahydrate with sulphuric acid (AnalaR grade 98%) and igniting at temperatures between 350 and 450°C for 7 hours.

This sulphuric acid treatment and ignition were repeated, producing a well-crystallised material which was the $\alpha$-form. Alternatively, the tetrahydrate could be dehydrated by heating, but the process gave a non-stoichiometric zirconium sulphate which could exist in several modifications, mainly the $\beta$ and $\gamma$ forms[138]. These forms are, however, metastable and equilibriate to the stable $\alpha$-$Zr(SO_4)_2$ phase.

Thermogravimetric, quantitative, chemical and X-ray diffraction analysis were used to study the properties of anhydrous and tetrahydrated zirconium sulphate and to determine their purity.

## 5.1 Thermogravimetric Analysis

Thermogravimetric analysis of zirconium sulphate tetrahydrate heated up to 410°C showed that water was evolved in three stages (Fig. 6, Curve A). In the range 115-190°C the weight loss was 13.29% (equivalent to 2.62 $H_2O$); at 190-250°C the weight loss was 6.27% (equivalent to 1.23 $H_2O$), and at 250-410°C the weight loss was 0.59% (equivalent to 0.11 $H_2O$).

Thermogravimetric analysis of "anhydrous" zirconium sulphate produced by treatment of zirconium tetrahydrate with concentrated sulphuric acid showed a small weight loss of 1.55% between 70-370°C (equivalent to 0.30 $H_2O$) (Fig. 6, Curve B).

Thermogravimetric analysis of zirconium sulphate tetrahydrate heated up to 750°C showed a weight loss of 53.9% (Calc. wt. loss for $2SO_3$ is 56.5% when $Zr(SO_4)_2.4H_2O$ become "anhydrous" and then it decomposes to $ZrO_2 + 2SO_3\uparrow$ after 410°C (Fig. 6, Curve C). That weight loss found was less than the calculated because the decomposition of $Zr(SO_4)_2$ was probably not completed at 750°C; it has been reported by Duval[118] that complete decomposition can be achieved at 800°C.

Figure 5. Absorbance at 620μ against concentration of copper ammonia complex

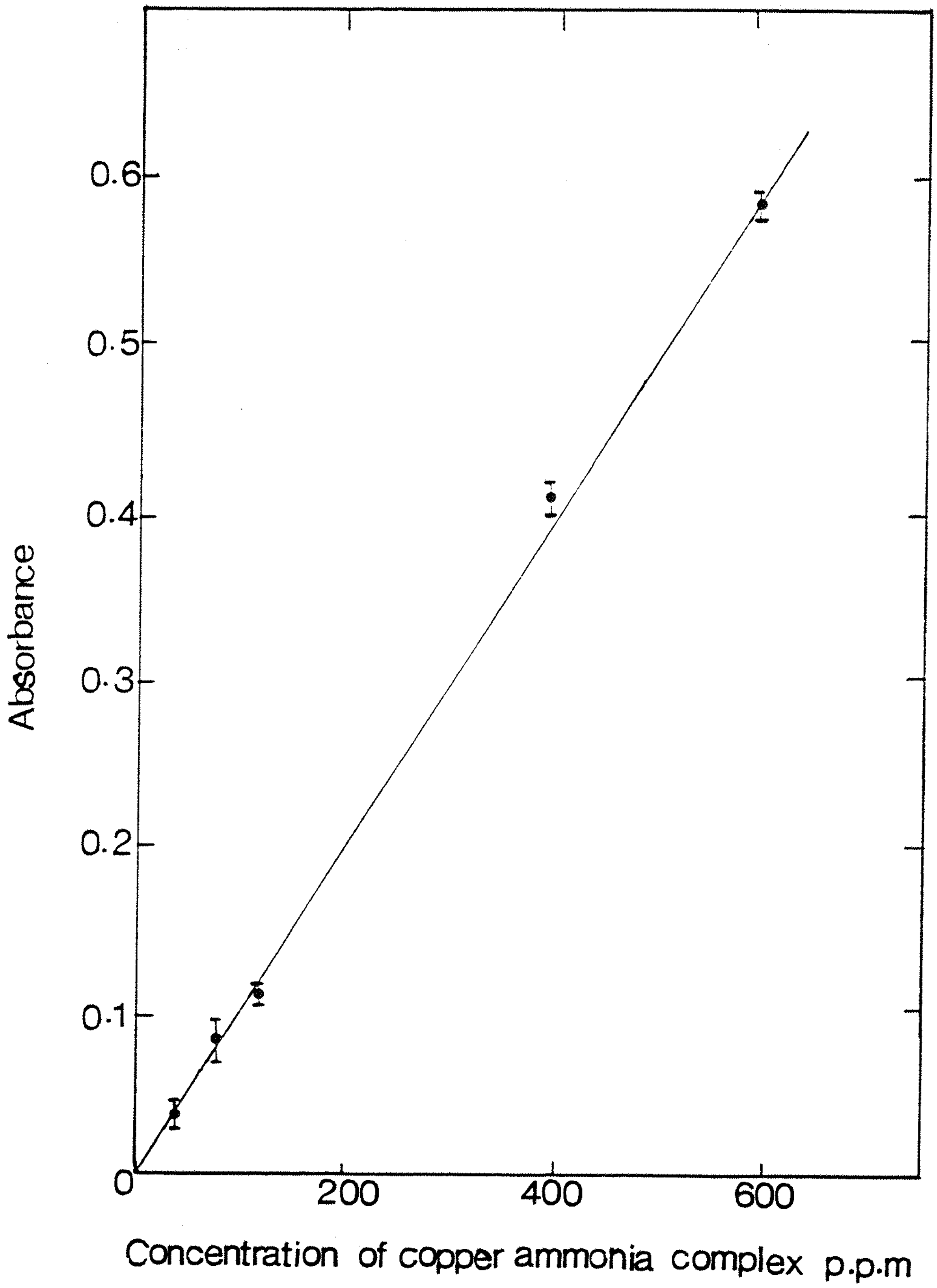
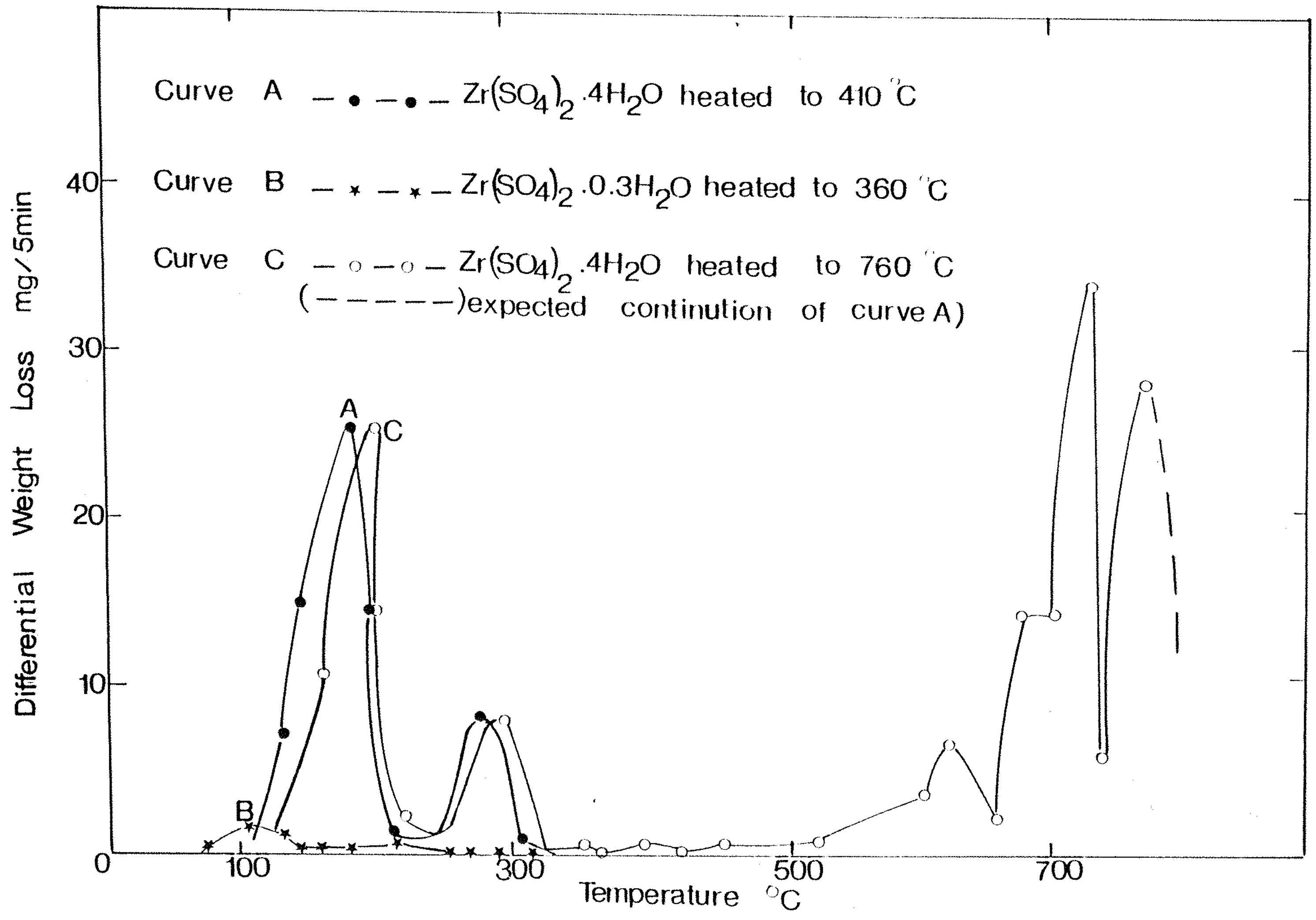


**Figure 6.** **Thermogravimetric analysis of ziroonium sulphate samples**



### 5.2. X-ray diffraction

A sample of $Zr(SO_4)_2.0.30H_2O$, obtained by treating $Zr(SO_4)_2.4H_2O$ with sulphuric acid[137], was subjected to X-ray powder diffraction analysis. The resulting d-values (relative intensities in brackets) were: 3.22Å (4.9), 3.5Å (6.7) and 2.72Å (8.5). These d-spacings compare favourably with values listed in J.C.P.D.S.: 3.23Å (100), 3.51Å (90) and 2.72Å (90). The intensities recorded in this work do not compare well with the literature values, however, these are subject to variation because of uncontrolled factors (such as orientation and size of crystallites) and also because of chance coincidence with other lines in a mixture of phases. Thus, for any given unknown pattern the strongest line may not be the strongest line of a pattern in the powder diffraction file (PDF), and consequently this pattern would only be found by trying various permutations of the strong lines of the unknown pattern.

$ZrO_2$ obtained from thermogravimetric analysis of a $\alpha$-$Zr(SO_4)_2.0.3H_2O$ was shown by X-ray to be monoclinic zirconium dioxide known as Baddeleyite with d-spacings of 3.15Å (100), 2.83Å (70) and 2.61Å (30) which corresponded to those of J.C.P.D.S. index 3.16Å (100), 2.84Å (64) and 2.62Å (22).

### 5.3. Quantitative chemical analysis

Zirconium sulphate tetrahydrate (BDH) was chosen as the source of zirconium. Analysis for zirconium by acidimetric titration, with and without complexation of zirconium with excess fluoride[139], gave 26.68% (Calc. for $Zr(SO_4)_2.4H_2O$ is 25.67%). Analysis for sulphate by precipitation of barium sulphate solution of this in excess EDTA and back titration with standard magnesium solution[140] gave 46.46% (Calc. for $Zr(SO_4)_2.4H_2O$ 48%).

# CHAPTER THREE

# REACTIONS OF SOME FIRST-ROW TRANSITION METAL COMPOUNDS IN PURE LITHIUM NITRATE-POTASSIUM NITRATE EUTECTIC

### 3.1. Copper(II) Sulphate Pentahydrate in Pure Lithium Nitrate-Potassium Nitrate Melt.

#### 3.1.1. Results

A blue coloured melt was obtained immediately on the addition of copper(II) sulphate pentahydrate (5 g) to the nitrate melt (10 g) at 137°C. After heating for 20 hours at 230°C, the colour of the melt changed to green and a black precipitate was formed.

When the experiment was repeated with anhydrous copper(II) sulphate (5 g) at 200°C, a green coloured melt was obtained. On heating the latter for 20 hours at 230°C, a black precipitate was formed. After dissolving the quenched melt in water, filtering and drying, both precipitate and filtrate were tested qualitatively showing the presence of Cu(II) in the black precipitate (probably copper(II) oxide) and the presence of nitrate and absence of oxide in the filtrate.

#### 3.1.2. Discussion

In a review of the chemistry of molten nitrates and nitrites, Kerridge[83] reported that the stability of copper(II) compounds in lithium nitrate-potassium nitrate is indicated by the determination of the solubilities of the chloride and nitrate at 160°C[84]. However, other workers using the same melt reported the precipitation of black copper(II) oxide at 143°C[85]. The copper(II) ion was also stated to oxidise iodide ions with the precipitation of brown copper(I) iodide, and silver metal with the formation of silver(I) ions and black copper(II) oxide, both reactions taking place at 150°C[86].

A kinetic study of the reaction of copper(II) ions in sodium nitrate-potassium nitrate at 310-350°C has been reported. The reaction was found to be autocatalysed

$$Cu^{2+} + 2NO_3^- \longrightarrow CuO + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots(36)$$

by the copper(II) oxide surface. Ferric oxide was also found to act as a catalyst for this reaction[87].

Frouzanfar and Kerridge[88] reported that copper(II) nitrate trihydrate has been successfully dehydrated in lithium nitrate-potassium nitrate eutectic at 140°C. At 300°C it commenced reaction as a Lux-Flood acid, precipitating copper(II) oxide. Copper metal was found by potential measurements to be surface-oxidised at 143°C in lithium nitrate-potassium nitrate[85], and no visible film was observed below 500°C[89]. In sodium nitrate-potassium nitrate copper(I) oxide may be formed at 250°C[90].

According to the results in this investigation and on the basis of what other workers have reported, the stoichiometries of the reactions of both copper(II) sulphate pentahydrate and anhydrous copper(II) sulphate in pure lithium nitrate-potassium nitrate eutectic for the overall reaction can be written as follows:

$$CuSO_4.5H_2O + 2NO_3^- \longrightarrow \underset{\text{black precipitate}}{\underline{CuO}} + 2NO_2 + \tfrac{1}{2}O_2 + 5H_2O + SO_4^{2-} \quad ...(37)$$

$$CuSO_4 + 2NO_3^- \longrightarrow CuO + 2NO_2 + \tfrac{1}{2}O_2 + SO_4^{2-} \quad ...(38)$$

The initial blue coloured melt was probably a copper(II) cation coordinated to nitrate groups as well as water molecules [i.e. $Cu^{2+}(NO_3^-)_x(H_2O)_y$]. The change of colour of the melt from blue in case of hydrated copper(II) sulphate to green in the case of anhydrous copper(II) sulphate probably means a loss of water or formation of intermediate basic suspension perhaps [$Cu(NO_3)_2.2Cu(OH)_2$] (the basic nitrate that was found when copper nitrate $Cu(NO_3)_2.3H_2O$ was heated only[118]) but the final product was copper(II) oxide.

## 3.2. Cobalt(II) Chloride Hexahydrate in Pure Lithium Nitrate-Potassium Nitrate Melt

### 3.2.1. Results

A dark blue coloured melt was obtained immediately on the addition of cobalt(II) chloride hexahydrate (0.5 g) to the nitrate melt (2 g ) at 396°C. At this temperature the reaction was very vigorous leading to the evolution of brown gas (nitrogen dioxide) and formation of a black precipitate (probably cobalt oxide).

### 3.2.2. Discussion

Cobalt(II) compounds are stable at 160°C in lithium nitrate-potassium nitrate as Kerridge[83] reported in his review of the chemistry of molten nitrates and nitrites, and some solubility values have been reported[84].

The spectrum of cobalt(II) chloride dissolved in lithium nitrate-potassium nitrate eutectic was reported by Gruen[91,92]. It was suggested that the cobalt species was possibly octahedral $Co(NO_3)_6^{4-}$. Alternative descriptions[93] of the cobalt species have involved coordination by four groups. In one model the 12 equidistant oxygens of tetrahedrally arranged nitrate groups gave rise to a cubic field, whereas in an alternative model two of the nitrate groups were bidentate and two were monodentate. The possibility of a species involving three bidentate nitrate groups was also considered[93]. The electronic spectrum has also been re-examined and attributed to dodecahedral coordination[94] rather than to octahedral. Evidence of complex formation with halide ions has been found in lithium nitrate-potassium nitrate at 145°C by polarography[95].

Brough[96] has reported that with increasing concentration of cobalt(II) chloride in the melt, the formation of chloro-complexes was increased, with visible spectra similar to those formed by addition of chloride to a melt solution of cobalt ion. Also Brough reported that vacuum or thermal dehydration of a hydrated transition metal nitrate does not normally give the anhydrous nitrate[97]. It was therefore necessary to show that during evacuation of the hydrated nitrates in the melt, no appreciable hydrolysis was occurring and that all water was removed. It was shown by trapping the water evolved while pumping down to $10^{-1}$ mm Hg, that the theoretical amount of water was removed from the melt and that the solidified solution showed no evidence of O-H bonds when examined by infrared spectroscopy. The condensed water was only slightly acid, eg that from melt containing 10.3 mol % $Co(NO_3)_2.6H_2O$ after three days at 160°C, had a pH of 1.5 and contained acid corresponding to 0.07% hydrolysis. Analysis of the slight black precipitate of cobalt oxide again indicated 0.07% hydrolysis. The kinetic data for the reaction

$$3Co^{2+} + 6NO_3^- \longrightarrow Co_3O_4 + 6NO_2 + O_2 \qquad ...(39)$$

has been obtained by Sláma[98] at 350-400°C in sodium nitrate-potassium nitrate. Extrapolation of his values to 160°C and their application to lithium nitrate-potassium nitrate indicated production of nitric acid fumes and cobalt oxide of the order of magnitude found. This indicated that complete dehydration of the anhydrous nitrates did occur without appreciable hydrolysis.

Frouzanfar and Kerridge[99] have established the temperature and stoichiometries of the reaction of cobalt(II) chloride with molten nitrate using infrared, x-ray diffractometry and thermogravimetric analysis. Tricobalt tetraoxide and nitrogen dioxide were produced together with oxygen and nitrite.

$$3Co^{2+} + 7NO_3^- \longrightarrow Co_3O_4 + NO_2^- + 6NO_2 + \tfrac{3}{2}O_2 \qquad ...(40)$$

Cobalt metal has been shown by potential measurements to form surface oxide film in lithium nitrate-potassium nitrate at 143°C[85], though this was not observed visually until 500°C[89].

The stoichiometry of the reaction of cobalt(II) chloride hexahydrate in pure lithium nitrate-potassium nitrate eutectic can be based on the results of this work together with the reports of other workers and can be proposed as follows:

$$3CoCl_2.6H_2O + 6NO_3^- \longrightarrow \underbrace{Co_3O_4}_{\text{black precipitate}} + 6NO_2 + O_2 + 18H_2O + 6Cl^- \qquad ...(41)$$

Because of the high concentration of nitrate ion (much more than water and chloride ion) the initial dark blue coloured melt was suggested to be a compound of cobalt(II) cation coordinated to nitrate groups, water molecules and possibly chloride ions as well. When the compound was reacted with nitrate ion, tricobalt(II) tetraoxide precipitate was the final product.

## 3.3. Nickel(II) Chloride Hexahydrate in Pure Lithium Nitrate-Potassium Nitrate Melt

### 3.3.1. Results

An olive green coloured melt was obtained immediately after the addition of nickel(II) chloride hexahydrate (0.5 g) to the melt (2 g) at 396°C. At this temperature the reaction was very vigorous initially; water vapour was evolved, and later brown nitrogen dioxide with the formation of a black precipitate of nickel(II) oxide

### 3.3.2. Discussion

In nitrate melts and at reasonably low temperatures, the nickel(II) oxidation state is stable[83]. The results of spectral investigation of solutions of nickel(II) in nitrate melts are compared[91,100,101] with the data for $Ni(NO_3)_4^{2-}$ in nitromethane[102] and $Ni(H_2O)_6^{2+}$ [103]. Gruen and McBeth[91,100,101] found two visible bands in binary nitrate eutectic, the one at lower energy being asymmetric with an ill-defined shoulder on the high-energy side. They identified the spectrum as being due to a complex involving four nitrate groups arranged tetrahedrally about the nickel such that the 12 oxygen atoms gave rise to a cubic field. Johnson and Piper[104] pointed out that such an arrangement would give rise to an energy splitting that is the inverse of that obtained for a six-coordinate octahedral field, and suggested an alternative model involving three bidentate nitrate groups. A further possibility suggested by Gruen[93] involved two monodentate and two bidentate nitrate groups. Smith et al.[105] examined the nickel(II) spectrum in the ternary nitrate melt and also a dimethylsulfone melt to which excess nitrate had been added.

In dimethylsulfone the changes observed both potentiometrically and spectrophotometrically on addition of the excess nitrate were shown to be compatible with the formation of dinitrato $Ni(NO_3)_2$ and trinitrato $Ni(NO_3)_3^-$ complexes. Recently solubility[84], chromatographic[106] and polarographic studies[95] have been carried out, the latter giving stability constants for the chloro and bromo complexes. A spectroscopic study in lithium nitrate-sodium nitrate-potassium nitrate eutectic[105] has confirmed the earlier octahedral assignment and because the spectrum was found to be identical with the 1:3 nickel(II) nitrate complex formed in dimethylsulphone, it was suggested that the octahedral environment was formed by three bidentate nitrate groups.

Earlier Brough[96] reported that a solution of nickel(II) chloride in lithium nitrate-potassium nitrate melt decomposed at 470°C to give nickel(II) oxide and nitrogen dioxide. The reaction may be formulated

$$Ni^{2+} + 2NO_3^- \longrightarrow NiO + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots(42)$$

The reaction was found to proceed at a much lower temperature in the presence of oxide donors such as sodium peroxide. Nickel metal was reported to form a film of nickel(II) oxide at 250°C in sodium nitrate-potassium nitrate[90], though a visible film was not found in lithium nitrate-potassium nitrate until 500°C[89].

From the results obtained in this work and according to what other workers have reported the stoichiometry of the reaction of nickel(II) chloride hexahydrate in pure lithium nitrate-potassium nitrate, can be written as follows:

$$NiCl_2.6H_2O+2NO_3^- \longrightarrow \underset{\text{black precipitate}}{\underline{NiO}}+2NO_2 + \tfrac{1}{2}O_2+6H_2O+2Cl^- \qquad \ldots(43)$$

Initially the olive-green coloured melt probably was a compound of nickel(II) cation coordinated to nitrate groups, water molecules and perhaps also chloride ions.

## 3.4. Iron(II) Sulphate Heptahydrate in Pure Lithium Nitrate-Potassium Nitrate Melt

### 3.4.1. Results

An orange-brown coloured melt was obtained immediately after the addition of iron(II) sulphate heptahydrate (2.8 g) to the nitrate melt (10 g) at 200°C with evolution of brown gas (nitrogen dioxide). The orange-brown melt was quenched and qualitatively tested[107] [distinctive tests for iron(II) and iron(III) salts in slightly acidic (hydrochloric acid) solution] (Table 2). The above results suggest that iron(III) has been formed (i.e. Fe(II) → Fe(III)) in the nitrate melt.

### 3.4.2. Discussion

It has been reported by Kerridge[83] in the Review of Chemistry of Molten Nitrates and Nitrites, that iron(III) is stated to be immobile on various chromatographic supports[106]. Gruen[108] recorded the spectrum of Fe(III) in lithium nitrate-potassium nitrate eutectic and reported that on addition of iron(III) chloride, no spectral maxima were obtained below 25 kK while there was complete absorption at higher energies. However, Kerridge and Khudhari[109] have studied the reactions of six compounds of iron in three different oxidation states (II), (III) and (VI) in lithium nitrate-potassium nitrate eutectic and in each case they found that the final product was iron(III) but there was evidence of intermediate formation of iron(III) oxide ($Fe_2O_3$) from potassium ferrate(VI) ($K_2FeO_4$), and ferrate(III) ($FeO_2^-$) from iron(III) oxide nitrate.

Brough[96] reported that anhydrous iron(II) chloride dissolved readily in the nitrate melt to give a clear orange-brown solution. Even at temperatures as low as 200°C, Fe(III) behaved as a weak Lux-Flood acid, slowly removing oxide ion from nitrate to form a red-brown oxide precipitate.

$$2Fe^{3+} + 3NO_3^- \longrightarrow Fe_2O_3 + 3NO_2^+ \qquad ...(44)$$

Table 2: Distinctive tests for iron(II) and (III) in the unwashed product obtained from reaction of iron(II) sulphate heptahydrate in pure lithium nitrate-potassium nitrate melt.

| Reagent Used | Observation on |  | Inference |
|---|---|---|---|
|  | Iron(II) sulphate heptahydrate $FeSO_4.7H_2O$ | Unwashed product from the experiment |  |
| 1. Potassium ferrocyanide solution | White or pale blue ppt | Deep blue ppt (prussian blue) | Presence of Fe(III) in the unwashed product |
| 2. Potassium ferricyanide solution | Deep blue ppt | No ppt<br>brown colouration | Absence of Fe(II) in the unwashed product |
| 3. Ammonium thiocyanate solution | Red clear solution | Deep red solution | Presence of Fe(III) in the unwashed product |
| 4. Ammonium hydroxide solution | Greenish ppt | Reddish-brown ppt | Presence of Fe(III) in the unwashed product |

Brough[96] also reported that the reaction of 0.1 M iron(III) chloride solution was slow at 200°C, being almost complete after six days. By increasing the temperature to more than 250°C or the addition of a base such as sodium peroxide or hydroxide, the reaction time was considerably reduced. No evidence was found of the formation of a lower oxidation state than Fe(III). The base appeared to react only through formation of sodium oxide and the consequent availability of oxide ion to $Fe^{3+}$. Anhydrous iron(II) chloride, even at low temperatures, was not stable in the melt, being immediately oxidised to a brown solution containing iron(III) with the production of nitrogen dioxide

$$Fe^{2+} + NO_3^- \rightarrow Fe^{3+} + NO_2 + O^{2-} \qquad ...(45)$$

This solution precipitated $Fe_2O_3$ more rapidly at 200°C than that of iron(III) chloride, the iron being almost totally removed from solution in about three hours. This was probably due to the availability of oxide ion from reaction (45).

Iron metal has been found to be generally inert, not forming an oxide film at 250°C in sodium nitrate-potassium nitrate[90], and not until 500°C in the lithium nitrate-potassium nitrate melt[89]. A less pure iron did however react in the latter melt at 400°C, the gases evolved consisted of carbon dioxide, nitrogen, nitrous oxide and nitrogen dioxide. In acidic melts reaction occurred at a lower temperature (0.1 M $K_2S_2O_7$ 180°C, 0.8 M $K_2Cr_2O_7$ 320°C) with the formation of iron(III)[89].

On the basis of what other workers reported together with the results obtained in this work, the stoichiometry of the reaction of iron(II) sulphate heptahydrate in pure lithium nitrate-potassium nitrate can be proposed as follows:

$$2FeSO_4.7H_2O + 4NO_3^- \longrightarrow \underset{\text{reddish-brown precipitate}}{Fe_2O_3} + 4NO_2 + \tfrac{1}{2}O_2 + 14H_2O + 2SO_4^{2-} \qquad ...(46)$$

Initially the orange-brown coloured melt was a compound of iron(II) cation coordinated with nitrate groups as well as water molecules and possibly sulphate ions also. The final product as suggested in (eqn. 46) is iron(III) oxide.

# CHAPTER FOUR

# REACTIONS OF SOME FIRST ROW TRANSITION METAL COMPOUNDS IN BASIC LITHIUM NITRATE-POTASSIUM NITRATE EUTECTIC

## 4.1. Introduction

The basic species in the nitrate melt have been studied by many workers (see 1.5) but perhaps the most unexpected results have been found by Zambonin and Jordan[39,40,41]. They claimed that the oxide ion exists in the nitrate melt, but only in very small concentration. They postulated that the basic species were in fact the peroxide and superoxide ions (eqn. 19 and 20), but other workers have assumed the existence of the orthonitrate[50] or pyronitrate[110,111,112] ions where the oxide ions are combined with one or two nitrate ions. More details of basic species in nitrate melt have been given in (1.5), but in this section the behaviour of basic solutes, like sodium peroxide and sodium hydroxide, will be discussed.

The first basic solute, sodium peroxide, has been reported by Habboush and Kerridge[113] to be slightly soluble in this melt with a change in colour at 260°C from yellow to colourless. They reported that the decomposition (eqn. 47) became more rapid above 300°C, but had ceased at 350°C.

$$Na_2O_2 \longrightarrow Na_2O + \tfrac{1}{2}O_2 \qquad \ldots (47)$$

This equation has a theoretical weight loss of 20.5%, but they found only a 10.7 weight loss, and concluded that this lower percentage weight loss was due to the formation of sodium monoxide on the surface of the peroxide where it was in contact with the melt. This surface layer eventually becomes thick enough to protect the peroxide at the centre of the particles from further attack. The reaction between sodium peroxide and molten equimolar lithium nitrate-potassium nitrate at 250°C has also been studied using a potentiometric titration technique[114], El-Hosary and El-Din reporting that melts containing lithium were more acidic than those with sodium or potassium ions. In particular they suggested[11] that sodium peroxide reacted with lithium nitrate as in equation 48,

$$\text{"}4LiNO_3 + 2Na_2O_2 \longrightarrow Li_4N_2O_7 + Na_4N_2O_7 + O_2\text{"} \qquad \ldots (48)$$

and on dissolving these solids in water, the lithium salt was more readily hydrolized (to lithium nitrate and lithium hydroxide) than the sodium salt[11].

The behaviour of sodium hydroxide in lithium nitrate-potassium nitrate has also been reported by Habboush and Kerridge[113]. They found that sodium hydroxide was stable in this melt up to 400°C, while above this temperature, it decomposed to sodium monoxide and water as in equation 49.

$$2NaOH \longrightarrow Na_2O + H_2O \qquad \ldots (49)$$

Thus addition of sodium peroxide or sodium hydroxide will increase the oxide concentration of a melt and also ultimately stabilise higher oxidation states. Several examples are now known where high oxidation states are stabilised in basic alkali metal nitrate eutectic solutions. For instance, bismuth is precipitated as bismuth(III) in pure nitrate eutectic but forms bismuthate(V) in highly basic lithium nitrate-potassium nitrate[115]. Manganate(VI) is stabilised in sodium nitrate-potassium nitrate melts[116] containing sodium peroxide, whereas reduction is rapid to manganese(IV) oxides in neutral melts. Neptunium is stable in neutral melts as neptunium(V) and can be oxidised to neptunium(VI) by addition of bromate. However, in very basic melts it is oxidised to neptunium(VII)[117].

## 4.2. Reaction of Hydrated and Anhydrous Copper(II) Sulphate in Lithium Nitrate-Potassium Nitrate Eutectic containing basic species.

### 4.2.1. Results in the Presence of Sodium Hydroxide

Copper(II) sulphate pentahydrate (0.1 molal) was observed to react with lithium nitrate-potassium nitrate eutectic (5 g) containing sodium hydroxide (4 molal), when it was added at 350°C, forming a black precipitate with evolution of brown nitrogen dioxide. No further changes were observed at 450°C.

### 4.2.2. Results in the Presence of Sodium Peroxide

The experiment was repeated several times using anhydrous copper(II) sulphate but with added sodium peroxide instead of hydroxide. A brown precipitate was formed each time. The unwashed, brown, quenched melt was ground and quantitatively analysed, giving the results listed in Table 3. Titration with sodium thiosulphate after addition of acid and excess potassium iodide, (see 2.6.2 no.3) estimated copper from the reduction of copper(II), i.e. $Cu^{2+} \rightarrow CuI$, together with any other oxidising agent (possibly copper(III) or peroxide) forming iodine, while titration with EDTA, after solution in acid (see 2.6.2 no.2), estimated copper(II) only.

It has been thought that possibly peroxide was affecting the results labelled "% Cu" obtained from titration of the unwashed brown quenched melt with sodium thiosulphate (see Table 3) because peroxide is a strong oxidising agent and reacts with iodide, thus increasing the volume of sodium thiosulphate used, i.e.

$$O_2^{2-} + 4H^+ + 2I^- \longrightarrow I_2 + 2H_2O \qquad \ldots (50)$$

Any cuprate (III) formed from reaction of copper(II) sulphate with nitrate melt containing sodium peroxide will also increase the titre, i.e. "% Cu" would also have an increased value (above the real % Cu) if copper(III) had formed during the reaction.

At this stage it was considered desirable to find a method to differentiate between peroxide and cuprate(III) so that the actual differences in values between column 5 and 6 of Table 3, could be properly attributed.

Thus calcium cuprate(III) $[Ca(CuO_2)_2.XH_2O]$ was prepared according to the method given by Prokopchick and Norkus[119] which is as follows:

Table 3 **Quantitative analysis of unwashed brown quenched melt obtained from reaction of copper(II) sulphate with nitrate melt containing sodium peroxide.**

| Run No | Wt of melt g | Conc. of $Na_2O_2$ molal | Conc. of $CuSO_4$ molal | "%Cu" Using $Na_2S_2O_3$ for titration | | %Cu using EDTA for titration |
|---|---|---|---|---|---|---|
| | | | | D | R | |
| 6 | 30 | 5.0 | 0.2 | 10.7 | N/A | 5.70 |
| 11 | 17 | 1.13 | 1.0 | 7.09 | N/A | 7.50 |
| 12 | 15 | 1.28 | 1.0 | 7.24 | N/A | 7.09 |
| 13 | 17 | 1.31 | 1.0 | 7.79 | N/A | 5.04 |
| | | | | 7.70 | N/A | 4.49 |
| | | | | N/A | 13.8 | 7.68 |
| 14 | 17 | 1.13 | 1.0 | 4.93 | N/A | 3.58 |
| | | | | N/A | 5.39 | 3.72 |
| 15 | 20 | 1.05 | 1.0 | N/A | 5.98 | 3.09 |
| | | | | N/A | 6.11 | 3.19 |

Note: D means direct procedure while R means reverse procedure (see 2.6.2, no.3)

About 0.5 g of calcium hydroxide was added to 24 ml of aqueous 0.2 M calcium hypochlorite and to the mixture, 5 ml of 0.1 M copper(II) chloride was added. The precipitated copper(II) hydroxide turned a dark purple-red and was kept at room temperature for 24 hr in a stoppered flask. The voluminous precipitate was then filtered and washed with about 120-150 ml of cold saturated calcium hydroxide solution until all the chloride had been washed out (qualitative test in silver nitrate solution slightly acidic with sulphuric acid, was carried out on the filtrate to ensure complete absence of the chloride ion). Calcium cuprate(III) was then dried in an oven at 110°C for about 5 mins.

Characterisation of unwashed and washed purple-red calcium cuprate(III), prepared according to the russian method[119], by using different techniques was done briefly, with the following results.

1. Quantitative analysis (titration using sodium thiosulphate, both direct (D) and reverse (R) procedure explained in 2.6.2 no.3). The results are listed in Table 4.

Table 4. Quantitative analysis of washed and dried calcium cuprate(III)

| Washed and dried calcium cuprate(III) | "% Cu" using $Na_2S_2O_3$ for titration | |
|---|---|---|
| Sample No. | R | D |
| 1 | 16.5 | 8.9 |
| 2 | 21.4 | 8.0 |
| 3 | 9.1 | 7.1 |

From Table 4, the average of three results, "% Cu" determined when titration was done reversibly = 15.6, nearly double "%Cu" determined when titration was done directly = 8.0. This is a proof of formation of cuprate(III).

2. Qualitative tests (for oxidising agent using manganous chloride reagent (Table 5).

**Table 5** **Qualitative tests for oxidising agents using manganous chloride reagent**

| Compound | Observations | Inference |
|---|---|---|
| 1. Washed dried calcium cuprate(III) | brown colouration | presence of oxidising agent probably $CuO_2^-$ |
| 2. Calcium hydroxide | pale-green colouration | absence of oxidising agent |
| 3. Copper oxide | pale-green colouration | absence of oxidising agent |
| 4. Copper chloride | bright-green colouration | absence of oxidising agent |
| 5. Calcium hypochlorite | brown colouration | presence of oxidising agent $ClO^-$ |

Since all the chloride has been washed out completely, no hypochlorite is present and the oxidising agent giving the positive test with manganous chloride was the cuprate(III) anion $CuO_2^-$ and not hypochlorite.

3. Raman spectroscopy

This technique analyses molecular rotations, vibrations and electronic transition in some particular cases. Yet, Raman Spectroscopy has not been developed as much as Infrared Spectroscopy and only comparatively few samples have been analysed with the Raman technique. Experimental problems have also arisen due to the monchromatic exciting source. The Raman experiment consists in observing the frequencies of the light scattered by a sample when illuminated by monochromatic radiation. Also coloured samples absorb visible radiation, become hot and decompose so that no Raman Spectroscopy can be observed.

Samples of different compounds were subjected to Raman spectroscopy giving certain vibrational frequencies are listed in Table 6 and shown by Fig 7, 8 and 9.

**Table 6 Frequencies of different compounds by Raman Spectroscopy**

| Compound | Colour | Frequency |
|---|---|---|
| 1. $Ca(CuO_2)_2.XH_2O$ (in solution) | purple-red | 723, 801 |
| 2. $Ca(OH)_2$ (solid/powder) | white | 723, 801 |
| 3. $Ca(ClO)_2$ (solid/powder) | white | 723, 801 |
| 4. $CuCl_2$ (solid) | green | |

The Raman technique was not greatly helpful for characterisation of calcium cuprate(III) for two reasons:

1. The sample was not very pure.
2. The strong colour caused absorption of the primary laser radiation, so Cu-O vibrational frequencies were not observed[143].

Since the frequencies for the three compounds in Table 6, are the same, and because of the absence of $\nu$(Cu-O) evidence , the explanination of the similarity in the frequencies is the presence of $\nu$ (Ca-O).

4. Infrared Spectroscopy

This technique is used to measure the absorption of radiation in the range 1-300 $\mu$m (most commonly 2.5 - 25 $\mu$m) caused by the excitation of molecular rotations or vibrations. Certain groups (e.g. carbonyl) have vibrational modes at characteristic frequencies whatever molecule they are in. Thus the IR (vibrational) spectrum of an organic molecule may give an indication of the groups it contains. IR reflectance methods are used to investigate molecules absorbed on surfaces.

In a reflectance IR experiment, a sample of unwashed calcium cuprate gave the frequencies 1453.4, 872.5 and 712.6, which correspond to $CaCO_3$, and 3650 which corresponds to $Ca(OH)_2$ (3644 is the O-H stretching frequency in metal hydroxide).

Figure 7. Raman spectroscopy of $Ca(CuO_2)_2.XH_2O$

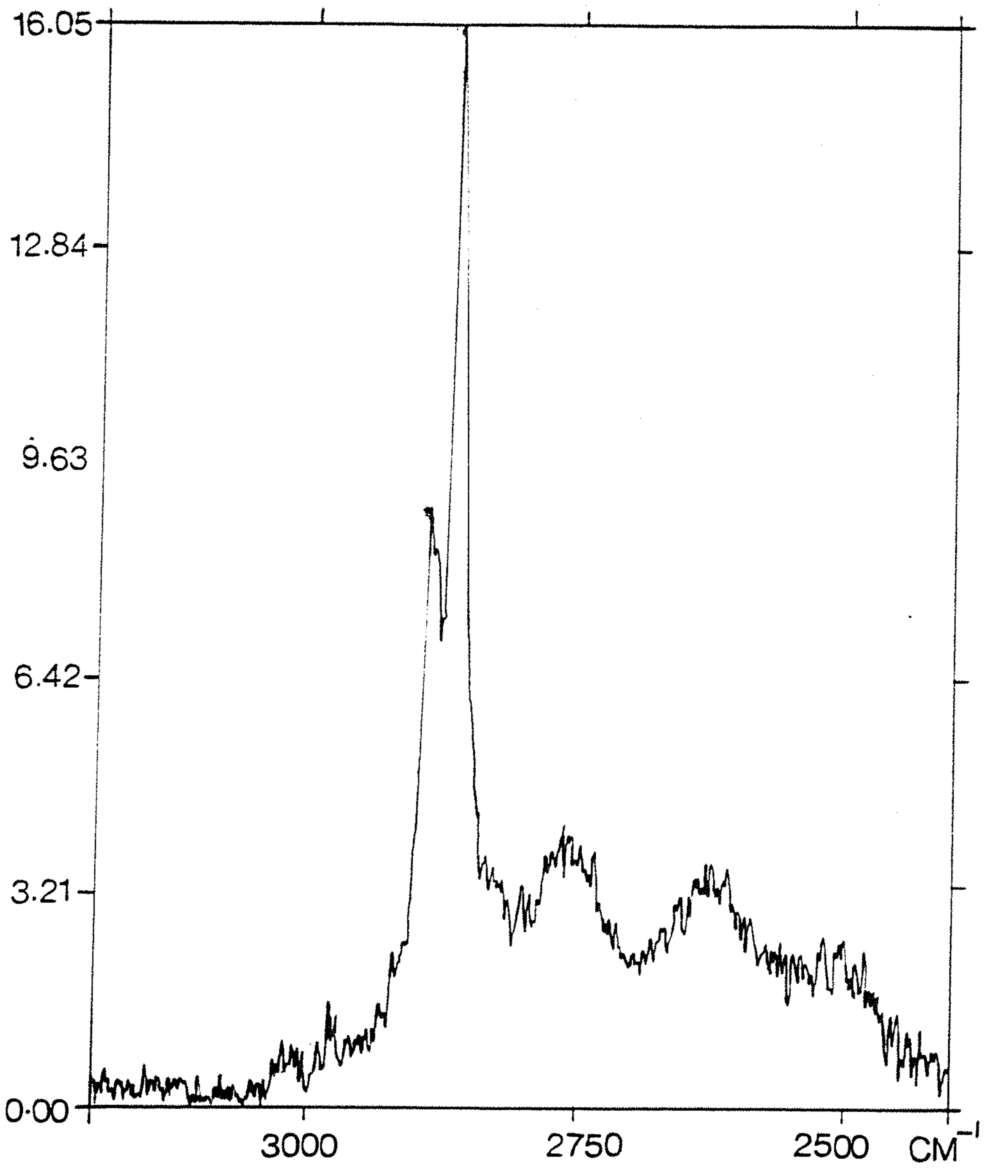


Figure 8. Raman spectroscopy of pure $Ca(OH)_2$

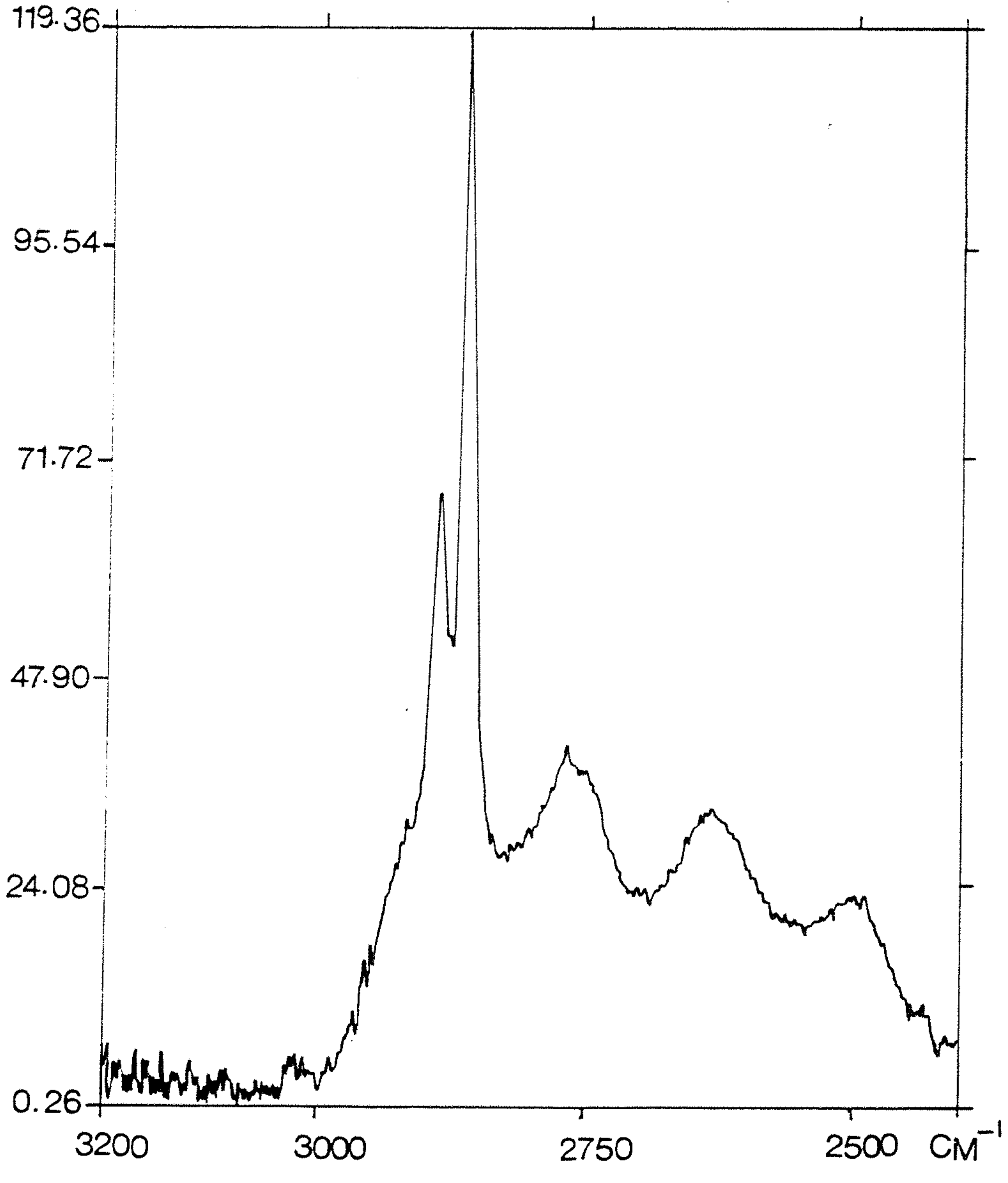
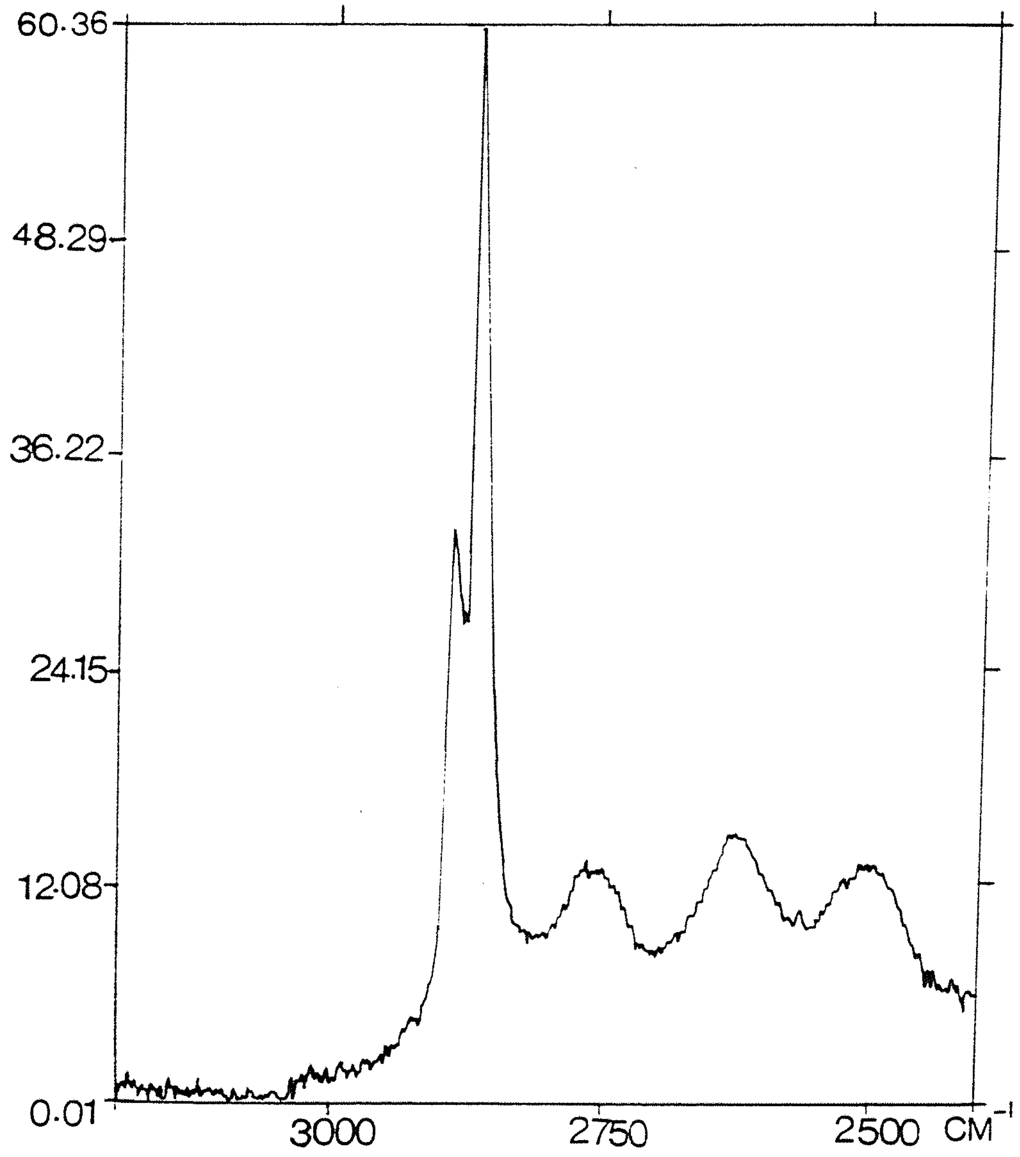


**Figure 9. Raman spectroscopy of $Ca(OCl)_2$**



Another sample (unwashed of calcium cuprate showed the frequencies, 874 and 715, which corresponded to $CaCO_3$, 3640 which corresponded to $Ca(OH)_2$ and finally 390 and 313 which corresponded to metal stretching (metal's stretching below 500), (Fig. 10, 11 and 12).

These results are clearly influenced by the presence of $Ca(OH)_2$ and $CaCO_3$ in the sample. There is no clear evidence for Cu(III) in this experiment.

The sample of calcium cuprate(III), prepared by the aqueous route, was then used to investigate the possibility of distinguishing between peroxide and copper(III).

Four volumetric methods, which can be used for the determination of peroxide, were investigated (at first qualitatively) to see if identical reactions occurred with copper(III). The volumetric methods were:

a. Analysis of sodium peroxide using standard 0.1 M potassium permanganate.
b. Oxidation with manganese(III) sulphate.
c. Titration with standard 0.1 M cerium(IV) sulphate and ferroin as indicator.
d. Titration with standard 0.1 M mercury(I) nitrate.

With calcium cuprate(III), peroxide and the unwashed quenched melt, the following results were obtained (Table 7).

Result 1, Table 7, means that the sodium peroxide sample is not very pure (purity percentage is 81 %), but the titre is much larger than in result 2, Table 7. To explain this low titre, the following hypothesis is suggested:

Copper(III) does not react with 0.1 M cerium(IV) sulphate and the titre of result 2, Table 7 was produced by impurities (where titre is of the size of a blank titration). If so, then result 3, Table 7, means there were less impurities in the unwashed precipitate and also that the unwashed precipitate contained virtually no peroxide.

Figure 10. Infrared spectroscopy of unwashed $Ca(CuO_2)_2$

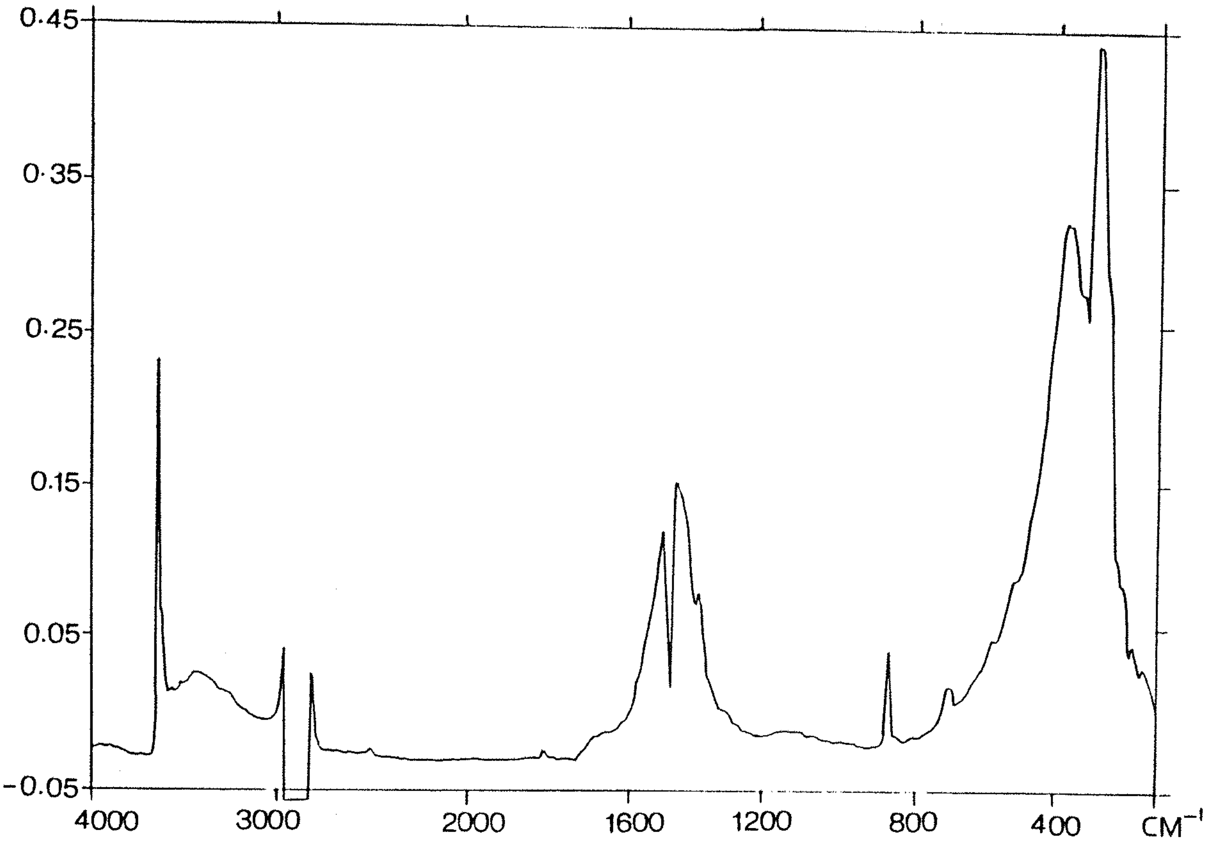


Figure 11. Infrared spectroscopy of CuO

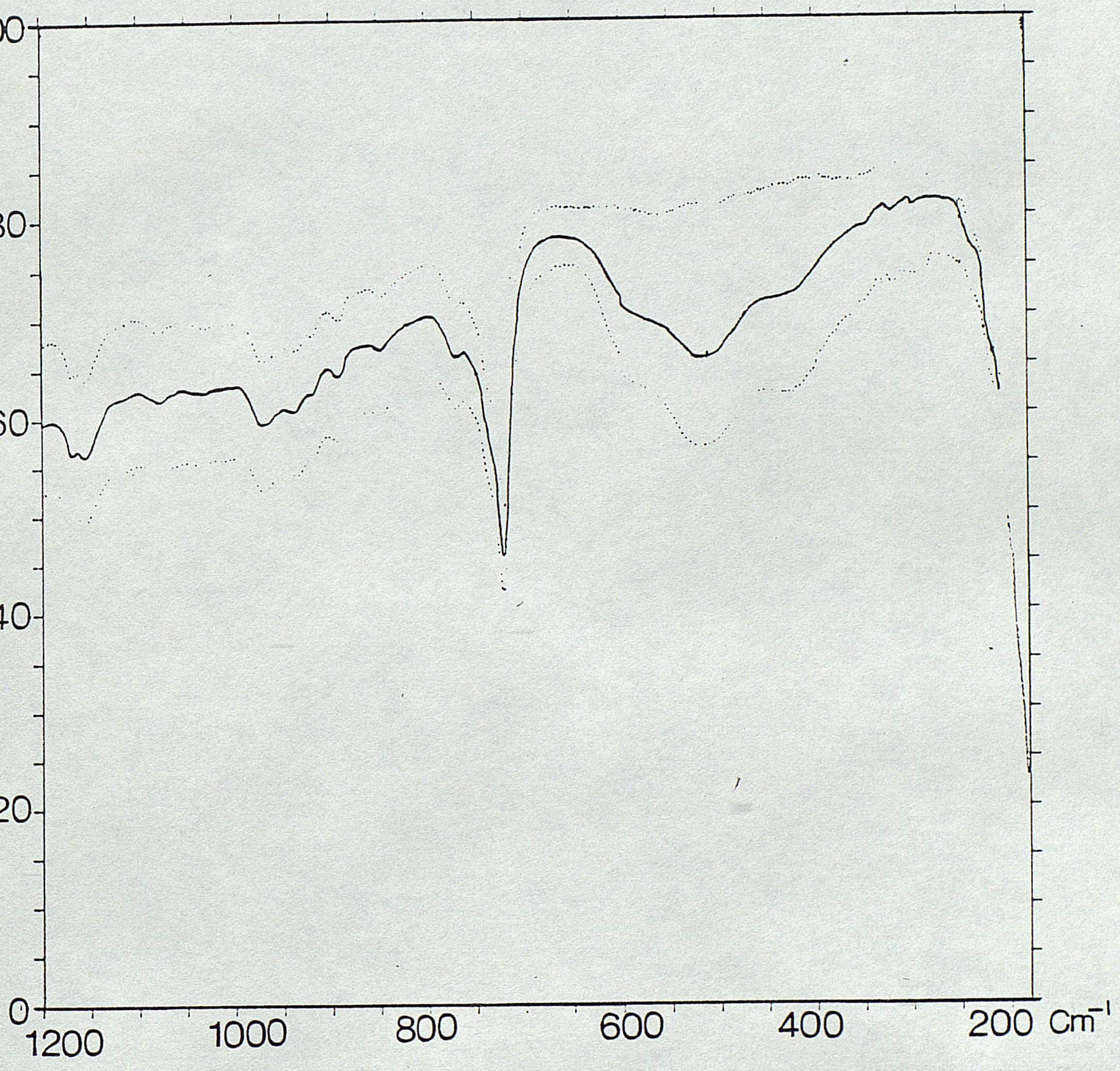


Figure 12. Infrared spectroscopy of unwashed $Ca(CuO_2)_2$
(Second Sample)

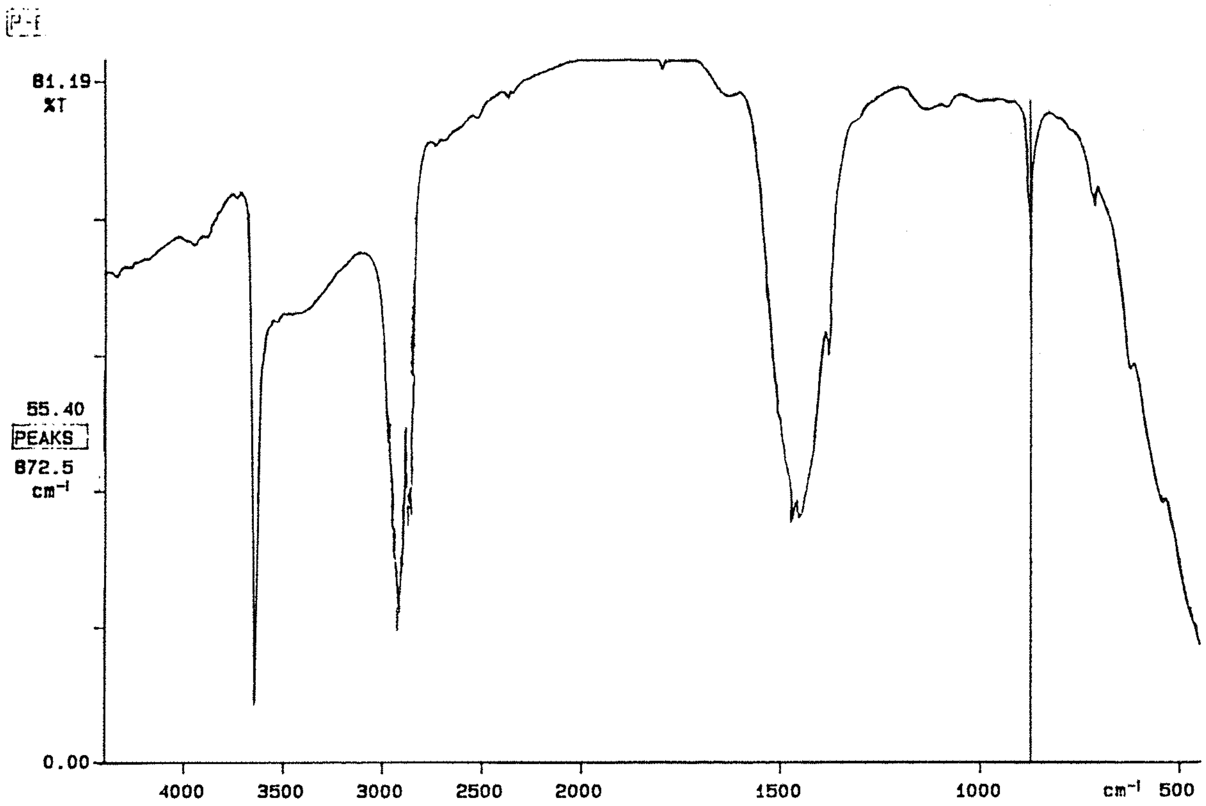


Table 7 Quantitative analysis of sodium peroxide, calcium cuprate(III) and unwashed quenched melt obtained from run 14 and 15 in Table 3

| No | Compound | Wt of sample<br>g | Volume of 0.1 M cerium (IV) sulphate required to get end point (ml) |
|---|---|---|---|
| 1 | Sodium peroxide | 0.2328 | 9.70 |
| 2 | Calcium cuprate | 0.1048<br>0.1059 | 0.18<br>0.22 |
| 3 | a. unwashed quenched melt from run 14 | 0.2668 | 0.07 |
|  | b. unwashed quenched melt from run 15 | 0.6007<br>0.6499 | 0.05<br>0.09 |

Thus, from the hypothesis, the differences between column 5 and 6 in Table 3, could not be due to peroxide in the unwashed precipitate and are suggested to be due to the presence of some copper(III).

An alternative way of removing peroxide (as well as excess melt) was to wash the quenched melt with water, though it was recognised that any copper(III) might also be hydrolysed. A procedure was established for washing the ground quenched melt for the minimum time with the minimum amount of water in the hope that all the copper(III) would not be decomposed before the peroxide and nitrate were washed out. The procedure devised was as follows:

About 2 g of unwashed quenched melt was weighed out. After grinding into very fine particles using a pestle and mortar, 25 ml of distilled water was added and the mixture was stirred for 2 minutes using a magnetic stirrer [to dissolve the nitrate as quickly as possible before hydrolysis of cuprate(III)] then filtered and dried in an oven at 110°C for about 10-15 minutes. Qualitative tests on the washed precipitate showed no nitrate or peroxide.

Table 8 Quantitative analysis of washed black precipitate (washed with water alone) obtained from reaction of copper(II) sulphate with nitrate melt containing sodium peroxide.

| Run No | Wt of melt g | Conc. of $Na_2O_2$ molal | Conc. of $CuSO_4$ molal | Colour of quenched melt | Colour of ppt after washing | "% Cu" using $Na_2S_2O_3$ for titration D | % Cu using EDTA for titration |
|---|---|---|---|---|---|---|---|
| 7 | 20 | 2 | 2 | black | black | 61.7 ± 0.9 | 65.4 ± 0.5 |
| 8 | 20 | 1 | 1 | brown | brown | N/A | N/A |
| 9 | 15 | 2 | 2 | brown-black | black | 82.8 ± 3.5 | 81.4 |
| 10 | 20 | 1 | 1 | brown | brown-black | N/A | N/A |

Table 9 X-ray diffraction of the washed black precipitate obtained from reaction of copper(II) sulphate with nitrate melt containing sodium peroxide from run 20.

| Washed black ppt | | From (J.C.P.D.S.) Index | | | | | |
|---|---|---|---|---|---|---|---|
| | | CuO | | $Cu_2(OH)_3NO_3$ | | $Cu(OH)_2$ | |
| d-spacings Å | I/Io | d-spacings Å | I/Io | d-spacings Å | I/Io | d-spacings Å | I/Io |
| 6.89 | 42 | | | 6.85 | 100 | | |
| 4.11 | 14 | | | 4.08 | 10 | (5.30 | 59) |
| 3.48 | 23 | | | 3.44 | 70 | (3.75 | 100) |
| 2.77 | 17 | | | 2.77 | 10 | (2.88 | 6) |
| 2.74 | 20 | 2.75 | 12 | | | | |
| 2.66 | 27 | | | 2.65 | 30 | 2.64 | 82 |
| 2.52 | 100 | 2.52 | 100 | | | 2.51 | 46 |
| 2.45 | 26 | | | 2.45 | 50 | | |
| 2.31 | 98 | 2.32 | 96 | 2.30 | 10 | 2.36 | 33 |
| 2.26 | 20 | | | 2.24 | 20 | 2.26 | 66 |
| 2.14 | 15 | | | 2.14 | 10 | | |
| 2.06 | 17 | | | 2.05 | 30 | 2.08 | 6 |
| 1.86 | 36 | 1.86 | 25 | | | | |
| 1.70 | 20 | 1.71 | 8 | | | 1.73 | 59 |
| 1.58 | 23 | 1.58 | 14 | 1.58 | 30 | | |
| 1.50 | 28 | 1.50 | 20 | 1.52 | 30 | 1.48 | 13 |
| 1.40 | 26 | 1.41 | 15 | | | 1.45 | 13 |
| 1.37 | 23 | 1.37 | 19 | | | 1.38 | 6 |

Quantitative analysis of the black precipitate washed with water alone gave the results listed in Table 8.

X-ray diffraction of the washed black precipitate from run 20, gave the d-spacings of CuO and other lines close to those of $Cu_2(OH)_3NO_3$ and possibly $Cu(OH)_2$ (Table 9)

Thermogravimetric analysis on the washed black precipitate from run 19, showed,

1. At low temperature, 46°C - 373°C, total weight loss found was 4.5% (Fig 13)
   a. Calculated weight loss for $1H_2O$ per $Cu(OH)_2$ is 18.45%, i.e.

$$Cu(OH)_2 \longrightarrow CuO + H_2O \qquad \ldots (51)$$

   b. Calculated weight loss for $3H_2O$, $2NO_2$ and 1O per $2Cu_2(OH)_3NO_3$ is 33.75%, i.e.

$$2Cu_2(OH)_3NO_3 \longrightarrow 4CuO + 3H_2O + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots (52)$$

2. At higher temperatures, 373°C - 430°C, a horizontal was obtained, i.e. there was no weight loss.
   Another thermogravimetric analysis on the washed black precipitate from run 20, (the same washed black precipitate was examined by X-ray diffraction) Table 9) showed as in Fig 14,

   1. At low temperature, 76°C - 660°C, weight loss found was 1.9%.
   2. There was no weight loss between 660°C - 1010°C.
   3. At extremely high temperatures, 1010°C, a further weight loss was found of 8.6% (calculated weight loss for 1O per 2CuO is 10.06%, when copper(II) oxide decomposes thermally to copper(I) oxide according to eqn 53)

$$2CuO \longrightarrow Cu_2O + \tfrac{1}{2}O_2 \qquad \ldots (53)$$

Figure 13. Thermogravimetric analysis of washed black precipitate from run 19.

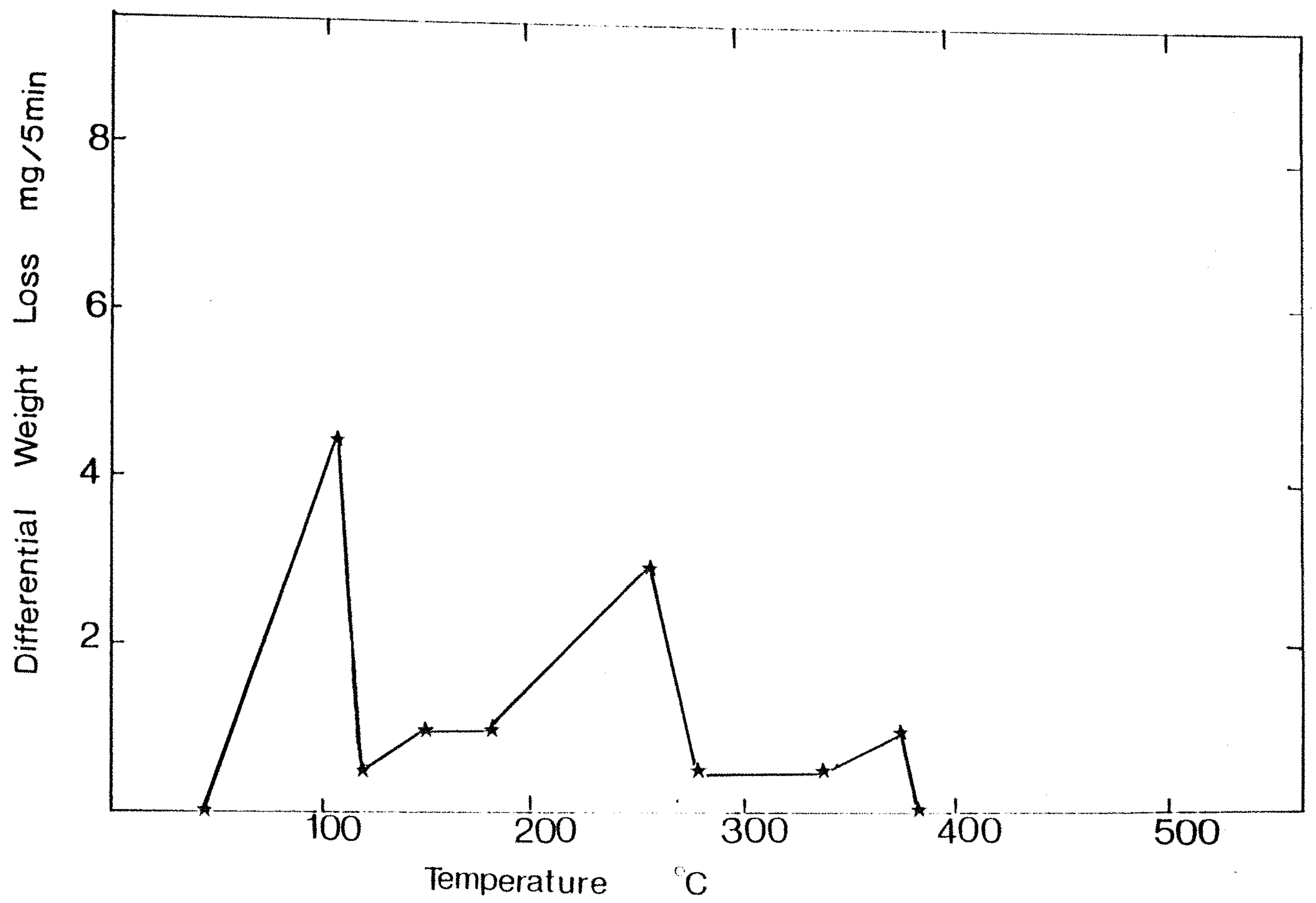
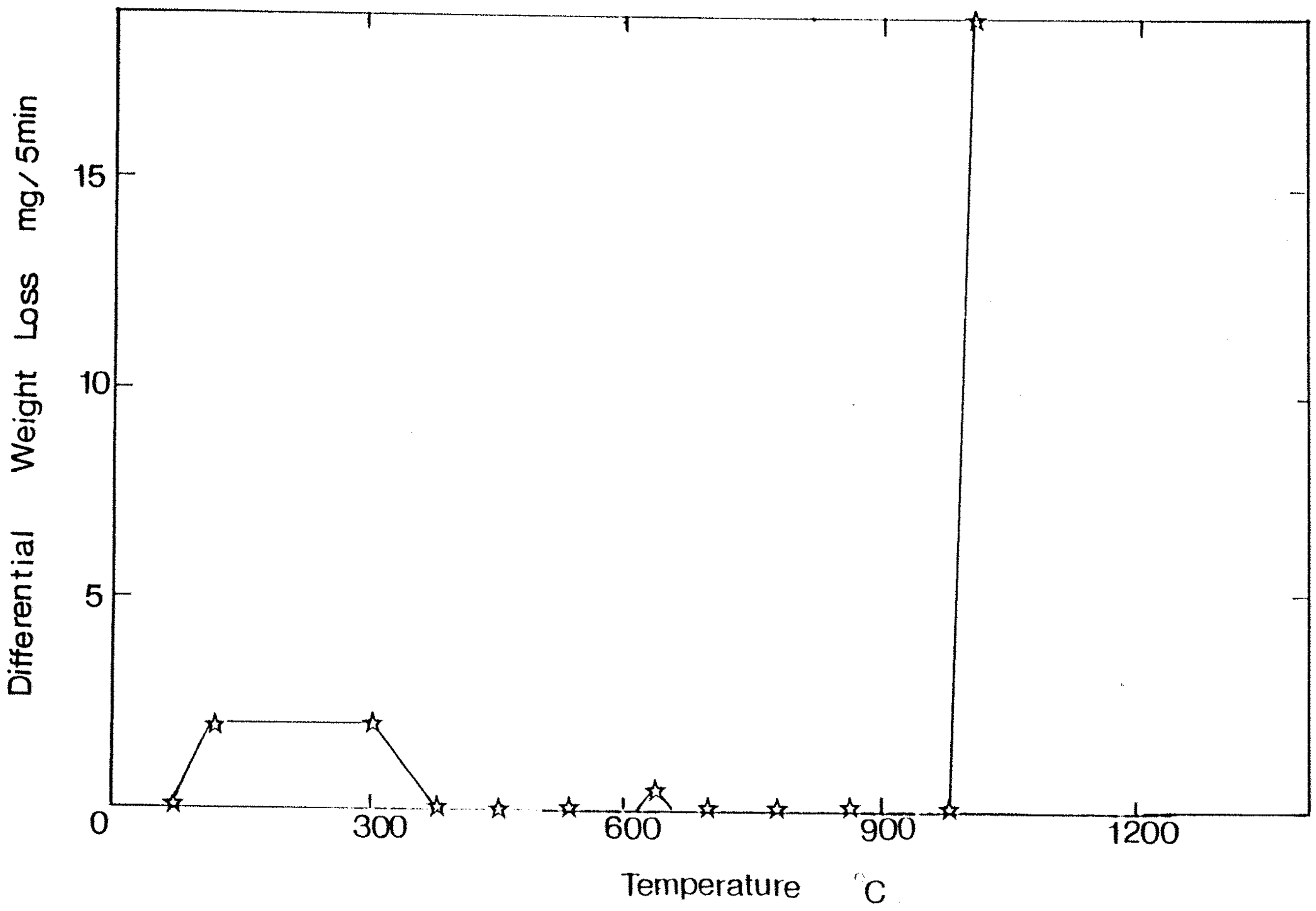


Figure 14. Thermogravimetric analysis of washed black precipitate from run 20.



Quantitative analysis for the black product after thermogravimetric analysis, gave (Found Cu, 84.3%, calculated for Cu in $Cu_2O$ 88.8%) which means copper(I) oxide was largely formed by thermal decomposition of copper(II) oxide.

### 4.2.3. Results in the Presence of Sodium Hydroxide and Peroxide

Similar reactions were carried out on hydrated copper(II) sulphate with nitrate melt containing both sodium hydroxide and peroxide, using different concentrations of reactants (Table 10). A black-brown precipitate was formed with evolution of brown nitrogen dioxide. It was noticed that with increasing concentration of bases, the colour of the precipitate became brown. No changes were observed on heating for ½ hour at 400°C. The brown quenched melt was ground into very fine particles then washed with water for 2 minutes to remove all unreacted nitrate melt and thus avoiding hydrolysis of cuprate(III) as much as possible. The solid was finally rinsed under suction with ethanol and then with ether (about 10 ml each) to dry the washed black precipitate instead of heating to 110°C, thus reducing the time for which the cuprate(III) was in contact with water. The washed black precipitate was finally dried in warm air for 5 minutes and analysed quantitatively with sodium thiosulphate and colorimetrically for copper (Table 10).

In the last runs (27-31), the reaction mixture was heated at 450°C for 3 hours producing a purple coloured product each time (colour of alkaline cuprate). Filtration in the centrifuge was suitable at this stage to obtain unwashed quenched melt (thus avoiding washing with water which causes hydrolysis of cuprate(III)) for the purpose of having it X-rayed. To start the filtration, the product was poured while hot (450°C) into the pre-heated inner tube which itself was placed in the outer tube to the furnace in the centrifuge (the filtration set is illustrated in Fig. 3).

Table 10 Quantitative analysis of washed precipitate (washed with water, ethanol and ether) obtained from reaction of hydrated or anhydrous copper(II) sulphate with nitrate melt containing sodium peroxide alone or both sodium hydroxide and peroxide.

| Run No | Wt. of melt | Conc. of NaOH | Conc of $Na_2O_2$ | Conc of $CuSO_4.5H_2O$ | Conc of $CuSO_4$ | Colour of quenched melt | | "%Cu" using $Na_2S_2O_3$ for titration | | % Cu using colorimetric method |
|---|---|---|---|---|---|---|---|---|---|---|
| | g | molal | molal | molal | molal | | | D | R | |
| 19 | 20 | N/A | 1 | N/A | 1.0 | black-brown | (1) | 71.5 ± 0.6 | N/A | 76.3 ± 1.3 |
| | | | | | | | (2) | 69.8 ± 0.3 | N/A | 65.3 |
| | | | | | | | (3) | N/A | 67.8 ± 1.0 | N/A |
| | | | | | | | (4) | N/A | 74.8 | N/A |
| 20 | 20 | N/A | 1 | N/A | 1.0 | black-brown | (1) | N/A | 75.4 ± 1.4 | N/A |
| | | | | | | | (2) | N/A | N/A | 65.3 ± 1.2 |
| 21 | 20 | N/A | 1 | N/A | 1.0 | black-brown | (1) | 72.8 ± 0.3 | N/A | 78.0 ± 1.0 |
| | | | | | | | (2) | N/A | 80.8 ± 2.4 | N/A |
| 22 | 20 | 4 | 2 | N/A | 1.0 | black-brown | (1) | N/A | 76.6 ± 1.5 | N/A |
| | | | | | | | (2) | N/A | N/A | 74.2 |
| 23 | 20 | 2 | 2 | N/A | 0.5 | brown | (1) | N/A | 71.3 ± 1.4 | N/A |
| | | | | | | | (2) | N/A | 70.8 ± 1.4 | N/A |
| | | | | | | | (3) | N/A | N/A | 67.0 ± 1.4 |
| 24 | 20 | 2 | 2 | N/A | 0.5 | brown | (1) | N/A | 68.1 ± 1.2 | N/A |
| | | | | | | | (2) | 69.6 | N/A | N/A |
| 25 | 10 | 8 | 8 | 0.14 | N/A | brown-reddish brown | N/A | N/A | N/A | N/A |
| 26 | 10 | 8 | 8 | 1.0 | N/A | violet | N/A | N/A | N/A | |

**Table 10 Continued**

| Run No | Wt. of melt | Conc. of NaOH | Conc of $Na_2O_2$ | Conc of $CuSO_4.5H_2O$ | Conc of $CuSO_4$ | Colour of quenched melt | "%Cu" using $Na_2S_2O_3$ for titration | | % Cu using colorimetric method |
|---|---|---|---|---|---|---|---|---|---|
| | g | molal | molal | molal | molal | | D | R | |
| 27 | 10 | 8 | 8 | N/A | 1 | purple | N/A | N/A | N/A |
| 28 | 10 | 8 | 8 | N/A | 0.15 | purple | N/A | N/A | N/A |
| 29 | 10 | 8 | 8 | N/A | 0.15 | dark purple | N/A | N/A | N/A |
| 30 | 10 | 8 | 8 | N/A | 0.15 | purple | N/A | N/A | N/A |

The centrifuge was then spun for about 5-10 minutes at 900 r.p.m. to get rid of most of the unreacted melt. The purple precipitate was scraped out, and the melt was discarded.

The unwashed purple precipitate obtained from filtration in the centrifuge was X-rayed. It showed the lines for sodium cuprate(III) $NaCuO_2$ in addition to the lines of nitrate melt $KNO_3$ and $NaNO_3$ (Table 11).

### 4.2.4 Discussion

In general, copper exists in three oxidation states, which are (I), (II) and (III). There are many examples of Cu(I), such as KCuO, CuI, $K[Cu(CN)_2]$ and $Cu_2O$. The latter can be obtained by thermal decomposition of copper(II) oxide above 800°C[121]. Oxidation state (II) is represented by $CuSO_4$, $K_2CuF_4$, $CuCl_2$ and CuO. Copper(II) oxide for example is obtained as a black crystalline solid by pyrolysis of copper(II) nitrate. Copper(III) is uncommon, being very easily reduced in solution to copper(II). Magee and Wood[122] reported that sodium dioxocuprate(III) was stable in basic solution, and the half-life of the $CuO_2^-$ ion was estimated to be 25 S, but Prokopchick and Norkus[119], prepared calcium cuprate in strongly basic solution in which it was evidently fairly stable. Copper(III) occurs in several crystalline compounds such as $NaCuO_2$, $KCuO_2$, $LiCuO_2$ and other alkali and alkaline-earth cuprates, which are obtained by heating the appropriate oxide mixture in an atmosphere of oxygen.

In melts, copper(II) oxide has been prepared from copper(II) nitrate trihydrate in molten nitrate at 300°C[88] or from copper(II) sulphate in molten nitrite starting at 120°C[123]. There is no information in the literature on the formation of copper(III) in any melt.

Table 11 X-ray diffraction of the purple product obtained from run 27, Table 10, by centrifugal separation.

| Sample from centrifuge | | Assigned (J.C.P.D.S.) index | | |
|---|---|---|---|---|
| d-spacings Å | I/Io | Compound | d-spacings Å | I.Io |
| 6.02 | 27 | | | |
| 5.50 | 21 | $NaCuO_2$ | 5.24 | 95 |
| 5.36 | 17 | | | |
| 4.70 | 28 | $KNO_3$ | 4.66 | 23 |
| 3.79 | 100 | $KNO_3$ | 3.78 | 100 |
| 3.76 | 61 | $KNO_3$ | 3.73 | 56 |
| 3.16 | 47 | $NaCuO_2$ | 3.17 | 80 |
| 3.05 | 74 | $NaNO_3$ | 3.03 | 100 |
| 2.98 | 23 | | | |
| 2.72 | 36 | $NaCuO_2$ | 2.72 | 70 |
| 2.65 | 83 | $NaCuO_2$ | 2.62 | 40 |
| 2.57 | 19 | $NaNO_3$ | 2.58 | 56 |
| 2.51 | 19 | | | |
| 2.45 | 19 | $NaCuO_2$ | 2.45 | 70 |
| 2.41 | 20 | $KNO_3$ | 2.40 | 7 |
| 2.37 | 27 | $KNO_3$ | 2.36 | 4 |
| 2.35 | 37 | $KNO_3$ | 2.33 | 9 |
| 2.29 | 24 | $NaNO_3$ | 2.31 | 25 |
| 2.27 | 20 | $KNO_3$ | 2.29 | 5 |
| 2.19 | 55 | $KNO_3$ | 2.19 | 41 |
| 2.06 | 20 | $NaCuO_2$ | 2.05 | 100 |
| 2.04 | 29 | $NaCuO_2$ | 2.04 | 35 |
| 1.94 | 31 | $KNO_3$ | 1.94 | 24 |

It would be noted that the results of Table 3, i.e. "% Cu" D or column 5 direct procedure, (see 2.6.2) were close to those of % Cu or column 6, except for run 6, where "% Cu" D was higher than % Cu possibly due to accidental errors, but that when the titration procedure with sodium thiosulphate was reversed (addition of excess potassium iodide to the brown quenched melt first and then dilute acid) the "% Cu" R was much higher than % Cu, Table 3. This was probably because of additional liberated iodine from reduction of copper(III) to copper(II), thus ultimately increasing the volume of sodium thiosulphate required. However, in contrast the titration with EDTA estimated only copper(II) because enough time was allowed for any copper(III) present in the dilute acidic aqueous solution to decompose to copper(II). Similarly when the brown quenched melt was washed with water alone, filtered and then dried. Closely similar results between "% Cu" D and % Cu (column 5, 7 and 8, Table 8) were obtained.

For run 7, it may be that the analysis is close to those for copper(II) hydroxide (calculated for Cu in $Cu(OH)_2$ 64.94%) but for run 9 the analysis is closer to copper(II) oxide (calculated for Cu in CuO 79.74%). This may be because of the difference in time and temperature of the runs (maximum temperature for run 7 was 294°C for 10 minutes while maximum temperature for run 9 was 380°C for 20 minutes). At the higher temperature the hydroxide would decompose to the oxide.

X-ray diffraction of the washed black precipitate obtained from run 20 (Table 9) showed a mixture of copper(II) oxide CuO, basic copper(II) nitrate $Cu_2(OH)_3NO_3$ and possibly copper(II) hydroxide $Cu(OH)_2$, suggesting that there was at least 5% of each compound present. From the intensities, the major component seems to be copper(II) oxide.

Thermogravimetric analysis on the washed black precipitate from run 19 showed that total weight loss found was 4.5%, which could be expected from about 25% of copper(II) hydroxide or about 15% of basic copper(II) nitrate with the remainder as copper(II) oxide. Alternatively the weight loss could be due to about 10.0% of copper(II) hydroxide and 5.5% basic copper(II) nitrate with the remainder as copper(II) oxide. This would be consistent with the three compounds indicated by x-ray diffraction. This mixture would have a copper analysis of 76.8%, which is in the range of values found (Table 10, run 19 and 20), and as are the values for the two binary mixtures above (76.0% and 75.7% Cu).

X-ray diffraction of the centrifuged, unwashed, purple quenched melt from run 27 (Table 10), showed the lines of sodium cuprate(III) $NaCuO_2$ and this proved the formation and stabilisation of the cuprate(III) in basic molten nitrate. It is clear that cuprate(III) can be easily decomposed within seconds when washed with water.

The formation of Cuprate(III) can be explained as follows:

Thermal decomposition of sodium peroxide and/or of sodium hydroxide are the likely sources of oxide ($O^{2-}$), i.e.

$$O_2^{2-} \longrightarrow O^{2-} + \tfrac{1}{2}O_2 \qquad \text{... (47)}$$

$$2OH^- \longrightarrow O^{2-} + H_2O\uparrow \qquad \text{... (49)}$$

Since the self-ionization of nitrate melt is very low at 250°C - 300°C (see 1.4), the oxidation would probably mainly be caused by sodium peroxide, suggesting the reaction:

$$Cu^{2+} + Na_2O_2 + 3NO_3^- + M^+ \longrightarrow MCuO_2 + Na_2O + 3NO_2\uparrow + O_2 \qquad \text{... (54)}$$

(where M is Li, K or Na)

The decomposition of cuprate(III) will probably be according to Prokopchick and Norkus'[119] suggestion,

$$MCuO_2 + 2H_2O \longrightarrow MOH + Cu(OH)_3 \longrightarrow CuO\downarrow + H_2O + \tfrac{1}{2}O_2 \quad \ldots (55)$$

and because of the excess nitrate, basic copper(II) nitrate formation is also possible [Duval[118], suggested a formula $CuX.3Cu(OH)_2.yH_2O$, in which x denotes $SO_4^{2-}$, $(NO_3)_2^{2-}$ or $(Cl)_2^{2-}$ when a base such as potassium hydroxide was added to solutions of copper(II) sulphate, nitrate or chloride resulting in the formation of basic salts].

[illegible]
CuX . 3 [illegible]

In nitrate melt containing sodium hydroxide alone, a black precipitate formed when copper(II) sulphate pentahydrate was added. This black precipitate might well be copper(II) hydroxide and/or copper(II) oxide, following the equation:

$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2 \longrightarrow CuO\downarrow + H_2O \quad \ldots (56)]$$

### 4.2.5 Conclusion

The investigation of copper(II) sulphate in basic molten nitrate showed that cuprate(III) was formed, but that it decomposed during the extraction when washed with water as proved by the analyses of washed black precipitate, Tables 8 and 10 and the x-ray diffraction results, Table 9.

The above facts are in agreement with the results of Magee and Wood[122] who showed that copper(III) can be present in aqueous solutions only in the presence of large stabilizing anions (such as periodate or tellurate) or in the presence of large concentrations of a base and that they are stable as dry solids but dissolve with decomposition in aqueous solutions.

Filtering off the purple precipitate in the centrifuge thus removing most of the unreacted nitrate melt as well as any other soluble species, will minimize the amount of water and time required to wash out nitrate melt before decomposition of copper(III) occurs.

To confirm that cuprate(III) has been formed, x-ray diffraction on the unwashed, quenched melt was carried out, and showed the lines for sodium cuprate(III).

It would also be worth using large stabilising anions as well as high concentration of a base in the course of the cuprate(III) preparation in molten nitrate.

## 4.3 Reaction of Hydrated and Anhydrous Cobalt(II) Chloride in Basic Lithium Nitrate-Potassium Nitrate Eutectic.

### 4.3.1. Results in the Presence of Sodium Hydroxide

Cobalt(II) chloride hexahydrate (0.1 molal) was observed to react with lithium nitrate-potassium nitrate eutectic (10 g) containing sodium hydroxide (8 molal), when it was added at 350°C forming a dark brown-black precipitate with the evolution of brown nitrogen dioxide. Heating to 450°C for 3 hours, the colour of the precipitate became black. Qualitative analysis on the unwashed quenched melt showed the presence of an oxidising agent.

### 4.3.2. Results in the Presence of Sodium Peroxide

Similar experiments were carried out, listed in Table 12, using twice the concentration of hydrated cobalt(II) chloride but with added sodium peroxide instead of hydroxide. A dark green solution was obtained. No changes were observed after heating for 5 hours at 450°C.

### 4.3.3. Results in the Presence of Sodium Hydroxide and Peroxide

A dark green solution was obtained when hydrated or anhydrous cobalt(II) chloride reacted with lithium nitrate-potassium nitrate eutectic containing both sodium hydroxide and sodium peroxide (see Table 12). Qualitative tests on the green quenched melt showed the presence of an oxidising agent which might be nitrate, peroxide or cobalt in a higher oxidation state than 2+. When water was added to the unwashed product, many colourless bubbles were observed, perhaps of oxygen, evolved from the high oxidation cobaltate thought to have been formed (the dark green solution obtained earlier) or possibly from unreacted sodium peroxide.

When the concentration of hydrated or anhydrous cobalt(II) chloride was increased (to more than 0.1 molal), using the same concentration of the bases (a ratio of 1:1), a black precipitate was formed.

In order to try and precipitate the species responsible for the dark green colour, presumed to be a cobaltate anion, the following experiment was repeated several times (see Table 13). A barium(II) chloride solution in lithium nitrate-potassium nitrate melt (1 molal), prepared and kept at 450°C, was added to the dark green solution of cobalt, also kept at 450°C, in the hope of precipitating a barium cobaltate species. A brown precipitate formed and was filtered off in the centrifuge. When the quenched product was tested qualitatively, it showed the presence of an oxidising agent, barium(II) and nitrate. It was incompletely soluble in water giving many colourless gas bubbles (possibly oxygen evolved from hydrolysis of a cobaltate or from unreacted sodium peroxide). It was completely soluble in concentrated acids.

The washed black precipitate after being dissolved in acid showed the presence of cobalt(II) when tested qualitatively (see section 2.6.1), perhaps because of the reduction of cobaltate to a simple salt of cobalt(II) possibly $Co(OH)NO_3$. This, with excess sodium hydroxide, could be converted to pink suspension of $Co(OH)_2$.

The filtered and washed black precipitate from run 5 was examined by X-ray diffraction which gave "d"-spacings close to those of $BaCO_3$ and $K_3Co(NO_2)_6$ (see Table 14).

**Table 12.** **Reaction of hydrated or anhydrous cobalt(II) chloride, with nitrate melt containing either sodium hydroxide alone or sodium peroxide alone, or both bases.**

| Run No | Wt of melt | Conc of NaOH | Conc of $Na_2O_2$ | Conc of $CoCl_2 6H_2O$ | Conc of $CoCl_2$ | Colour of solution | Colour of quenched melt | Colour of ppt |
|---|---|---|---|---|---|---|---|---|
| | g | molal | molal | molal | molal | | | |
| 2 | 10 | 8 | - | 0.1 | - | - | grey | black |
| 3 | 5 | - | 9 | 0.2 | - | dark green | pale-green | - |
| 4 | 5 | - | 8 | - | 0.3 | grey green | pale-green | - |
| 5 | 5 | - | 8 | - | 0.3 | dark green | pale green | - |
| 6 | 5 | - | 8 | - | 0.3 | dark green | pale green | - |
| 7 | 5 | 4 | 4 | 0.1 | - | dark green | pale green | - |
| 8 | 5 | 4 | 4 | 0.1 | - | dark green | pale green | - |
| 9 | 10 | 8 | 8 | 0.1 | - | dark green | pale green | - |
| 10 | 10 | 8 | 8 | 0.1 | - | dark green | pale green | - |
| 11 | 10 | 8 | 8 | - | 0.2 | dark green | pale green | - |
| 12 | 10 | 8 | 8 | - | 0.1 | dark green | pale green | - |
| 13 | 10 | 8 | 8 | - | 0.1 | light green | green | - |
| 14 | 10 | 8 | 8 | - | 0.1 | dark green | pale green | - |
| 15 | 10 | 8 | 8 | - | 0.6 | - | dark grey | black |
| 16 | 2 | 8 | 8 | 2.0 | - | - | dark grey | black |
| 22 | 11 | 8 | 8 | 0.1 of hydrated $CoSO_4$ | - | - | grey | black |

Table 13 Reaction of hydrated or anhydrous cobalt(II) chloride with nitrate melt containing either sodium hydroxide or sodium peroxide, or both with the addition of barium chloride solution in nitrate melt

| Run No | Wt of melt g | Conc of NaOH molal | Conc of $Na_2O_2$ molal | Conc of $CoCl_2.6H_2O$ molal | Conc of $CoCl_2$ molal | Conc of $BaCl_22H_2O$ molal | Colour of solution before addition of $BaCl_2.2H_2O$ solution | Colour of ppt formed after addition of $BaCl_2.2H_2O$ soln |
|---|---|---|---|---|---|---|---|---|
| 4 | 5 | - | 8 | - | 0.3 | 1.0 | dark green | grey |
| 5 | 5 | - | 8 | - | 0.3 | 1.0 | dark green | brown |
| 8 | 5 | 4 | 4 | 0.1 | - | 1.0 | dark green | brown |
| 9 | 10 | 8 | 8 | 0.1 | - | 1.0 | dark green | brown |
| 12 | 10 | 8 | 8 | - | 0.1 | 1.0 | dark green | brown |
| 13 | 10 | 8 | 8 | - | 0.1 | 1.0 | light green | brown |
| 14 | 10 | 8 | 8 | - | 0.1 | 0.5 | dark green | dark grey |
| 16 | 10 | - | 8 | 0.3 | - | 0.5 | dark brown-black | black |
| 17 | 10 | - | 8 | - | 0.3 | 0.5 | brown-grey | black |
| 19 | 5 | - | 8 | - | 0.3 | 0.5 | black-grey | black |
| 20 | 10 | 8 | 8 | - | 0.2 | 1.0 | dark green-black | black |
| 21 | 10 | 8 | 8 | - | 0.1 | 1.0 | brown-grey | black |

A similar experiment was carried out but on hydrated cobalt(II) sulphate instead of cobalt(II) chloride (see Table 12). A black precipitate was formed with evolution of brown nitrogen dioxide. No changes were observed on heating for 3 hours at 450°C. The reaction product was spun in the centrifuge to filter off the precipitate. The unwashed grey quenched melt was examined by X-ray diffraction (Fig 13), and gave "d"-spacings close to those of $K_3Co(NO_2)_6$ in addition to the lines of $KNO_3$ and $LiNO_3$, also $NaNO_3$, $KNO_2$, $LiNO_2$, $Na_2O$, $K_2O$, LiOH and $Co(OH)_2$ (Table 15) and Fig. 15.

### 4.3.4. Discussion

In general, the most common oxidation state for cobalt is (II) e.g. compounds such as CoS, $CoCl_2$ and CoO and complexes such as $[Co(NH_3)_6Cl_2$ and $[Co(CN)_5]^{3-}$. Cobalt(II) oxide for example can be prepared by heating cobalt(II) carbonate or nitrate[121]. Oxidation state(III) is relatively unstable in simple complexes (called high-spin complexes) because of four unpaired electrons in the d orbitals and this will cause the decrease in crystal field splitting energy and ultimately decrease the stability of the complex. On the other hand cobalt(III) low-spin complexes are stable, because unpaired electrons have been forced to pair and this will increase the crystal field energy which increases the stability of the complex, as in $[Co(NH_3)_6]Cl_3$, $Cu_3[Co(CN)_6]$ and $K_3[Co(NO_2)_6]$. Having mentioned that, $[CoF_6]^{3-}$ is a high-spin complex but found to be stable. In molten salts, and in particular molten nitrate and nitrite, cobalt(II) and (III) compounds or complexes have been obtained. Tricobalt tetraoxide has been prepared from $Co(NO_3)_2$ in lithium nitrate potassium nitrate eutectic at 350°C[99]. Potassium hexanitro cobaltate(III) has been obtained from cobalt(II) chloride in lithium nitrite-potassium nitrite at 120°C[123].

Figure 15. X-ray diffraction of the unwashed grey quenched melt obtained from run 22.

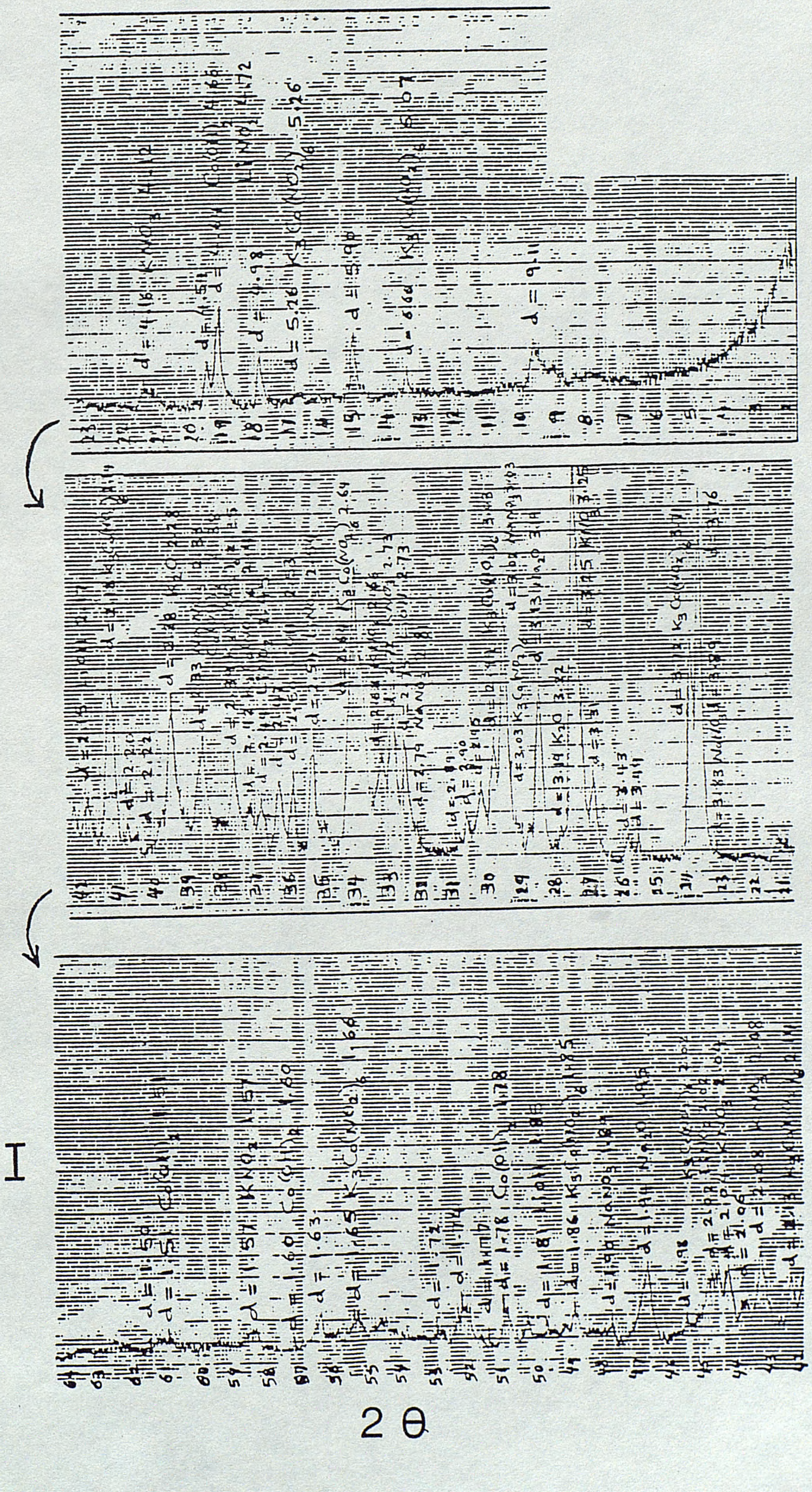


Table 14 X-ray diffraction for washed black precipitate obtained from the reaction of $CoCl_2$ in lithium nitrate-potassium nitrate eutectic containing sodium peroxide with the addition of $BaCl_2.2H_2O$ solution.

| Washed black precipitate | | From J.C.P.D.S. Index | | | |
|---|---|---|---|---|---|
| | | $BaCO_3$ | | $K_3Co(NO_2)_6$ | |
| d-spacings | $I/I_o$ | d-spacings Å | $I/I_o$ | d-spacings Å | $I/I_o$ |
| 4.55 | 26 | 4.56 | 9 | | |
| 3.70 | 98 | 3.72 | 100 | 3.71 | 60 |
| 3.20 | 27 | 3.21 | 15 | | |
| 2.61 | 44 | 2.62 | 24 | 2.62 | 100 |
| 2.14 | 36 | 2.15 | 28 | 2.14 | 75 |
| 2.02 | 29 | 2.04 | 10 | 2.02 | 16 |
| 2.01 | 33 | 2.01 | 21 | | |
| 1.95 | 21 | 1.94 | 15 | | |
| 1.93 | 30 | 1.94 | 15 | | |
| 1.85 | 20 | 1.85 | 3 | 1.85 | 18 |
| 1.65 | 22 | 1.67 | 5 | 1.66 | 20 |
| 1.51 | 22 | 1.52 | 4 | | |

Table 15 X-ray diffraction of the reaction of hydrated cobalt(II) sulphate in lithium nitrate-potassium nitrate eutectic containing sodium hydroxide and sodium peroxide

| Unwashed grey quenched melt | | Assigned (J.C.P.D.S.) Index | | |
|---|---|---|---|---|
| d spacings Å | $I/I_o$ | Compound | d-spacings Å | $I/I_o$ |
| 9.11 | 22 | | | |
| 6.60 | 16 | $K_3Co(NO_2)_6$ | 6.07 | 30 |
| 5.90 | 25 | | | |
| 5.26 | 12 | $K_3Co(NO_2)_6$ | 5.26 | 35 |
| 4.98 | 20 | | | |
| 4.64 | 31 | $Co(OH)_2$ | 4.66 | 70 |
| | | $LiNO_2$ | 4.72 | 100 |
| 4.54 | 18 | | | |
| 4.16 | 14 | $KNO_3$ | 4.12 | 40 |
| 3.83 | 11 | $NaNO_3$ | 3.89 | 6 |
| 3.72 | 59 | $K_3Co(NO_2)_6$ | 3.71 | 60 |
| 3.49 | 14 | | | |
| 3.43 | 14 | | | |
| 3.31 | 29 | | | |
| 3.25 | 100 | $KNO_3$ | 3.25 | 100 |
| 3.19 | 16 | $K_2O$ | 3.22 | 75 |
| 3.13 | 53 | $Na_2O$ | 3.19 | 40 |
| 3.03 | 30 | $K_3Co(NO_2)_6$ | 3.03 | 25 |
| 3.02 | 68 | $NaNO_3$ | 3.03 | 100 |
| 2.99 | 38 | $K_3Co(NO_2)_6$ | 3.03 | 25 |
| 2.95 | 27 | | | |
| 2.90 | 21 | | | |
| 2.89 | 15 | | | |
| 2.79 | 15 | $NaNO_3$ | 2.81 | 16 |
| 2.75 | 37 | LiOH | 2.73 | 100 |
| 2.72 | 44 | $KNO_3$ | 2.73 | 80 |
| 2.68 | 36 | $KNO_3$ | 2.66 | 41 |
| 2.64 | 78 | $K_3Co(NO_2)_6$ | 2.64 | 100 |
| 2.54 | 39 | $LiNO_3$ | 2.54 | 75 |
| 2.50 | 31 | LiOH | 2.53 | 70 |
| 2.47 | 28 | | | |
| 2.44 | 24 | $LiNO_2$ | 2.45 | 40 |
| 2.42 | 23 | $K_3Co(NO_2()_6$ | 2.41 | 14 |
| 2.39 | 36 | $K_3Co(NO_2)_6$ | 2.35 | 45 |
| | | $Co(OH)_2$ | 2.38 | 100 |
| 2.33 | 39 | $NaNO_3$ | 2.33 | 25 |
| 2.28 | 49 | $K_2O$ | 2.28 | 100 |
| 2.22 | 17 | | | |
| 2.20 | 19 | | | |
| 2.18 | 58 | $K_3Co(NO_2)_6$ | 2.14 | 75 |
| 2.15 | 25 | LiOH | 2.17 | 40 |

Table 15 Continued/...

| Unwashed grey quenched melt | | Assigned (J.C.P.D.S.) Index | | |
|---|---|---|---|---|
| d spacings Å | $I/I_o$ | Compound | d-spacings Å | $I/I_o$ |
| 2.13 | 25 | $K_3Co(NO_2)_6$ | 2.14 | 75 |
| 2.08 | 30 | $KNO_3$ | 2.08 | 60 |
| 2.06 | 19 | | | |
| 2.04 | 26 | $KNO_3$ | 2.04 | 60 |
| 2.02 | 27 | $LiNO_2$ | 2.02 | 95 |
| | | $K_3Co(NO_2)_6$ | 2.02 | 16 |
| 1.98 | 15 | | | |
| 1.94 | 27 | $Na_2O$ | 1.95 | 100 |
| 1.90 | 15 | $NaNO_3$ | 1.89 | 16 |
| 1.86 | 18 | $K_3Co(NO_2)_6$ | 1.85 | 18 |
| 1.81 | 15 | $LiOH$ | 1.85 | 50 |
| 1.78 | 19 | $Co(OH)_2$ | 1.78 | 19 |
| 1.77 | 7 | | | |
| 1.65 | 17 | $K_3Co(NO_2)_6$ | 1.66 | 20 |
| 1.60 | 12 | $Co(OH)_2$ | 1.60 | 50 |
| 1.57 | 14 | $KNO_2$ | 1.57 | 18 |
| 1.51 | 13 | $Co(OH)_2$ | 1.51 | 8 |

The reaction of cobalt(II) chloride with lithium nitrate-potassium nitrate eutectic containing sodium hydroxide, probably gave a black precipitate of tricobalt tetraoxide, because cobalt(II) cation presumably behaved as a Lux-Flood acid (i.e. oxide acceptor) and sodium hydroxide or nitrate as Lux-Flood base (i.e. oxide donor) forming cobalt (II, III) oxide $Co_3O_4$. Partial oxidation is also involved.

The behaviour of sodium hydroxide in nitrate melt has been discussed earlier in this chapter (see section 3.2.1). Thermal decomposition of hydroxide will provide oxide ($O^{2-}$i.e.

$$2OH^- \longrightarrow O^{2-} + H_2O\uparrow \qquad \ldots (49)$$

As Duke suggested, a self-ionization of nitrate melt also takes place (section 1.4), i.e.

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \quad K = 2.7 \times 10^{-26} \text{ at } 250°C$$
$$K = 5.7 \times 10^{-24} \text{ at } 300°C \qquad \ldots (11)$$

Since, the self ionization of nitrate melt is very low, sodium hydroxide will be the main source of oxide ($O^{2-}$). In addition, an oxide acceptor would act as an acid by displacing the equilibrium (II) to the right and increasing the nitryl ion concentration. The nitryl ion was thought to react with excess of nitrate, thus

$$NO_2^+ + NO_3^- \rightleftharpoons [N_2O_5] \longrightarrow 2NO_2\uparrow + \tfrac{1}{2}O_2 \qquad \ldots (12)$$

Formation of tricobalt tetraoxide can reasonably be represented by the following equation:

$$3Co^{2+} + 2NaOH + 6NO_3^- \longrightarrow Co_3O_4 + Na_2O + 6NO_2$$
$$+ H_2O\uparrow + O_2 \qquad \ldots (57)$$

Thus addition of sodium hydroxide to nitrate melt will increase the concentration of oxide ($O^{2-}$) and ultimately stabilise any higher oxidation states formed.

From results in 4.3.3 (Table 14), barium carbonate (identified by X-ray diffraction) is probably formed from reaction of soluble barium cation ($Ba^{2+}$) in nitrate melt with carbonate anion ($CO_3^{2-}$) (possibly present as impurity in sodium hydroxide or sodium peroxide), to form insoluble barium carbonate, i.e.

$$Ba^{2+} + CO_3^{2-} \longrightarrow BaCO_3 \qquad \ldots (58)$$

The second product, identified also by X-ray diffraction, was potassium hexanitro cobaltate(III) and this probably was formed in the following way. Zambonin, Jordan and Kerridge[39-46], suggested that according to eqn. (19), oxide is oxidised to peroxide ($O_2^{2-}$) in molten nitrates,

$$O^{2-} + NO_3^- \rightleftharpoons NO_2^- + O_2^{2-} \quad K \simeq 3 \qquad \ldots (19)$$

The behaviour of sodium peroxide in nitrate melt has been reviewed in this chapter (see section 3.2.1). Thermal decomposition of sodium peroxide will be as follows:

$$O_2^{2-} \longrightarrow O^{2-} + \tfrac{1}{2}O_2\uparrow \qquad \ldots (47)$$

So the concentration of oxide ($O^{2-}$) will be increased causing displacement in the equilibrium (19) to the right and ultimately will increase the concentration of nitrite ($NO_2^-$) and favour the formation of $K_3[Co(NO_2)_6]$.
The overall reaction can be reasonably written as follows:

$$Co^{3+} + 6NO_2^- + 3K^+ \longrightarrow K_3[Co(NO_2)_6]\downarrow \qquad \ldots (59)$$

Potassium hexanitrocobaltate(III) was formed in nitrate melt as a black precipitate, in nitrite melt[123] as insoluble yellow-green, and in aqueous[124] solution as a yellow precipitate, and its formation was probably because Co(II) was oxidised to Co(III) by either nitrate or peroxide and because Co(III) is a complex- former showing a particular affinity for nitrogen donors (the majority of its complexes contain $NH_3$, ethylenediamine, $NO_2$ group etc.). The oxidation of Co(II) → Co(III) in the presence of $NO_2^-$ causes the formation of the stable black precipitate of potassium hexanitrocobaltate(III) $K_3[Co(NO_2)_6]$.

When hydrated cobalt(II) sulphate reacted with nitrate melt containing both sodium hydroxide and peroxide (run 22 Table 7), potassium hexanitrocobaltate(III) was identified by X-ray diffraction together with many other compounds (Table 15). These compounds possibly were formed, because lithium, sodium and potassium were available in the presence of sodium hydroxide and peroxide. Cation exchange could easily have happened and this caused great difficulty in matching the lines and intensities of the compounds formed with those from the (J.C.P.D.S.) index (because X-ray was done on the unwashed product obtained from run 22, Table 7).

## 4.4. <u>Reaction of Anhydrous and Hydrated Nickel(II) Chloride in Basic Lithium Nitrate-Potassium Nitrate Eutectic</u>

### 4.4.1. Results in the Presence of Sodium Hydroxide

About 5 g of lithium nitrate-potassium nitrate eutectic was transferred to a pyrex tube with a B24 socket and placed in a furnace at 200°C. Sodium hydroxide (4 molal) was added at 250°C forming a milky suspension with evolution of water vapour. At 350°C anhydrous nickel(II) chloride (0.2 molal) was added with formation of a black precipitate and brown nitrogen dioxide with no change in colour up to 450°C. The product was grey-black at room temperature. The product was ground and washed with water for 2 minutes (which is the minimum time to dissolve the unreacted nitrate melt while avoiding the hydrolysis of the product obtained).

The washed black precipitate was washed again initially with ethanol and secondly with ether then dried. Qualitative tests showed the black precipitate was an oxidising agent and contained nitrate but not peroxide. The black precipitate was insoluble in water but completely dissolved in concentrated sulphuric acid.

### 4.4.2. Results in the Presence of Sodium Peroxide

A similar reaction was carried out with anhydrous nickel(II) chloride (2 molal) and sodium peroxide (4 molal) added at 306°C. A black precipitate formed immediately with the evolution of brown nitrogen dioxide. There were no changes on heating at 450°C for 1 hour. After cooling the black product was ground, washed with water for 2 minutes (to remove unreacted melt and other soluble species), then with ethanol and ether. After drying the black precipitate, qualitative tests showed the presence of oxidising agent, nitrate and absence of peroxide. The black precipitate was insoluble in water but dissolved completely in concentrated hydrochloric acid.

Corresponding reactions with nickel(II) chloride hexahydrate gave similar results (Table 16).

### 4.4.3. Results in the Presence of Sodium Hydroxide and Peroxide.

About 11 g of lithium nitrate-potassium nitrate was transferred to a pyrex tube with B24 socket and placed in a furnace. Sodium hydroxide (8 molal) was added at 252°C forming a milky suspension with evolution of water vapour. At 350°C, sodium peroxide (8 molal) and nickel(II) chloride hexahydrate (0.1 molal) were added giving a black precipitate with the evolution of brown nitrogen dioxide. When the temperature reached 450°C, the reaction mixture was heated for 5 hours but no changes were observed. The quenched product (unwashed) was tested qualitatively showing the presence of oxidising agent, nitrate and peroxide. The product was insoluble in water.

## 4.5. Reaction of Hydrated Nickel(II) Sulphate in Lithium Nitrate-Potassium Nitrate Eutectic containing Sodium Hydroxide and Sodium Peroxide

### 4.5.1. Results

About 10 g of lithium nitrate-potassium nitrate eutectic was weighed and then transferred to a pyrex tube with a B24 socket and placed in a furnace at 170°C. Sodium hydroxide (3 molal) was added at 240°C which formed a milky suspension with the evolution of water vapour, which collected on the neck of the drying tube. When the temperature had reached 350°C both sodium peroxide (8 molal) and the hydrated nickel(II) sulphate (0.1 molal) were added forming a black mixture and brown nitrogen dioxide gas which was continuously evolved. The temperature of the reaction was increased to 450°C, and the mixture was heated for 3 hours giving a black precipitate.

This was filtered off by spinning the mixture in the modified centrifuge (using the apparatus shown earlier in Fig 3, section 2.4) for 10 minutes with a maximum speed of 900 r.p.m.. The black precipitate remaining was transferred to a porcelain dish. The colour of the product was grey after cooling. X-ray diffraction of the ground product gave d-spacings close to those for $LiNiO_2$ (Table 17).

The quenched product was dissolved in water (to remove unreacted melt and other soluble species), then filtered. The washed black product gave d-spacings which corresponded quite closely to those for $LiNiO_2$ (Table 18).

Repetition of the experiment with different concentrations of bases (Table 19), gave similar black products. Qualitative tests on the latter (both unwashed and washed) showed that they were oxidising agents and insoluble in water, in addition to the presence of lithium. X-ray diffraction of washed black precipitate obtained from both run 9 and 10 (see Table 19) also gave d-spacings corresponding to those of $LiNiO_2$.

### 4.5.2. Discussion

In general, nickel exists in several oxidation states, though by far the most common and stable is (II), (e.g. NiO), which can be prepared by heating $Ni(NO_3)_2.6H_2O$ to 800°C[121]. Nickel (O) is represented by $Ni(CO)_4$ and a yellow cyano complex $K_4[Ni(CN)_4]$. The latter can be obtained by reduction of $K_2[Ni(CN)_4]$ in liquid ammonia with excess potassium, and oxidises immediately on exposure to air.

TABLE 16: Reaction of hydrated nickel(II) chloride with nitrate melt containing sodium hydroxide alone or sodium peroxide alone or both bases.

| Run No. | Wt. of melt g | Conc. of NaOH molal | Conc. of $Na_2O_2$ molal | Conc. of $NiCl_2$ molal | Conc. of $NiCl_2.6H_2O$ molal | Colour of product |
|---|---|---|---|---|---|---|
| 2 | 5.0 | 4 | - | 0.2 | - | Black |
| 3 | 5.5 | - | 4.0 | 0.2 | - | Black |
| 4 | 4.6 | 4 | - | - | 0.2 | Black |
| 5 | 4.6 | - | 6.8 | - | 0.2 | Black |
| 6 | 11.0 | 8 | 8.0 | - | 0.1 | Grey-black |

Table 17. X-ray diffraction of unwashed grey product obtained from the reaction of hydrated nickel(II) sulphate in the melt in the presence of sodium hydroxide and sodium peroxide.

| Grey Product (unwashed) | | $LiNiO_2$ from J.C.P.D.S. Index (A.S.T.M.) | |
|---|---|---|---|
| d-spacings Å | I/Io | d-spacings Å | I/Io |
| 4.65 | 25 | 4.72 | 100 |
| 2.04 | 24 | 2.04 | 95 |
| 2.49 | 16 | 2.45 | 40 |
| 1.94 | 24 | 1.96 | 118 |

Table 18. X-ray diffraction of the washed black product obtained from the reaction of hydrated nickel(II) sulphate in the melt in the presence of sodium hydroxide and sodium peroxide

| Black product (washed) | | $LiNiO_2$ from J.C.P.D.S. Index (A.S.T.M.) | |
|---|---|---|---|
| d-spacings Å | I/Io | d-spacings Å | I/Io |
| 4.78 | 100 | 4.72 | 100 |
| 2.02 | 85 | 2.04 | 95 |
| 2.43 | 55 | 2.45 | 40 |
| 2.36 | 25 | 2.36 | 12 |

Nickel(I) is uncommon, e.g. dark red $K_4[Ni_2(CN)_6]$ which can be made by sodium amalgam reduction of aqueous $K_2[Ni(CN)_4]$. Higher oxidation states are nickel(III) and nickel(IV) and occur in a few compounds such as nickel(III) oxide hydroxide NiO(OH), or in complex fluorides such as $K_3[NiF_6]$, $K_2[NiF_6]$.

$NiO_2.xH_2O$ is another example of Ni(III) which can be made from oxidation of alkaline nickel sulphate solution by NaOCl which gives a black "peroxide" $NiO_2.xH_2O$. This is unstable being readily reduced by water. Nickel(III) is also represented by sodium nickelate $NaNiO_2$ and several related compounds which can be prepared by bubbling oxygen through molten alkali metal hydroxides contained in nickel vessels at about 800°C. Other oxides and oxide phases[121] can be made by heating NiO with alkali or alkaline earth oxides in oxygen. These mixed oxides evolve oxygen on treatment with water or acid.

In molten salts, in particular molten nitrates and nitrites, nickel(II) oxide has been prepared as a black precipitate when solutions of nickel(II) chloride, sulphate and nitrate in lithium nitrate-potassium nitrate decomposed (at 470°C for chloride and at 440°C for nitrate[96]). Nickel(II) oxide has been formed from nickel(II) chloride in lithium nitrite-potassium nitrite[123].

From results obtained in section 4.a.1. and 4.a.2, reaction of nickel(II) chloride in lithium nitrate-potassium nitrate containing either sodium hydroxide or peroxide, probably gave a black precipitate of nickel(II) oxide NiO, according to the following sequence.
Sodium hydroxide will decompose thermally,

$$2OH^- \longrightarrow O^{2-} + H_2O\uparrow \quad ...(49)$$

$$\text{and} \quad O^{2-} + Ni^{2+} \longrightarrow NiO \quad ...(60)$$

Table 19: Reaction of hydrated nickel(II) sulphate with nitrate melt in the presence of sodium hydroxide and sodium peroxide.

| Run No. | Wt. of melt g | Conc. of NaOH molal | Conc. of $Na_2O_2$ molal | Conc. of $NiSO_4.4H_2O$ molal | Colour of product |
|---|---|---|---|---|---|
| 7 | 10 | 4 | 4 | 0.1 | Black |
| 8 | 10 | 4 | 4 | 0.1 | Black |
| 9 | 10 | 8 | 8 | 0.1 | Black |
| 10 | 10 | 8 | 8 | 0.1 | Black |
| 11 | 10 | 8 | 8 | 0.1 | Black |

The overall reaction represented:

$$Ni^{2+} + 4NaOH + 2NO_3^- \longrightarrow NiO + 2Na_2O + 2NO_2 + 2H_2O\uparrow + \tfrac{1}{2}O_2 \qquad ...(61)$$

When sodium peroxide was used instead of hydroxide, probably the black precipitate is nickel(II) oxide also. The reactions are:

$$O_2^{2-} \rightarrow O^{2-} + \tfrac{1}{2}O_2\uparrow \qquad ...(47)$$
$$Ni^{2+} + O^{2-} \longrightarrow NiO \qquad ...(62)$$

or, overall,

$$Ni^{2+} + Na_2O_2 + 2NO_3^- \longrightarrow NiO + Na_2O + 2NO_2 + O_2 \qquad ...(63)$$

But, in nitrate melt containing both sodium hydroxide and peroxide, a black precipitate of lithium nickelate(III) was identified by X-ray diffraction because the concentration of oxide ($O^{2-}$) will be high due to the decomposition of both bases and the oxidation of nickel(II) cation will be possible,

$$Ni^{2+} + 2NaOH + Na_2O_2 + 3NO_3^- + Li^+ \longrightarrow LiNiO_2 + 2Na_2O$$
$$3NO_2\uparrow + H_2O\uparrow + O_2 \qquad ...(64)$$

High concentration of oxide ($O^{2-}$) is responsible for stabilisation of higher oxidation states such as lithium nickelate(III).

## 4.6. Reaction of Iron(II) Sulphate Heptahydrate in Lithium Nitrate - Potassium Nitrate Eutectic containing Sodium Hydroxide and Peroxide.

### 4.6.1. Results

About 10 g of lithium nitrate-potassium nitrate eutectic was transferred to a pyrex tube with a B24 socket and placed in a furnace. Sodium hydroxide (4 molal) was added at 243°C forming a milky suspension with water vapour evolution. At 300°C sodium peroxide (4 molal) was added and a yellowish-white thick mixture was formed with bubbles. When the temperature reached 320°C, iron(II) sulphate heptahydrate (0.1 molal) was added and a brownish-beige coloured solution was formed with evolution of brown nitrogen dioxide. As the temperature increased to 450°C the colour of the solution changed to beige. Qualitative tests on the unwashed product showed that it was insoluble in water and a brown precipitate formed. The solution of the latter in dilute acid contained iron(III) and peroxide.

The experiment was repeated several times using different concentrations of the reactants but always with a ratio of (1:1) sodium hydroxide to sodium peroxide and the same concentration of iron(II) sulphate heptahydrate, (Table 15) and the beige solid quenched was obtained each time.

On repetition of the experiment (run 6, Table 20), the colour of the solution was reddish-brown with the evolution of brown nitrogen dioxide and oxygen.

The unwashed product was insoluble in water and qualitative tests showed the absence of peroxide and the presence of an insoluble reddish-brown precipitate of iron(III) oxide.

### 4.6.2. Discussion

In general, iron exists in several oxidation states the highest being (VI). Potassium ferrate(VI) $K_2FeO_4$ was prepared as black crystals by the method of Thompson et al.[125] or by oxidation of iron(III) nitrate in strong alkali solution[126]. The only oxidation states of importance in aqueous and related chemistry of iron are (II) and (III). Iron (III) oxide hydroxide FeO(OH) contains $FeO_6$ octahedra[127]. They are generally red-brown gels and are a major constituent of soils. Oxidation of $Fe^{2+}$ in basic solutions or from $Fe(OH)_2$ by air can lead to the formation of $FeO(OH)$ and also $Fe_3O_4$. The iron(III) oxide hydroxide is soluble in acids and to some extent in bases. When iron(III) oxide hydroxide was heated, $Fe_2O_3$ was obtained[121].

Iron(III) is also represented by ferrites(III) [i.e. mixed oxides with octahedral Fe(III)][128]. Examples are the spinels $M^{II}Fe_2O_4$, $BaFe_{12}O_{19}$ and $Ba_2Mn^{II}{}_2Fe_{12}O_{22}$. Ferrites can be made by fusing $Fe_2O_3$ with carbonates or by hydrothermal methods from $Fe(OH)_2$ or $FeO(OH)$ suspensions in the presence of metal ions[129]. In molten nitrate, $Fe_2O_3$ has been prepared from iron(III) chloride in lithium nitrate-potassium nitrate eutectic at 200°C as a reddish-brown insoluble oxide.

According to the results in this work, (Table 20), the beige solid is suggested to be ferrate(III), because iron(III) was soluble in the nitrate melt giving a beige solution. Kerridge and Khudhari[109] reported that a colourless melt was obtained when iron(III) oxide nitrate reacted with nitrate melt at 160°C after heating for 24 hours, and it was suggested that ferrate(III) might have been formed at a high temperature and the latter was decomposed after washing the quenched product. Because lithium and potassium ions are available, the formation of $LiFeO_2$ and $KFeO_2$ was thought to be possible, but in the presence of sodium hydroxide and sodium peroxide in the nitrate melt, the possibility of $M_2FeO_4$ [ferrate(VI)] would be more considerable because of high concentration of oxide($O^{2-}$).

Table 20: Reaction of hydrated iron(II) sulphate with nitrate melt containing sodium hydroxide and sodium peroxide.

| Run No | Wt. of melt g | Conc. of NaOH molal | Conc. of $Na_2O_2$ molal | Conc. of $FeSO_4 7H_2O$ molal | Colour of solution | Colour of quenched |
|---|---|---|---|---|---|---|
| 2 | 10 | 2 | 2 | 0.1 | Brownish-beige | Beige |
| 3 | 10 | 4 | 4 | 0.1 | Brownish-beige | Beige |
| 4 | 10 | 8 | 8 | 0.1 | Brownish-beige | Beige |
| 5 | 10 | 4 | 4 | 0.1 | Brownish-beige | Beige |
| 6 | 10 | 2 | 2 | 0.5 | Reddish-brown | Brown |

The stoichiometries of the reactions of iron(II) sulphate heptahydrate in nitrate melt containing both bases could reasonably be as follows:

$$2OH^- \longrightarrow O^{2-} + H_2O\uparrow \qquad \ldots(49)$$

$$O_2^{2-} \longrightarrow O^{2-} + \tfrac{1}{2}O_2\uparrow \qquad \ldots(47)$$

$$Fe^{2+} + 2NaOH + Na_2O_2 + 4NO_3^- + 2M^+ \longrightarrow M_2FeO_4 + 2Na_2O + 4NO_2 + H_2O + \tfrac{1}{2}O_2 \qquad \ldots (65)$$

Looking again at Table 20 , the reddish-brown insoluble iron(III) is suggested to be iron(III) oxide ($Fe_2O_3$) because iron(II) sulphate dihydrate was reported[109] to react with nitrate melt at high temperature forming iron(III) oxide. The stoichiometry was:

$$2FeSO_4.2H_2O + 4NO_3^- \longrightarrow Fe_2O_3 + 2SO_4^{2-} + 4H_2O + 4NO_2 + \tfrac{1}{2}O_2 \qquad \ldots (66)$$

But, in this work two bases were used (sodium hydroxide and sodium peroxide), and the reddish-brown precipitate was suggested to be a mixture of iron(III) oxide and iron(III) oxide hydroxide. The stoichiometry can be proposed as follows:

$$4Fe^{2+} + 4NaOH + Na_2O_2 + 8NO_3^- \longrightarrow Fe_2O_3 + 2FeO(OH) + H_2O + 3Na_2O + 8NO_2 + 3/2O_2 \qquad \ldots (67)$$

# CHAPTER FIVE

# REACTIONS OF THE THE SECOND-ROW TRANSITION METAL ZIRCONIUM IN LITHIUM NITRATE-POTASSIUM NITRATE (PURE AND BASIC) AND SODIUM NITRITE-POTASSIUM NITRITE EUTECTIC

## 5.1 Introduction

The chemistry of the second-row transition metals zirconium, yttrium, etc has been relatively little studied in molten nitrates, because it was natural at the outset to choose a molten salt solvent containing simple spherical ions with single, or at the worst, identical charges on cation and anion, and with small covalent interactions. However, this has resulted in concentrating much attention on the alkali metal halide melts.

Zirconium metal is mainly used in nuclear reactors, due to its extremely low thermal neutron cross section combined with exceptional corrosion resistance. In addition, it has relatively high strength at the elevated temperatures arising in thermal reactors. Fluoride melts are favoured for this application.

One observation reported for zirconium in nitrate media is that zirconium hydrogen phosphate ($Zr(HPO_4)_2.H_2O$) used as an ion-exchange medium, was stable up to 350°C in sodium nitrate-potassium nitrate, above which temperature alkali metal ions are exchanged for hydrogen. The release of phosphate did not commence until 500°C[144].

Potassium hexafluorzirconate(IV) as a cryoscopic solute was apparently stable in potassium nitrate at 330°C, but in molten silver nitrate at 212°C produced a depression equivalent to five particles[145] ($2K^+$, $2F^-$ and $ZrF_4$ were suggested).

Now, because there is little information reported on zirconium compounds in molten nitrate and nothing on molten nitrite, the third aim in this work was to investigate the reactions of zirconium compounds in molten nitrate (pure and basic) and in molten nitrite.

## 5.2 Reactions in Pure Lithium Nitrate-Potassium Nitrate Eutectic.

## 5.3 Results

### a. Zirconium(IV) Sulphate Tetrahydrate

A white suspension was produced with evolution of white fumes containing nitric acid, when zirconium(IV) sulphate tetrahydrate (BDH) (0.2 molal), was added to lithium nitrate-potassium nitrate just above 94°C. Thermogravimetric analysis (Fig 16, Curve A) showed weight loss beginning at lower temperatures as expected for a hydrolysis reaction with the first stage of weight loss consisting of several, but overlapping, reactions. The second stage was similar to that for anhydrous zirconium(IV) sulphate (see section b). The total weight loss was found to be 88.2%.

### b. Anhydrous Zirconium(IV) Sulphate

When anhydrous zirconium(IV) sulphate (prepared as discussed in Chapter 2) reacted with lithium nitrate-potassium nitrate eutectic (0.2 molal), brown nitrogen dioxide was evolved and a white suspension was formed at a temperature above the melting point of the eutectic (132°C). On raising the temperature a renewed vigorous evolution of nitrogen dioxide occurred around 400°C. Thermogravimetric analysis showed two main stages of weight loss (Fig 16, Curve B):

| | | |
|---|---|---|
| a. | 190-350°C (max. rate at 270°C) | 51.7% |
| b. | 350-450°C (max. rate at 400°C) | 23.5% |

The total weight loss was 75.2%.

### c. Zirconium(IV) oxide

$ZrO_2$ was prepared by reacting either hydrated or anhydrous zirconium(IV) sulphate with molten nitrate (see a. and b. above). When $ZrO_2$, prepared in this way, was heated in $LiNO_3.KNO_3$ eutectic, a slow reaction began above 440°C. $ZrO_2$ obtained commercially (MEL and Co.) showed similar behaviour, but the weight loss began at 470°C (Fig. 17, Curve A). The situation is then complicated by the simultaneous decomposition of the nitrate solvent. These reactions of $ZrO_2$ with nitrate melts are believed to involve the formation of zironate (see Discussion section).

Figure 16. Thermogravimetric analysis of hydrated and anhydrous zirconium sulphate in lithium nitrate potassium nitrate eutectic

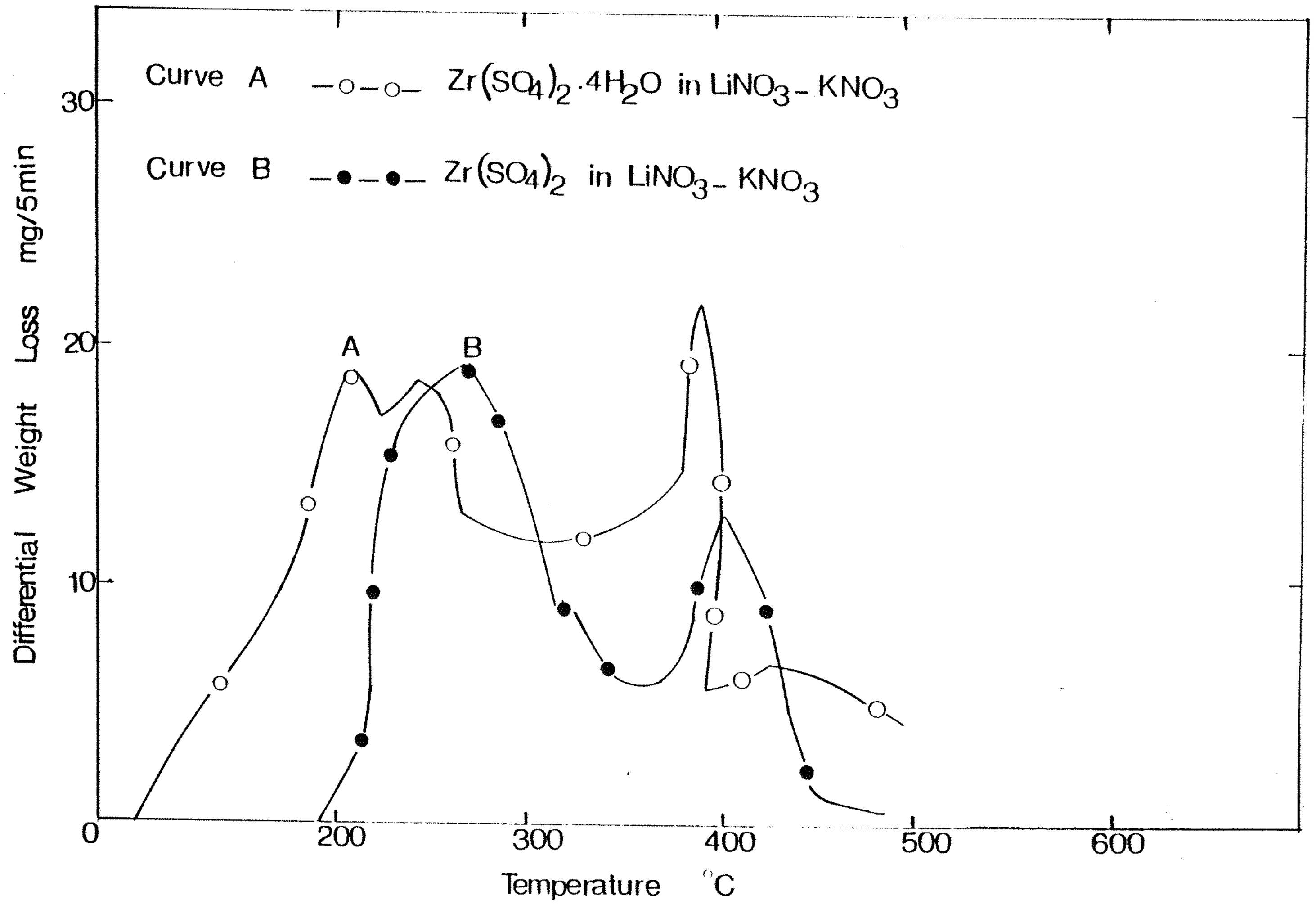
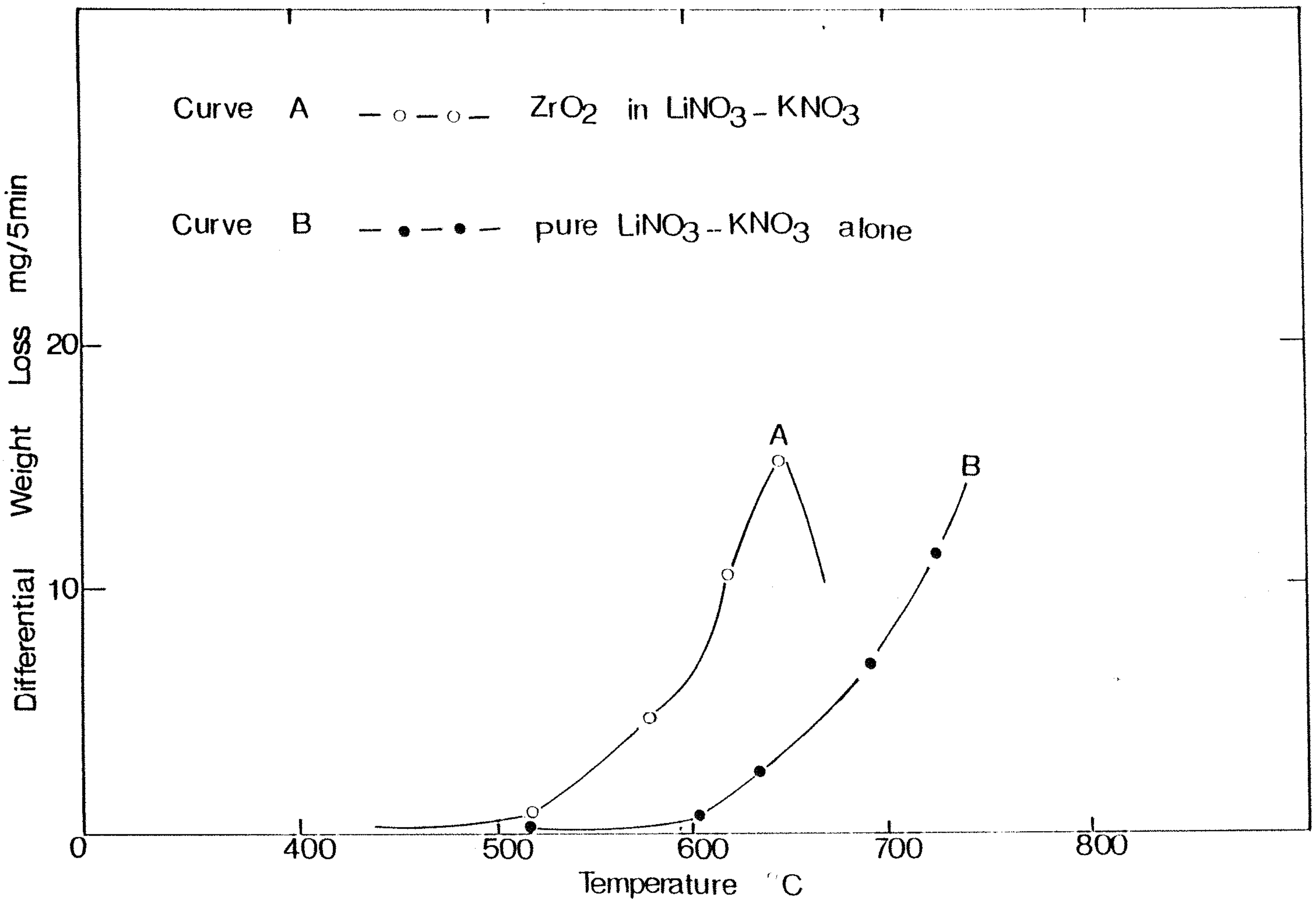


Figure 17. Thermogravimetric analysis of zirconium dioxide in lithium nitrate-potassium nitrate eutectic



### 5.4 Reactions in Basic Lithium Nitrate-Potassium Nitrate Eutectic

Anhydrous zirconium(IV) sulphate (0.2 molal) in lithium nitrate-potassium nitrate containing potassium nitrite (1 molal) when analysed thermogravimetrically, showed three stages of weight loss; the first maximum was at 250°C, the second maximum at 290°C and the third maximum at 350°C (Fig 18). The total weight loss found was 54.8%.

### 5.5 Reaction in Pure Sodium Nitrite-Potassium Nitrite Eutectic

Anhydrous zirconium(IV) sulphate in sodium nitrite-potassium nitrite (0.2 and 0.4 molal in two experiments), when analysed thermogravimetrically (Fig 19, Curve A and B) showed a weight loss maximum almost at the melting point of the nitrite eutectic (220°C). No further weight loss occurred above 270°C (until the melt itself began to decompose). The total weight loss found was 41.9%.

### 5.6 Extraction of Zirconium(IV) Dioxide from the Melt

To extract zirconium(IV) dioxide from the previous reactions, the following washing procedure was applied.

To the quenched melt containing zirconium(IV) dioxide, 25 ml of distilled water was added and left for about an hour to dissolve all the nitrate or nitrite. The suspension was then filtered using a No. 4 sintered crucible and a water pump. To the white precipitate in the crucible was added 3-4 times 25 ml of distilled water at intervals of half an hour until no more nitrate was found in the filtrate (diphenylamine reagent was used to test for nitrate and nitrite). 15 ml of 4 **M** $H_2SO_4$ was then used (to break the big agglomerates of zirconium(IV) dioxide), followed by further quantities of water. The suspension was then filtered and the precipitate left to dry in a desiccator overnight.

Figure 18. Thermogravimetric analysis of zirconium sulphate in basic molten nitrate

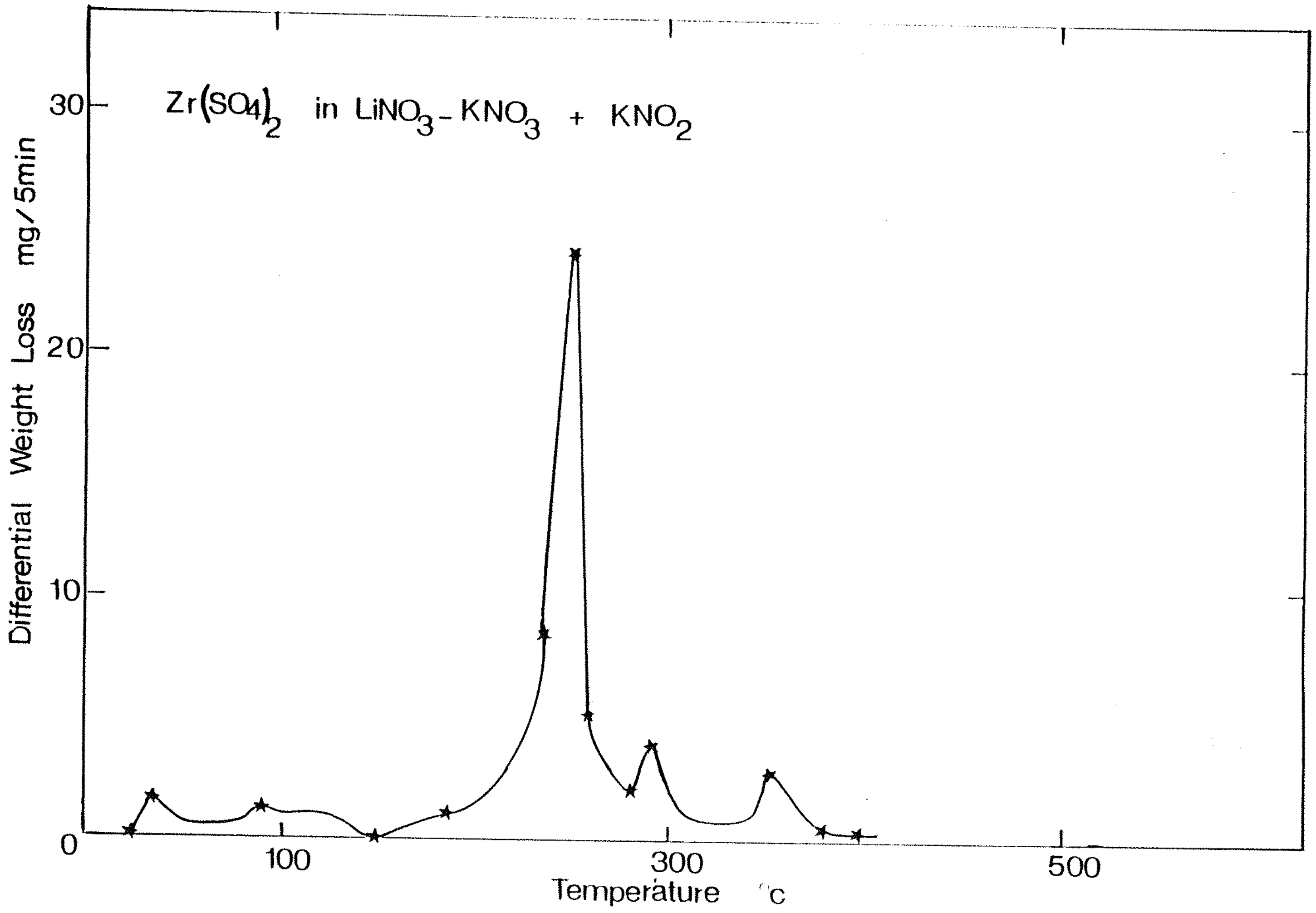
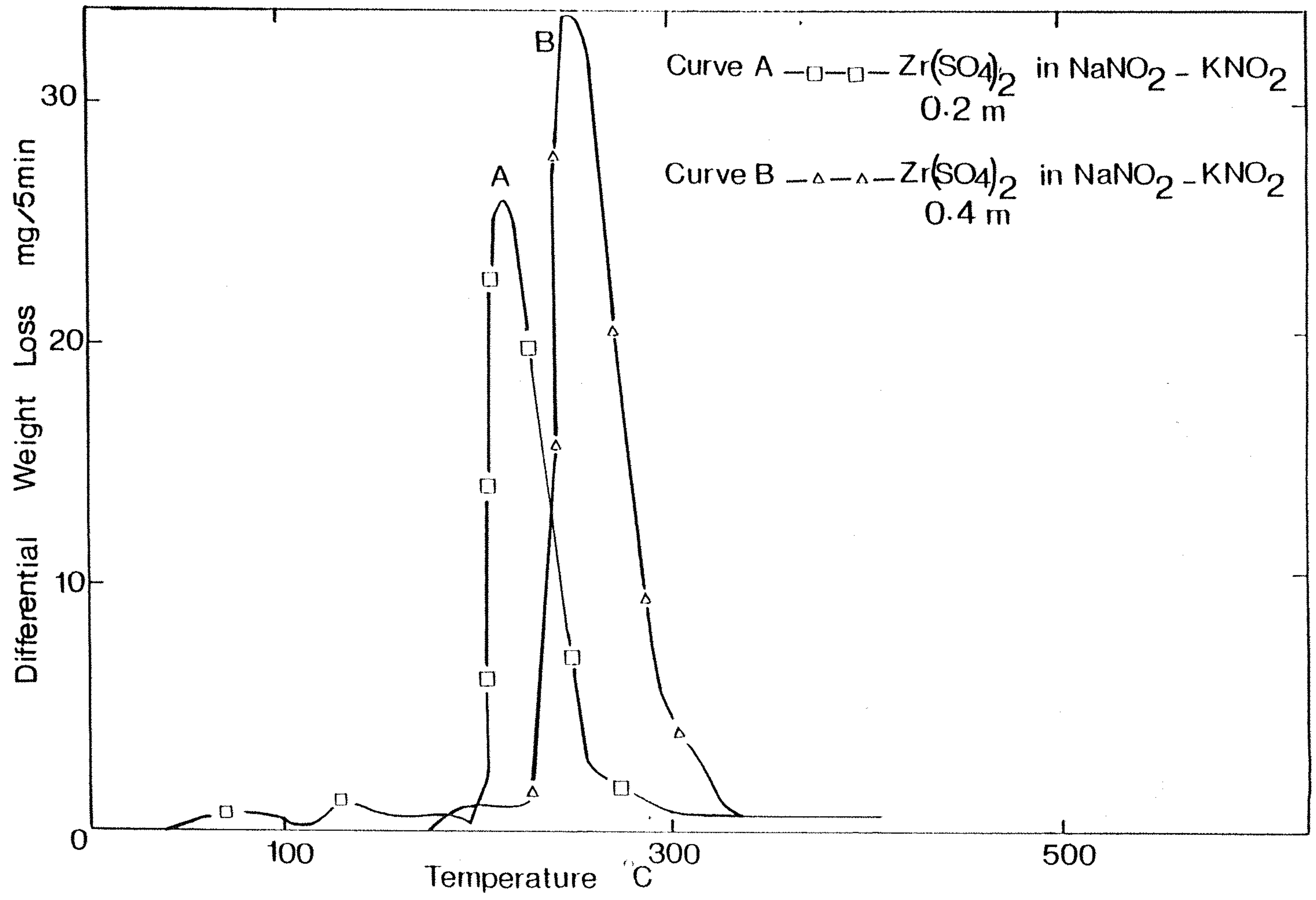


Figure 19. Thermogravimetric analysis of zirconium sulphate in molten nitrite



## 5.7 Discussion

The $Zr^{4+}$ ion is relatively large, highly charged and spherical with no partially filled shell to give it stereochemical preferences. Zirconium has more basic oxides than titanium, having somewhat more extensive aqueous chemistry and more commonly attaining higher coordination numbers 7 and 8. Both zirconium and titanium have limited chemistry of the (III) oxidation state, the most common oxidation state is (+4).

In this work, zirconium(IV) behaved as Lux-Flood acid in the molten nitrate eutectic, reacting as follows:

a. $Zr(SO_4)_2.4H_2O + 4NO_3^- \longrightarrow ZrO_2 + 2SO_4^{2-} + 4H_2O$
$+ 4NO_2 + O_2$ ...(68)

(Calculated weight loss of $4H_2O + 4N + 10O$ per $Zr(SO_4)_2.4H_2O$ is 81.1%).

The weight loss found, 88.2%, was rather higher than the calculated weight loss, probably due to reaction of some of the water vapour with nitrate ion to give $HNO_3$ and $OH^-$:

$NO_3^- + H_2O \longrightarrow HNO_3 + OH^-$, ...(69)

followed by reaction of $OH^-$ with $Zr^{4+}$.

b. $Zr(SO_4)_2 + 4NO_3^- \longrightarrow ZrO_2 + 2SO_4^{2-} + 4NO_2 + O_2$ ...(70)

(Calculated weight loss of $4N + 10O$ per $Zr(SO_4)_2$ is 76.3%).

The weight loss found, 75.2%, was close to the calculated weight loss.

c. The reaction of $ZrO_2$ with nitrate above 440 °C is believed to be as follows:[67]

$ZrO_2 + 2MNO_3 \longrightarrow M_2ZrO_3 + 2NO_2 + \frac{1}{2}O_2$ ...(71)

(see Fig. 17). Since the pure eutectic is itself decomposing at a significant rate in the same temperature range, it is not possible to use the weight loss as evidence for reaction (71). However, reaction of $ZrO_2$ with pure molten sodium nitrate gave a product which was identified by XRD as sodium zirconate, $Na_2ZrO_3$.

Zirconates are normally made by combining $ZrO_2$ with oxides, hydroxides, nitrates, etc, of other metals and firing the mixture at 1000° - 2500°C. $CaZrO_3$ is isomorphous with perovskite. By dissolving $ZrO_2$ in molten KOH and evaporating off the excess of solvent at 1050°C, the crystalline compounds $K_2Zr_2O_5$ and $K_2ZrO_3$ may be obtained. The former contain $ZrO_6$ octahedra sharing faces to form chains that in turn, share edges and corners with other chains. The latter contains infinite chains of $ZrO_5$ square pyramids[121].

In aqueous solutions, addition of hydroxide to zirconium(IV) solutions causes the precipitation of white gelatinous $ZrO_2.nH_2O$, where the water content is variable. On strong heating, this hydrous oxide gives hard, white, insoluble $ZrO_2$ called zirconia. This has an extremely high melting point (2700°C), exceptional resistance to attack by both acids and alkalis, and good mechanical properties. It is used as ceramic material for crucibles, furnace cores, electrical devices, etc.

Zirconium(IV) dioxide (zirconia) exhibits three polymorphs (materials having the same chemical composition but a different crystal structure), the monoclinic, tetragonal and cubic phases. The change from one structure to another is referred to as polymorphic transformation. The monoclinic phase is stable up to 1170°C where it transforms to the tetragonal phase which is stable up to 2370°C. The cubic phase exists up to the melting point of 2680°C. The monoclinic to tetragonal phase transformation is accompanied by a large volume change that results in internal stresses in the $ZrO_2$ body large enough to cause fracture or substantial weakening. In attempts to avoid this problem, it was discovered that appropriate additions of MgO, CaO or $Y_2O_3$ to $ZrO_2$ produced a cubic form from room temperature to the melting point that did not undergo a transformation and was thus useful over a broader temperature range. This is referred to as fully stabilised zirconia.

Stabilised $ZrO_2$ has low fracture toughness and poor resistance to impact. By not adding enough MgO, CaO or $Y_2O_3$ to stabilise the $ZrO_2$ completely and by careful control of particle sizing and processing, mixtures of the stabilised cubic phase and the unstable (tetragonal or monoclinic or both) will be formed to achieve very high fracture toughness. This type of material is referred to as partially stabilised zirconia (psz).

Industrially, it is desirable to avoid the necessity for high reaction temperatures and long reaction times on grounds of cost. A low temperature route is preferred. It is also desirable to prepare $ZrO_2$ in the cubic form for better mechanical strength. However, as explained above, this has to be stabilised, otherwise it may transform to the monoclinic form with resultant cracking. If $ZrO_2$ is prepared using nitrate or nitrite melt, as described above, the stabilising ions (calcium, magnesium or yttrium) can be added to the melt and co-precipitated with the $ZrO_2$. This possibility of making stabilised zirconia by a low-temperature route is one of the major reasons why this work was undertaken.

X-ray diffraction of zirconium(IV) dioxide formed from reaction of zirconium(IV) sulphate in molten nitrate showed a mixture of two phases, monoclinic and tetragonal (Fig 20), while zirconium dioxide (MEL Co), as supplied, was shown by X-ray diffraction to contain the monoclinic phase only (Fig 21, A). However, when this material was suspended in molten nitrate, a partial transformation to the tetragonal phase was observed (Fig 21, B).

When potassium nitrite was added to the nitrate eutectic as a base, to produce more oxide anion (it has a dissociation constant of $10^{10}$ larger than that of nitrate under equivalent conditions), this resulted in reaction in less time and at lower temperature as was proved by thermogravimetric analysis (see Section 5.4). The total weight loss found was 54.8% which corresponds closely to the equation:

$Zr(SO_4)_2 + 4NO_2^- \longrightarrow ZrO_2 + 2SO_4^{2-} + 2NO_2 + 2NO$ ...(72)
(Calculated weight loss for 4N + 6O per $Zr(SO_4)_2$ is 53.7%)

X-ray diffraction of zirconium(IV) dioxide formed in basic molten nitrate showed the presence of tetragonal phase only (Fig 22) despite the increase in the basicity.

To further increase the basicity of the melt, pure sodium nitrite-potassium nitrite eutectic was used. The weight loss then found, 41.9%, was very close to that given by the following equation:

$Zr(SO_4)_2 + 6NO_2^- \longrightarrow ZrO_2 + 2SO_4^{2-} + 2NO_3^- + 4NO$ ...(73)
(Calculated weight loss for 4N + 4O per $Zr(SO_4)_2$ is 42.4%).

X-ray diffraction of zirconium(IV) dioxide formed in molten nitrite, also showed the presence of tetragonal phase only (Fig 23) even with increased concentration of the solute $Zr(SO_4)_2$.

Table 21 shows a summary of the X-ray diffraction results (phases present).

In all the previous reactions, in molten nitrate (pure and basic) or in molten nitrite, the oxidation state of zirconium was +4; no higher oxidation state has been formed because +4 is the group valency of zirconium.

Figure 20. X-ray diffraction of $ZrO_2$ obtained from (0.2m) $Zr(SO_4)_2$ in $LiNO_3.KNO_3$

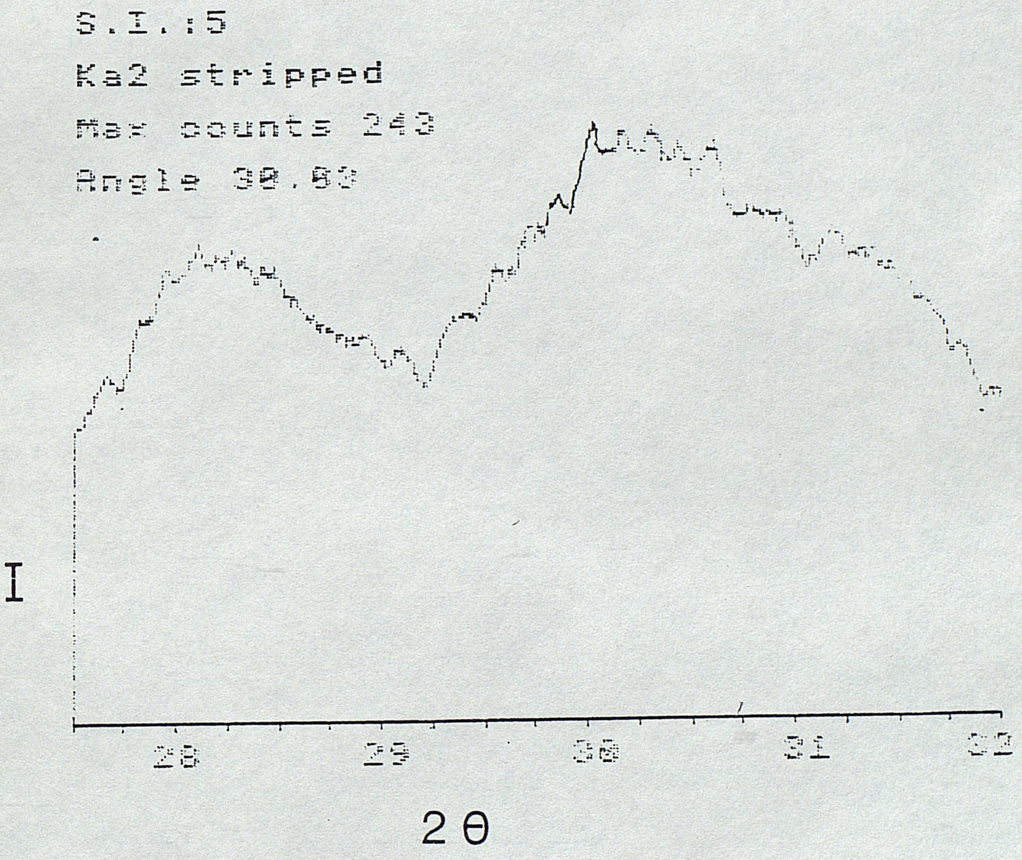


**Figure 21.** X-ray diffraction of:
A. pure $ZrO_2$ (MEL Co.)
B. (0.2m) $ZrO_2$ in $LiNO_3.KNO_3$

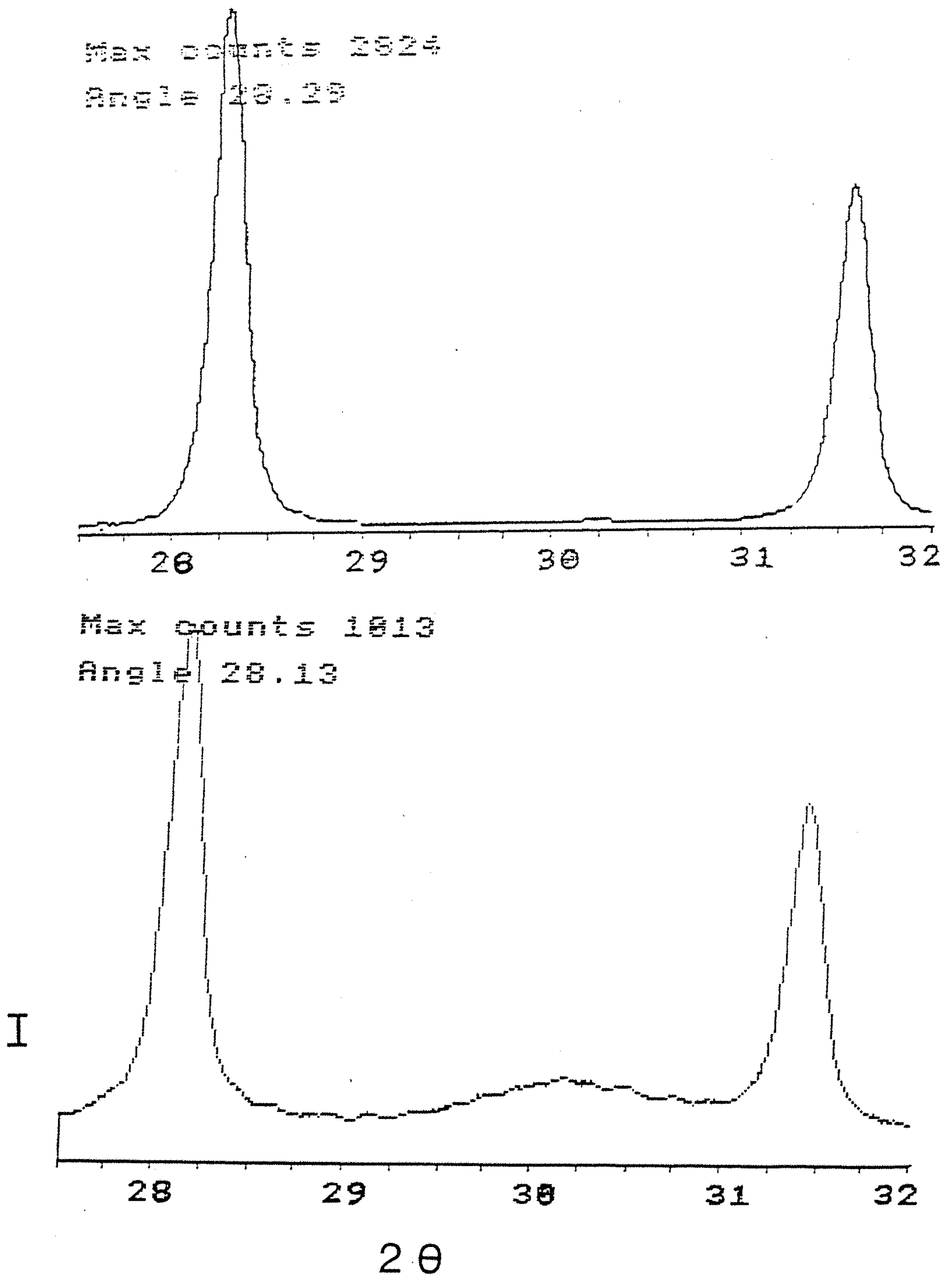


Figure 22. X-ray diffraction of $ZrO_2$ obtained from $Zr(SO_4)_2$ in basic nitrate melt.

A. $LiNO_3$-$KNO_3$ + (1m) $KNO_2$

B. $LiNO_3$-$KNO_3$ + (2m) $KNO_2$

C. $LiNO_3$-$KNO_3$ + (4m) $KNO_2$

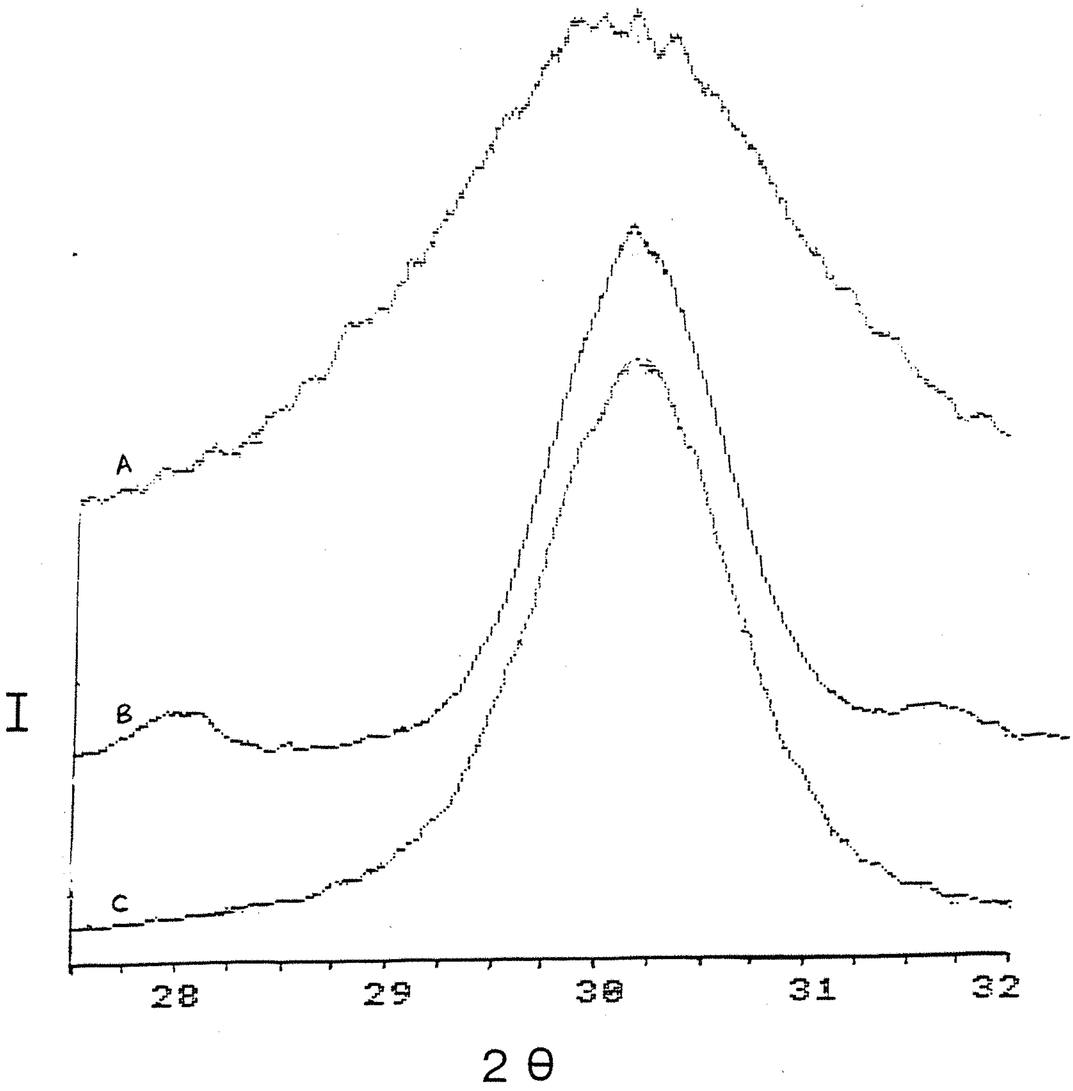


Figure 23. X-ray diffraction of $ZrO_2$ obtained from $Zr(SO_4)_2$ in molten nitrite.
A. (0.1m) $Zr(SO_4)_2$ in $NaNO_2$-$KNO_2$
B. (0.2m) $Zr(SO_4)_2$ in $NaNO_2$-$KNO_2$
C. (0.6m) $Zr(SO_4)_2$ in $NaNO_2$-$KNO_2$

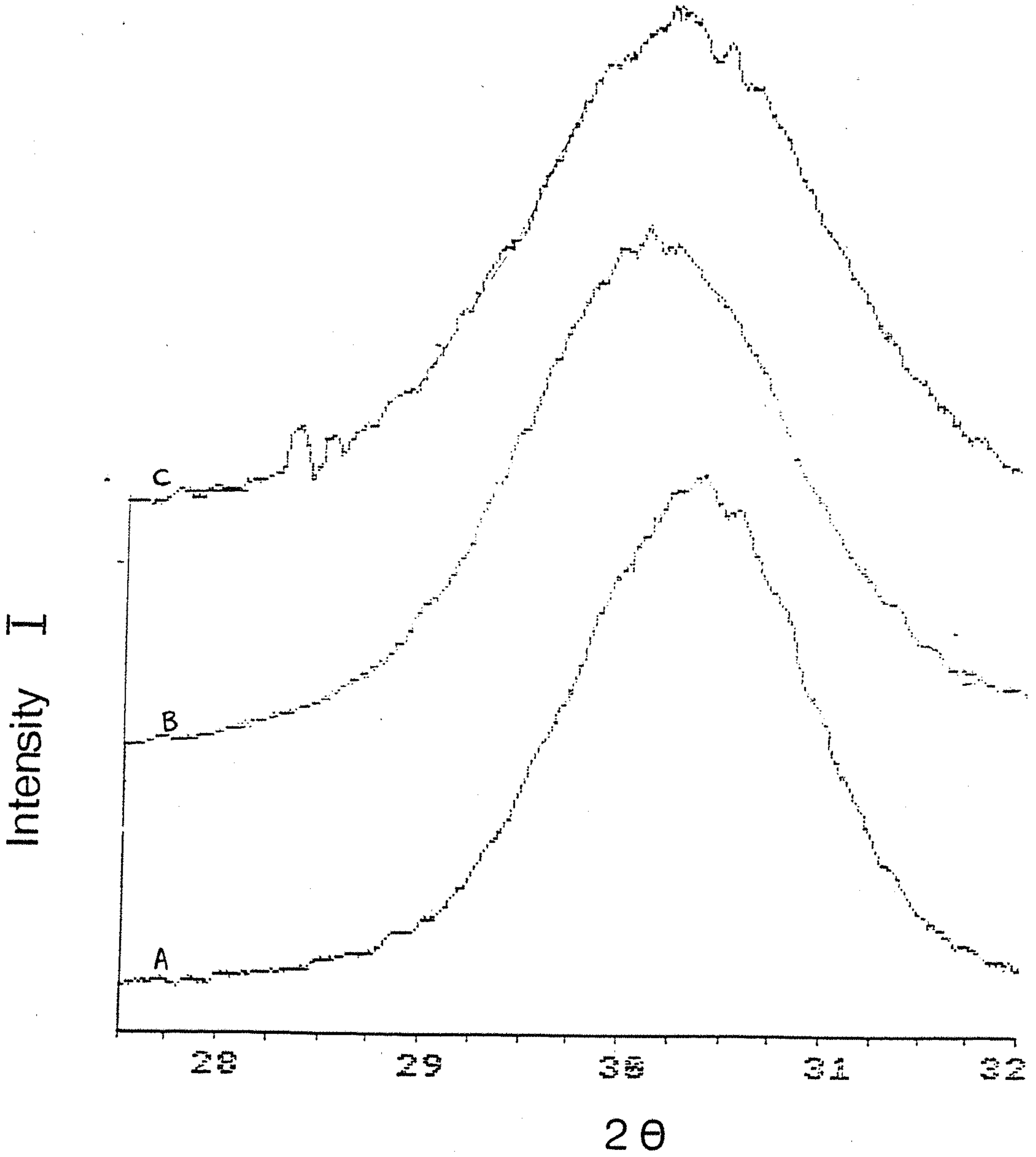


Table 21. Summary of the X-ray Diffraction Results.

| Solvent | Solute & Conc. (m) | Base added & Conc. (m) | $ZrO_2$ phase(s) |
|---|---|---|---|
| $LiNO_3.KNO_3$ | $Zr(SO_4)_2$ (0.2) | - | t + m |
| - | $ZrO_2$ (MEL. Co) | - | m |
| $LiNO_3.KNO_3$ | $ZrO_2$ (0.2) | - | t + m |
| $LiNO_3.KNO_3$ | $Zr(SO_4)_2$ (0.2) | $KNO_2$ (1) | t |
| $LiNO_3.KNO_3$ | $Zr(SO_4)_2$ (0.2) | $KNO_2$ (2) | t |
| $LiNO_3.KNO_3$ | $Zr(SO_4)_2$ (0.2) | $KNO_2$ (4) | t |
| $NaNO_2.KNO_2$ | $Zr(SO_4)_2$ (0.1) | - | t |
| $NaNO_2.KNO_2$ | $Zr(SO_4)_2$ (0.2) | - | t |
| $NaNO_2.KNO_2$ | $Zr(SO_4)_2$ (0.6) | - | t |

(t = tetragonal; m = monoclinic)

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