SOME ASPECTS OF THE CHEMISTRY OF MOLTEN NITRITES

by

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ABSTRACT

FACULTY OF SCIENCE

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by Sabah Saleh Al-omer

The Lux-Flood acid-base behaviour and oxidation-reduction properties of nitrite melts were investigated. These studies showed the nitrite melt to be a moderately strong base and also to exhibit both reducing and oxidizing properties.

Seven vanadium compounds were studied, potassium disulphatovanadate (III), vanadyl (IV) sulphate and vanadium (IV) oxide being initially oxidized to metavanadate while vanadium pentoxide initially reacted to give both metavanadate and vanadium (IV) oxide. Metavanadate then reacted further at 300°C to yield orthovanadate which was found to catalyze the decomposition of nitrite melt.

Sodium cobaltinitrite underwent cation exchange in nitrite eutectics with melting points below its decomposition temperature (170°C) to yield potassium cobaltinitrite as an intermediate which decomposed at 220°C to form Co_3O_4. However, in the higher melting Na/KNO_2 (220°C) considerable thermal decomposition of sodium cobaltinitrite took place below the melting point. Hexamminecobalt (III) chloride initially decomposed in nitrite eutectics, producing cobalt (II) chloride which

reacted with the melt to form potassium cobaltinitrite.

The electronic spectra of nickel (II) and copper (II) in molten Li/KNO_2 were obtained. The spectrum of nickel (II) complex was consistent with a regular octahedral coordination suggested to be $[Ni(NO_2)_3(ONO)_3]^{4-}$. The reflectance spectra for the solid showed a change in the nature of coordination which suggested the formation of $[Ni(NO_2)_4(ONO)_2]^{4-}$. From the spectrum of copper (II) a distorted octahedral complex, $[Cu(NO_2)_4(ONO)_2]^{4-}$ is suggested.

The behaviours of six lead compounds as well as metallic lead in Na/KNO_2 eutectic were studied. Metallic lead was only surface oxidized and lead monoxide was inert, whereas lead dioxide oxidized the nitrite ion to nitrate ion. Red lead, Pb_3O_4, reacted with the nitrite melt, forming lead monoxide. Based on thermogravimetric analysis, the reaction is suggested to take place through the formation of both $Pb(NO_2)_2$ and $Pb(NO_2)_4$. Lead (II) nitrite decomposed stepwise in a nitrite melt to yield lead monoxide as the final product. The compounds $2Pb(NO_2)_2.PbO$ and $Pb(NO_2)_2.2PbO$ are proposed as intermediates. Both lead nitrate and lead chloride underwent anion exchange at and slightly below the melting point to form lead (II) nitrite.

The reactions of sodium orthotungstate, tungsten trioxide, tungsten hexacarbonyl and metallic tungsten were investigated. Sodium orthotungstate was inert, whereas tungsten trioxide reacted below the melting point forming orthotungstate. Tungsten metal acted as a reducing agent, orthotungstate, nitrogen, nitrous oxide and nitric oxide being formed according to the conditions. Tungsten hexacarbonyl underwent sublimation and appeared to be unreactive in the melt. Zirconium metal did not react with a nitrite melt up to 400°C, even on the addition of sodium peroxide. Potassium permanganate reacted to form the unstable, green manganate (VI) ion which then decomposed to form manganate (IV).

The stoichiometries of the Lux-Flood acid-base reactions of $(NaPO_3)$, $Na_3(PO_3)_3$, $Na_4(PO_3)_4$, $NK_4P_2O_7$, $Na_5P_3O_{10}$ and P_4O_{10} were studied. All these phosphate compounds, except pyrophosphate, initially depolymerized below the melting point to pyrophosphate. The latter then degraded further at 300°C to produce orthophosphate.

The reactions of peroxide ion with a nitrite melt was investigated and the equilibrium constant of the reaction

$$O_2^{2-} + NO_2^- = NO_3^- + O^{2-}$$

was determined to be $\simeq 0.1$ in a zirconium crucible. The attack on a platinum crucible by the presence of peroxide ion in a nitrite melt was found to produce platinum (IV) oxide and the corrosive species is suggested to be the peroxonitrite ion.

CONTENTS

INTRODUCTION

From the earliest times, chemical reactions at high temperature have been employed, such as those occurring in glass making and the extraction of common metals and many of these reactions are in fact taking place in molten salts.

One of the most important early scientific studies in this field was carried out in 1807 by Sir Humphry Davy.(1) In these, he found that perfectly dried potassium hydroxide was virtually a non-conductor but it could be rendered conductive by a very slight addition of moisture. In this slightly moist state it was fused by a high current density and electrolized yielding metallic potassium.

However Michael Faraday,(2) was the first person to study a number of molten salts in a systematic and scientific manner, and obtained a comparative electrochemical force series of the elements in these salts and also established the fundamental laws of electrolysis. Since then, electrolytic processes have been developed for the production of large amounts of electropositive metals from their molten salts. As an example, more than 8 x 10^6 tons of aluminium are produced annually by the electrolysis of alumina Al_2O_3 dissolved in molten cryolite Na_3AlF_6.(3) Similarly sodium, magnesium, etc., are extracted from their fused salts. Molten salts are also used in other high temperature metallurgical processes such as brazing, coating and soldering.

Despite such early study, the chemical properties of molten salts have only generated intense interest in the last thirty years and the investigations which have been carried out have involved both industrial and scientific aspects. For example, the increasing demand for the less common metals, such as titanium, zirconium, niobium and tantalum by the nuclear reactor and aerospace industries has meant extensive study of the economics of molten salt production techniques.

The application of molten salts to nuclear technology was in fact begun in the early 1940s in the United States(4) as a part of a programme to develop nuclear power for both military and commercial uses. Molten fluorides appeared particularly appropriate because of their high solubility for uranium, 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 860°C using a fuel salt mixture of NaF, ZrF_4 and UF_4.(4) 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 temperatures greater than 625°C.

Corrosion can present a major problem when molten salts are used in a nuclear reactor. In the molten fluoride reactor, corrosion of structural metals was observed and it was found that chromium metal was attacked more readily than other metal alloys.(5)

In addition to nuclear reactors, the industrial corrosion problems which occur on the fire side of the coal and oil fueled boilers has also provoked interest in molten salts. In thermal power stations the boilers corrode severely in the flue gas cooling system, due to the formation of compounds which are particularly corrosive at temperature over 600°C.(6) Analysis has shown that these were a mixture of sulphates, e.g. $KAl(SO_4)_2$, Na_2SO_4, K_2SO_4 etc.(6,7,8), which are molten at temperature above 600°C.

The mechanism of this type of corrosion has been studied by several workers(9,10,11,12) and has been suggested that the corrosion started with the transfer of electrons from the metal to sulphur trioxide formed in the molten sulphate, the relevant equations being

$$SO_4^{2-} = SO_3 + O^{2-} \qquad (1)$$

$$M + SO_3 = MO + SO_2 \qquad (2)$$

where M represents the metallic element.

It therefore appeared that the extent of corrosion could be reduced by controlling the acidity of the melt by introducing higher concentration of a basic substance, such as magnesium oxide.

Molten salts have also been used as the electrolyte in fuel cells for the conversion of chemical energy into electrical power.(13) One type of fuel cell is the lithium-chlorine battery for producing a large amount of current from a small cell volume. The cell with a molten lithium chloride electrolyte operates at 650°C.(14)

The limited use of molten salts in present day industry is in part due to the lack of information on the chemical reactivities and physical properties of these solvents and the chemistry of solutes in such solvents, which has sometimes hindered or prevented the industrial use of an otherwise attractive process.

Being highly ionic, molten salts are a special case of liquids and, hence, of solvents. It is useful, therefore, to make a comparison between the properties of these liquids and those of aqueous media. In general molten salts often have quite different solvent properties from water as well as a wider liquid temperature range which depends of course to some extent on the nature of the eutectic. For example, in nitrite eutectics, the subject of the present study, the binary sodium nitrite-potassium nitrite eutectic has a liquid range of about 330°C from the melting temperature (220°C) to the decomposition temperature (550°C), whereas water is limited to a liquid range of 100°C.

Other eutectics used in this study similarly provide larger liquid ranges, e.g. sodium nitrite-potassium nitrite-barium nitrite (m.p. 170°C) with a liquid range limited to 190°C because of the lower decomposition temperature (360°C) and lithium nitrite-potassium nitrite (m.p. 110°C) with a range of 290°C.

Interesting information on the properties of molten salts can be obtained by studying the chemical reactions which occur when these molten media are used as solvents. It has been found that many reactions in oxyanion melts are analogous to acid-base type reactions in aqueous chemistry, and an operational acid-base definition has been formulated for oxyanion systems. According to Lux,(15) acids and bases can be defined on the basis of the equation

$$\text{Base} = \text{Acid} + O^{2-} \qquad (3)$$

The above equation is analogous to the acid-base definition of Bronsted for the protolytic system in which the acid is characterized by its tendency to transfer a proton and a base by its tendency to accept a proton. Analogously, in molten systems, a base was defined as that which could donate oxide ions, and an acid was defined as that which could accept oxide ions.

An early application of this acid-base definition was made by Flood and co-workers(16,17,18,19), and his name is often used in conjunction with Lux when these systems are discussed.

Investigations have been made on pure molten sodium nitrite (m.p. 284°C) as well as other various lower melting nitrite eutectics. These investigations are much less extensive than those carried out in molten nitrates. From the similar Lux-Flood behaviour of both nitrate and nitrite melts it has been suggested that the ionisation of molten nitrite was also similar to that of molten nitrate,(20) i.e., for the nitrate ion(21)

$$NO_3^- = NO_2^+ + O^{2-} \tag{4}$$

and for the nitrite ion

$$NO_2^- = NO^+ + O^{2-} \tag{5}$$

the nitrosyl ion, however, exists only at low concentration since it was reported to react with the nitrite ion to form volatile products

$$NO^+ + NO_2^- = [N_2O_3] \tag{6}$$

N_2O_3 is not seen as such, but rather, dissociates into NO_2 and NO, i.e.

$$[N_2O_3] \rightarrow NO_2 + NO \tag{7}$$

The postulated ionisation of molten nitrate (equation 4) has been criticised by Topol et al.(22) who claimed to have found no evidence for the nitryl ion in sodium nitrate-potassium nitrate at 280 - 350°C and suggested the following equilibrium

$$2NO_3^- = 2NO_2 + \frac{1}{2}O_2 + O^{2-}$$

though it has not been accepted in recent literature.

It has been suggested that the basic species in the nitrite melt is the oxide ion,(20) but other workers(23) assumed the existence of the orthonitrite ion where the oxide ion is combined with a nitrite ion. Correspondingly, in nitrate melts, the oxide ion has been suggested to be present in the form of the orthonitrate(24) or in the form of pyronitrate.(25) However, Jordan and Zambonin(26,27,28) found the oxide ion to be unstable, being oxidized to peroxide and superoxide.

Acid-base reactions in molten nitrites have received some attention in the last few years. These studies have shown that nitrite melts are much more basic than nitrate melts. For example, the reaction of potassium dichromate(29) was found to commence below the melting point of the sodium nitrite-potassium nitrite eutectic. The fundamental stoichiometry was found to be

$$Cr_2O_7^{2-} + 2NO_2^- \rightarrow 2CrO_4^{2-} + NO_2 + NO \qquad (8)$$

Comparison of this reaction with the analogous reaction of the same Lux-Flood acid in lithium nitrate-potassium nitrate eutectic, which commenced at 400°C, provided evidence of the more basic character of nitrite melt. The ratio of NO to NO_2 produced from reaction (8) has been studied and found to be greater than unity, being lowest when the gases were rapidly removed.(30) Potassium trichromate and chromium (VI) oxide have also been found to react below the melting point of the sodium nitrite-potassium nitrite eutectic forming chromate.

$$Cr_3O_{10}^{2-} + 4NO_2^- \rightarrow 3CrO_4^{2-} + 2NO_2 + 2NO \qquad (9)$$

and

$$CrO_3 + 2NO_2^- \rightarrow CrO_4^{2-} + NO_2 + NO \qquad (10)$$

Among other transition metal compounds which have been the subject of investigation in nitrite melt are iron (II) chloride and iron (III) chloride, both of which behaved as Lux-Flood acids. Iron (III) reacted at the melting point whereas iron (II) reacted at 280°C. The higher reaction temperature for iron (II) was attributed to its very low solubility.(31)

Cobalt metal has been reported to form a dark red melt when used as the cathode in a sodium nitrite melt at 302°C.(32) On dissolving the melt in water after cooling, cobalt (III) was identified. However cobalt (II) chloride(31) has been found to react at the melting point according to the equation

$$3CoCl_2 + 6NO_2^- \rightarrow Co_3O_4 + 6Cl^- + 2NO_2 + 4NO \qquad (11)$$

On the other hand, it was reported that cobalt (II) chloride is stable in lithium nitrate-potassium nitrate at 160°C.(33) In the present work it was found that no soluble species of cobalt (II) or cobalt (III) were obtained in nitrite melts because of the formation of insoluble potassium cobaltinitrite. In addition to the transition metal compounds mentioned above, nickel (II) chloride has been found to behave as a Lux-Flood acid reacting at 220°C according to the equation.(31)

$$NiCl_2 + 2NO_2^- \rightarrow NiO + 2Cl^- + NO + NO_2 \qquad (12)$$

In the present work, the author has found that coordination in low melting point nitrite melt is possible and stable species of nickel (II) and copper (II) complexes were obtained. Nickel (II) has also been found stable in nitrate melt at lower temperature.

Silver compounds are also among the compounds which have been studies in nitrite melts. Silver nitrite was found to be very soluble and stable up to 250°C whereupon decomposition occurred with the formation of silver metal, nitrate ions and both nitrogen dioxide and nitric oxide. The solution of silver nitrite in a nitrite melt was found to be more stable than solid silver nitrite since the latter commenced decomposition at 200°C. The silver (I) nitrate reaction also occurred at a temperature lower than of the thermal decomposition of the pure salt which was considered to indicate substantial coordination of silver by nitrite ions.(34) The solubility of silver chloride in a nitrite melt has been determined as approximately $\sim 7 \times 10^{-3}M$ which is close to its extrapolated solubility in a nitrate melt at 300°C ($5.8 \times 10^{-3}M$).(35)

In addition to the basic nature of nitrite melts, a very important additional aspect of their chemistry is the oxidation-reduction power of these solvents. Acting as an oxidizing agent, molten nitrite oxidized iron (II) to iron (III), chromium (III) to chromium (VI) and cobalt (II) to cobalt (III).(29,31) It was suggested -that the mechanism of these oxidation reaction commenced with the self dissociation of nitrite ion into oxide ion and nitrosyl ion followed by oxidation by the nitrosyl ion.(36)

On the other hand, nitrite ion has also been found to act as a reducing agent, it having been reported that chromium (III) was formed from the reaction of chromium (VI) in a nitrite melt. This initial reduction of chromium (VI) had not been reported previously in nitrite melt.(29) A similar phenomena has now been observed in the reaction between vanadium pentoxide and nitrite eutectic. Here vanadium (IV) dioxide was produced which once again was oxidized to vanadium (V) at higher temperature.(37)

There have been only a few studies of the solvent properties of molten nitrites. In general low solubilities were observed. For example, sodium sulphate is soluble and stable in these melts; and sodium orthovanadate was found to be moderately soluble.(37) The solubility of sodium carbonate in sodium nitrite has also been determined at various temperatures. The molal solubilities were found to be 0.561 m at 318°C, 0.615m at 328°C and 0.668m at 338°C. The solubilities of these compounds in a nitrite melt is less than that in water.(38)

The solubility of gases in molten salts, as in more conventional solvents, appears to be of two types, physical solubility and solubility resulting in a chemical change. The extent of physical solubility appears to be related to the size of the free volumes (holes) in the melt which is relative to the solute ion radius and is generally low, but increases with increasing temperature. Where solvation or ionization was possible, solution results in a new species being formed in the melt. As an example of solubility associated with chemical changes, sulphur dioxide was found to react with nitrite melt forming sulphate ions together with nitrogen dioxide and nitric oxide.(39)

A further aspect of the limited work already carried out on molten nitrites is the spectroscopic measurements of some soluble species of transition metal oxyanions. It has been found that potassium chromate in sodium nitrite-potassium nitrite melt has an absorption maximum at 24000 cm^{-1}(29) whereas the green-yellow melt which was produced on the addition of chromium (VI) oxide to the melt gave an absorption band at 16600 cm^{-1}. It was reported that the addition of potassium permanganate to a nitrite melt yielded a semistable blue coloured solution which was rendered stable on the addition of sodium peroxide or sodium hydroxide. The spectra of the quenched blue solution has shown an absorption band at 30500 cm^{-1} and 15000 cm^{-1} which were attributed to the presence of MnO_4^{3-}(40). In the present work, the spectra of nickel (II) chloride and copper (II) chloride are reported. These are the first successful spectral measurements of non-oxyanionic transition metal compounds in molten nitrite.

Some reactions of organic compounds in nitrite melts have also been investigated, an example is the oxidation of sodium formate and sodium acetate in molten sodium nitrite forming sodium carbonate with the evolution of N_2O, N_2 and H_2O.(41) In recent work it was found that oxalate ion was oxidized in a nitrate melt producing nitrite ion which also oxidized the oxalate ion with the evolution of CO_2,NO and N_2O.(42) In contrast, the phase diagrams of sodium formate and acetate with sodium nitrite have been reported with no mention of any reaction have been observed(43) which might be due to the slow rate of reaction of these compounds with nitrite melt.

From the foregoing discussion of the nitrite melt it is clear that the amount of work so far done in this field is small and there are many questions yet to be answered regarding the behaviour of nitrite salt in the molten state.

Therefore the aim of the present investigation was to clarify the oxidation-reduction behaviour of nitrite melt, to obtain additional information about the acid-base reactions of such solvent, and to evaluate the role of the peroxide ion in a nitrite melt.

CHAPTER I

THE MELT

PREPARATION AND PROPERTIES

I.1 INTRODUCTION

Pure alkali metal nitrites as well as binary and ternary nitrite systems have been the subject of investigation which includes the use of the melts as media for chemical reactions. It has been found that the melting points of the pure alkali metal nitrites increase markedly with atomic weight as for example the melting points of $LiNO_2$, 222°C; $NaNO_2$, 284°C and KNO_2, 438°C. In the binary eutectics, the melting point also increases with the average atomic weight, but to a lesser extent, as shown by, for example $LiNO_2/KNO_2$, (45:55 mol%) m.p 98°C, $LiNO_2/NaNO_2$, (62:38 mol%), m.p 151°C, and $NaNO_2/KNO_2$, (65:35 mol%), m.p 220°C.(44,45,46)

Many other nitrite systems, both binary and ternary, have been studied by several workers.(47,48) The eutectic point temperatures of the binary system have been found to vary from 102°C for the ceasium nitrite-potassium nitrite system to 221°C for the barium nitrite-potassium nitrite system. For ternary systems the eutectic point temperatures range from 98°C for the potassium nitrite-lithium nitrite-strontium nitrite system to 168°C for barium nitrite-potassium nitrite-sodium nitrite system. These systems and other nitrite systems which have been investigated are listed in Table 1.

Table 1

Eutectic composition and melting points

system	composition mol%	eutectic m.p. °C
$Ba(NO_2)_2$ - KNO_2	31.6	221
$Ba(NO_2)_2$ - KNO_2 - $LiNO_2$	0.25 - 59.15 - 40.6	106
$Ba(NO_2)_2$ - KNO_2 - $NaNO_2$	21.2 - 42.4 - 36.4	162
$Ba(NO_2)_2$ - $LiNO_2$	20.5	182
$Ca(NO_2)_2$ - KNO_2	25	185
$Ca(NO_2)_2$ - $LiNO_2$	9.6	205
$Ca(NO_2)_2$ - $NaNO_2$	32.4	200
$CsNO_2$ - $LiNO_2$	60	102
$CsNO_2$ - $TlNO_2$	25	162
KNO_2 - $LiNO_2$	59.3	104
KNO_2 - $LiNO_2$ - $Sr(NO_2)_2$	61.2 - 36.7 - 2.0	98
KNO_2 - $NaNO_2$	35	218
KNO_2 - $Sr(NO_2)_2$	73.2	213
$LiNO_2$ - $NaNO_2$	63	149
$LiNO_2$ - $NaNO_2$ - $Sr(NO_2)_2$	55.1 - 36.7 - 8.2	137
$NaNO_2$ - $Sr(NO_2)_2$	71	218
$NaNO_2$ - $TlNO_2$	18	140
$Sr(NO_2)_2$ - $TlNO_2$	12.7	142

In the present work three nitrite eutectic mixtures were used as solvents. Sodium nitrite-potassium nitrite eutectic was used in most studies because of its lower melting point, by comparison with pure nitrite melts, and its ease of preparation in comparison with other eutectics. However, the nitrite ion in this eutectic exhibited high reactivity as a Lux-Flood base even at the melting point so that insoluble metal oxides, rather than soluble complex species, were formed by reacting with metal compounds. To obtain a solution containing transition metals, the low melting sodium nitrite-potassium nitrite-barium nitrite eutectic was tried, but re-crystallization of barium nitrite from the melt on handling at room temperature for a few seconds imposed a higher working temperature and, as a result, insoluble transition metal oxides were formed. However, the lithium nitrite-potassium nitrite binary eutectic which has a lower melting point than the ternary sodium nitrite-potassium nitrite-barium nitrite eutectic was found to form soluble solutions with some transition metal compounds, and visible spectra were determined successfully.

The densities (49) of these molten nitrites of lithium, sodium, potassium, rubidium and cesium have been determined and their molar volumes calculated. These measurements were, of course, carried out over the temperature range in which the melts were thermally stable.

I.2 PREPARATION OF NITRITE EUTECTICS

I.2.1 Sodium nitrite-potassium nitrite eutectic

Reagent grade potassium nitrite (Hopkins and Williams G.P.R.)

and Analar sodium nitrite (B.D.H.) were dried 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 nitrite eutectic of 35 mol% KNO_2.$^{(46)}$ 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 about 270°C using a No. 4 porosity sinter funnel with an attached B24 drip cone in the top of a conical flask. A side arm on the filter funnel terminated in a B10 cone, which was connected through a socket to a water pump via an outlet in the roof of the oven. This technique achieved a rapid, efficient filtration.

The melt was solidified after filtration and then broken into small lumps and stored in a desiccator over silica gel. Before using the melt in chemical reactions it was finally dehydrated by evacuation at less than 10^{-2} torr and about 220°C for 20 hours. The dehydration procedure was as follows.

The melt was contained in a Pyrex tube with a B24 socket to which a B24 cone was fitted. The B24 cone terminated with a B14 socket and had a side arm with a stopcock. The side arm terminated with a B10 cone which was attached to the vacuum pump through a flexible joint of pressure tubing <u>via</u> a liquid nitrogen trap. It was found that sudden evacuation of the crude melt always led to violent evolution of the residual water causing splashing of a large amount of melt onto the upper, cooler parts of the apparatus where it solidified. To avoid this, either the solid eutectic was evacuated for about five hours, then the temperature gradually raised to 220°C or if starting with the fused eutectic, the pressure was gradually reduced using an Edwards needle valve inserted in the B14 socket. By gradually closing the needle valve over about 30 minutes, rapid evacuation was avoided. When the valve was completely closed it was replaced by a Pirani gauge and the pressure then maintained at 10^{-2} torr for about 20 hours. These methods invariably yielded a clear yellow coloured melt.

I.2.2 Preparation of sodium nitrite-potassium nitrite-barium nitrite eutectic

This ternary eutectic was prepared from reagent grade potassium nitrite (Hopkins and Williams, G.P.R.). Analar sodium nitrite (B.D.H.) and reagent grade barium nitrite (Hopkins and Williams, G.P.R.). The reagents were dried separately at 130° for 30 hours then mixed in the eutectic proportions quoted by Protsenko(50) (4.24 mol% KNO_2, 36.4 mol% $NaNO_2$ and 21.2 mol% $Ba(NO_2)_2$). The mixture was fused at 200°C for several hours and then filtered through a No. 4 sinter as described above. The filtered melt was solidified by cooling, ground into small pieces and then dehydrated under vacuum for 20 hours as described previously. As the melting point of this mixture was found to be 170°C, six degrees higher than that quoted by Protsenko (164°C), a cation analysis was carried out to accurately determine the percent composition. The results of the analysis are presented later in this chapter.

The ternary eutectic was found more convenient, than the sodium nitrite-potassium nitrite binary eutectic since it has a lower melting point. The difficulty faced in using it was the precipitation of barium sulphate whenever potassium pyrosulphate, a reagent frequently used for rendering melts acidic, was added.

I.2.3 Preparation of lithium nitrite-potassium nitrite eutectic

Since several transition metal compounds were observed to react with both sodium nitrite - potassium nitrite eutectic and the ternary sodium nitrite-potassium nitrite-barium nitrite eutectic at or below their melting points, it was considered desirable to prepare a much lower melting alkali metal nitrite eutectic to determine if a soluble transition metal species could be obtained. Lithium nitrite-potassium nitrite eutectic with a melting point of 107°C was chosen for this purpose. Since lithium nitrite is expensive and not locally available, it was found more convenient to prepare the compound. The preparation procedure is described below.

The eutectic was prepared as follows: After drying the lithium nitrite and potassium nitrite to a constant weight at 150°C, they were mixed in the proportion given by Protsenko(48) (60 mol% KNO_2), melted at 130°C and filtered in a similar manner as to that used for sodium nitrite-potassium nitrite eutectic. The eutectic was then dehydrated again at a vacuum of 10^{-2} torr at 110°C for ten hours, solidified and stored in a dry box. The melting point was determined and found to be (110°C ±2°C).

I.2.4 Preparation of lithium nitrite

Two methods were employed for the preparation of lithium nitrite which was reported by Ball(51) to crystallize with a molecule of water to form $LiNO_2.H_2O$. It was found that the first method of preparation, from lithium sulphate and barium nitrite was inconvenient because of difficulties in removing the fine barium sulphate particles. Therefore, a second method using potassium nitrite was tried and found more convenient. Equal molar quantities of reagent grade potassium nitrite (Hopkins and Williams, G.P.R.) and lithium sulphate were mixed in a concentrated aqueous solution and the preciptated potassium sulphate filtered through a No. 4 sinter. The filtrate was evaporated to dryness and the lithium nitrite extracted from the residue with absolute alcohol, in which residual potassium sulphate was much less soluble. The alcoholic solution was evaporated under vacuum using a rotating evaporator at about 50°C.

Since thermal dehydration at 160°C of hydrated lithium nitrite resulted in some decomposition, vacuum dehydration was preferred. The salt was placed in a B24 test tube and evacuated at room temperature for about six hours. The temperature was then raised to 110°C over about four hours and salt was kept evacuated at this temperature for six hours. The salt was then examined for the water of hydration by using a thermogravimetric balance. No weight loss was observed up to 140°C. The purity of the salt was determined by analytical methods to be described later in the analysis section. (Found Li = 12.8% and NO_2^- = 81.2%. Calculated for $LiNO_2$, Li = 13.2% and NO_2^- = 86.7%).

I.2.5 Preparation of sodium nitrate-potassium nitrate eutectic

Analar sodium nitrate (B.D.H.) and Analar potassium nitrate (B.D.H.) were dried at 120°C for six hours, cooled, and mixed in the eutectic proportions.(21) The remainder of the preparation and filtration was carried out as in the preparation of sodium nitrite-potassium nitrite eutectic. The melting point of the eutectic was found to be 218 ± 2 °C.

I.3 ANALYSIS

I.3.1 Analysis of nitrate in the presence of nitrite

The analytical method(52) used here is adapted for the determination of small amounts of nitrate when nitrite forms the bulk of the sample. First the nitrite ion was decomposed with sulphamic acid according to the equation

$$NaNO_2 + NH_2SO_3H \rightarrow NaHSO_4 + N_2 + H_2O \qquad \text{... I.1}$$

The nitrite solution was added dropwise to an ice cooled sulphamic acid solution in order to avoid either the formation of additional nitrate from the formation of nitrogen dioxide and nitric oxide, or the destruction of the nitrate already present in the solution. After the destruction of the nitrite ion, the nitrate ion is reduced by an excess of iron (II) sulphate according to the equation

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O \qquad \text{... I.2}$$

by boiling for three minutes in the presence of sodium chloride. The excess iron (II) ions were back titrated with standard potassium dichromate solution. In every analysis, between 10 - 15 g of the nitrite eutectic were dissolved in water and made up to 250 ml. Using a burette, 25 ml of this solution were added dropwise to 30 ml of an aqueous 15% sulphamic acid solution. During the addition, the latter solution was continuously stirred and kept in an ice water bath. This method of addition eliminated the production of nitrogen dioxide and nitric oxide in amounts which would have interfered in the analysis. After complete addition, the solution was made up to 100 ml.

Two grams of sodium chloride and ten ml of 0.02M iron (II) sulphate were added to 25 ml of the nitrite-free solution and the mixture boiled for three minutes. After cooling the solution was titrated with 0.1M potassium dichromate using ferroin as an indicator. The nitrate content was calculated from the difference in dichromate used for the blank and the sample. The analysis of different batches of nitrite eutectic showed a different nitrate and oxide ion concentration depending on the nature of thermal treatment the eutectic had undergone. The oxide ion was determined by titration the aqueous solution with 0.1M sulphuric acid.

I.3.2 Determination of lithium nitrite

Nitrites react in warm acid solution with permanganate solution to produce manganese (II) and nitrate.(53) About 0.8 - 1 g of lithium nitrite were dissolved in distilled water and diluted to 250 ml in a volumetric flask. 10 ml of standard 0.01M potassium permanganate were introduced into a 500 ml conical flask, 300 ml of 1M sulphuric acid were added and the solution heated to 40°C on a stirring hot plate. The nitrite solution was added slowly from a burette with a constant stirring until the permanganate solution was just decolorised. Lithium was determined gravimetrically as lithium sulphate after converting to the sulphate by evaporating with concentrated sulphuric acid.

I.3.3 Analysis of sodium nitrite-potassium nitrite-barium nitrite eutectic

Since the ternary sodium nitrite-potassium nitrite-barium nitrite eutectic was found to have a melting point higher than that quoted by Protsenko(50) analysis was carried out for the cations present to determine accurately the percentage composition. Barium was determined gravimetrically as barium sulphate by the addition of an excess of dilute sulphuric acid to a hot aqueous solution of the eutectic. The precipitate was weighed after ignition at 900°C.

An E.E.L. Flame spectrometer was used for the determination of sodium and potassium. The calibration curve for sodium and potassium was prepared using standard solutions of Analar sodium and potassium chlorides. The analysis gave results as follows:
K = 15.6%, Na = 7.9% and Ba = 25.2%. (Calculated for $Na/K/Ba(NO_2)_2$
K = 15.0 %, Na = 7.6% and Ba = 26.3%.)

I.4 EXPERIMENTAL TECHNIQUE

Experiments in molten nitrite were carried out in a Pyrex test tube with B24 socket closed with a silica gel drying tube. In some reactions a supply of dry oxygen-free nitrogen, purified by passage through chromium (II) chloride solution and then dried by passing through a concentrated sulphuric acid tower and a phosphorus pentoxide tube, was passed over the melt during a reaction. The reaction test tube fitted snugly into an electric furnace connected to an Ether Transitrol controller, by which the furnace temperature was regulated to ± 4°C. The furnaces used in most of the experiments consisted of a 3½ inch deep steel pot of the required internal diameter which was wound with a nichrome wire threaded through insulating refractory beads and embedded in alumina cement. The pot was held in a square asbestos box and the free space filled with micafil insulator. Such a furnace had a temperature range up to 600°C, depending on the resistance wire and the number of windings.

For the study of the reactions of a nitrite melt containing sodium peroxide in a zirconium crucible, the glass tube holding the crucible was immersed in a constant temperature bath. This bath was a well insulated stainless steel pot containing approximately 15 Kg of sodium nitrite-potassium nitrite eutectic placed on a 500 watt hot plate controlled by an Ether Transitrol. A mechanical stirrer was used to ensure a uniform temperature throughout this molten bath. The temperature of the bath was measured with a 360°C mercury thermometer as well as a thermocouple and Transitrol.

In carrying out a chemical reaction, between 10 to 15 grams of melt were used. The occurrence of chemical reactions after the addition of reagents was monitored every 15 minutes by tests on small samples taken either by inserting a cool glass rod into the reaction melt or using a piece of a glass tubing plugged with a glass wool filter. Alternatively a quantitative and/or qualitative analysis of the products was performed on the whole melt on completion of reaction, usually after dissolving in water, making up to the appropriate volume and using portions for analysis. Insoluble reaction products were analysed after removing the nitrite melt with water.

I.5 DISCUSSION OF PROPERTIES

In view of the hygroscopic nature of the anhydrous nitrites, particularly when its eutectics contained lithium, it is necessary to avoid, as far as possible, contact with the atmosphere in holding or transferring operations. The purified melt was therefore poured directly from the preparation tube into an evaporating basin in a small desiccator and the desiccator immediately evacuated and placed in a dry box. The solidified melt was rapidly ground in the dry box and then stored in closed sample bottles in a desiccator.

To carry out a weighing of the melt on a balance, a silica crucible with a tightly fitting polythene cover was used, all transfers being carried out inside the dry box. The covered crucible containing the melt was kept in a desiccator except when being weighed. Contact of air with the melt during the weighing was found by thermogravimetric analysis to have almost no effect on the eutectic.

Sodium nitrite-potassium nitrite eutectic was found to be reasonably stable up to 500°C, though the upper limit of investigation was normally 400°C at which temperature attack on the Pyrex containers became appreciable resulting in opacity and ultimately cracking of the glass. Silica was more resistant but also became etched after several days at 400°C. The presence of sodium peroxide renders the melt more corrosive, even at the melting temperature, and it was found that the corrosion speed was dependent on both the concentration of peroxide and the temperature of the melt. Etching was noticed after 20 minutes at 250°C with a peroxide concentration of 9×10^{-4}m, thus it is undesirable to use silica cells for spectroscopic measurements of peroxide in the melt since the etching led to a loss in transmission.

A further troublesome property of nitrite melts was their expansion on solidification, which could cause fracture of a glass tube, spectroscopic cell, or other closed container. This made storage of reacted melt, which had been cooled to room temperature, impossible in such vessels. A technique used for small amounts was to allow the melt to solidify against the wall of the vessel rather than in contact with both walls and the bottom, by tilting the tube while the eutectic was still liquid. In this way expansion on cooling merely lifted the globule of melt off the side of the tube.

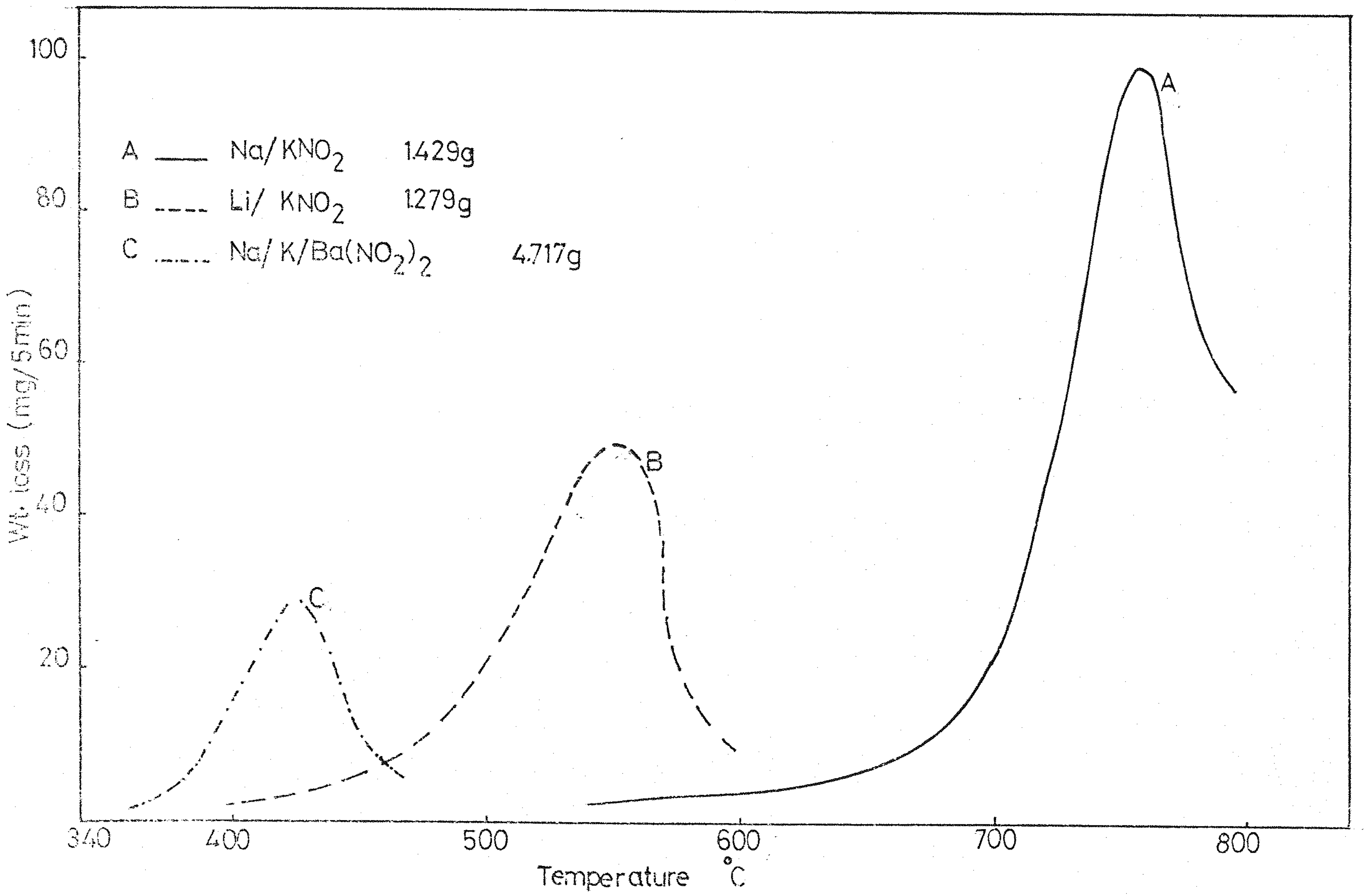
I.5.1 Decomposition of nitrite eutectics

The decomposition of the alkali nitrites are of considerable importance in view of their use as solvents. Apart from the large scale rapid decomposition of the melt at higher temperature which imposed an upper temperature limit on their use, the slow thermal decomposition of sodium nitrite-potassium nitrite, lithium nitrite-potassium nitrite and sodium nitrite-potassium nitrite-barium nitrite eutectics at much lower temperatures under atmospheric conditions were investigated using a Stanton T.R.1 thermobalance. The ternary sodium nitrite-potassium nitrite-barium nitrite eutectic was shown to have a lower decomposition temperature than the other two eutectics as seen in Figure I curve **C**. The decomposition of this melt started at 360° ± 10 with a weight loss increasing slowly until it reached a maximum around 425°C.

Protsenko(54) who studied the thermal decomposition of pure barium nitrite in air using differential thermal analysis reported decomposition to occur at 410° - 440°C, whereas the present work showed that the decomposition of the same compound commenced at 370° ± 10°C. The decomposition of the ternary eutectic at 360°C was thus probably due to the thermal decomposition of barium nitrite, as

Fig . I

T.G.A. of nitrite eutectics



both sodium nitrite and potassium nitrite decompose at higher temperatures.

No weight loss was observed on heating the lithium nitrite-potassium nitrite eutectic until $400^{\circ} \pm 10$. The velocity of the decomposition increased with temperature until it reached a maximum at 550° (Figure I curve B). Thermogravimetric analysis of pure lithium nitrite showed weight loss to begin at $240^{\circ} \pm 10$. The presence of potassium nitrite in the eutectic proportions increased the thermal stability of lithium nitrite as it shifted the decomposition temperature to $400^{\circ}C$. The nature of this stabilization is not clear.

The thermal stability of sodium nitrite-potassium nitrite eutectic was found to be higher than that of the ternary sodium nitrite-potassium nitrite-barium nitrite and the lithium nitrite-potassium nitrite eutectics as shown in Figure I curve A. The decomposition started at $550 \pm 10^{\circ}C$ with a maximum weight loss around $760^{\circ}C$.

The decomposition of pure potassium nitrite was investigated and was found to commence around $520 - 560^{\circ}C$.

The thermal decomposition of pure sodium nitrite has been studied over the temperature range of $650 - 780^{\circ}C$(55) and the decomposition gases were found to consist of nitrogen and oxygen as well as a small amount of nitric oxide and nitrogen dioxide. During the initial stages of decomposition nitrogen was found to be the predominant gas formed; however, as the reaction progressed the relative quantity of oxygen increased. Sodium superoxide was suggested as an intermediate product during the course of decomposition and the increased proportion of oxygen as the decomposition of sodium nitrite proceeded was attributed to the decomposition of superoxide to monoxide and oxygen. Traces of nitrogen dioxide and nitric oxide observed during the decomposition is in qualitative agreement with the results reported by Oza.(56)

On the basis of these thermogravimetric studies, upper working temperatures of 360°C, 400°C and 550°C for sodium nitrite-potassium nitrite-barium nitrite, lithium nitrite-potassium nitrite and sodium nitrite-potassium nitrite eutectics were adopted which provided liquid ranges of 170 - 360°, 110 - 400° and 220 - 550° respectively.

I.5.2 Volatility

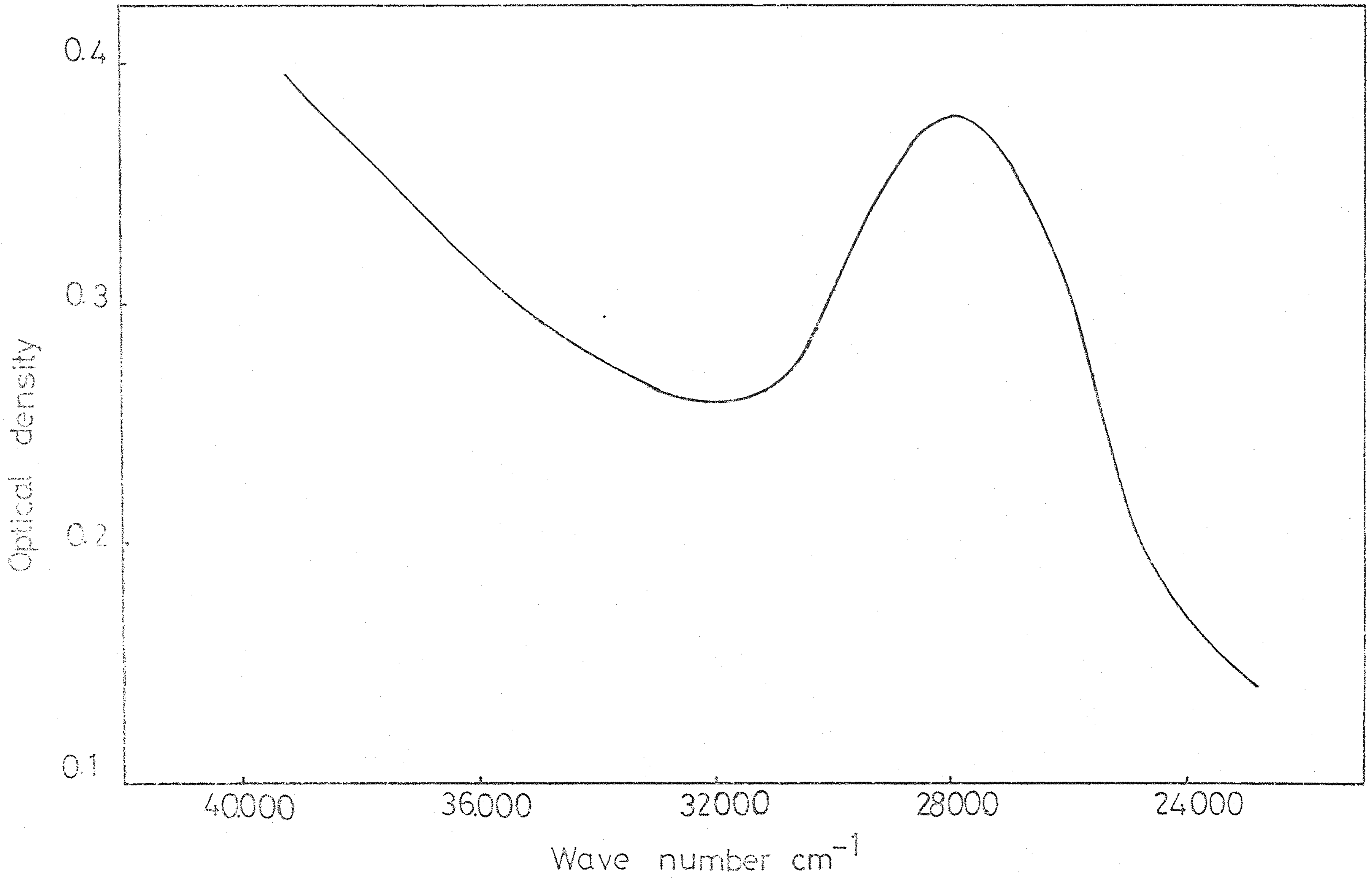
The volatilities of sodium nitrite and potassium nitrite have been studied by Hardy and Field.(57) They showed that both alkali metal nitrites can be distilled from their melts, without significant decomposition, at a pressure of 5×10^{-3} torr in the temperature range 300 - 500°C. This effect, although not serious in qualitative experiments, introduced errors when evacuating a standard melt for long periods of time above 350°C, as slow loss of melt occurred. The effect of melt evaporation could be minimized by carrying out reactions in vacuo below 350°C. This precaution was normally followed in the present work.

I.5.3 Ultraviolet spectra

Ultraviolet spectroscopy of sodium nitrite-potassium nitrite melts was carried out on a Unicam S.P. 700 modified for use up to 1000°C. The absorption spectra of the melt against air was determined

Fig. 2

U.V spectra of nitrite melt



by first filling the spectroscopic cell with melt and then emptying it, the measurements being made on the thin film which remained on the cell. The spectra shows an absorption band at 28000cm^{-1} which has been attributed to a charge transfer within the nitrite ion.(58) (Figure 2).

CHAPTER II

REACTIONS OF VANADIUM COMPOUNDS

II.1 INTRODUCTION

Vanadium compounds present an interesting field of study in molten salt chemistry because of their oxidation-reduction behaviour and their acid-base properties. These two behaviours of the vanadium compounds were demonstrated in the present investigation where sodium nitrite-potassium nitrite eutectic was used as a reaction medium.

Analogous investigations have been carried out on the reactions of vanadium compounds in other molten salts, though sometimes with rather different results. In molten nitrate, the reactions of vanadium compounds have been studied. Shams El din and El Hosary(59) studied the reaction of vanadium pentoxide in a pure potassium nitrate melt at 350°C using an acid-base titration technique and they reported that the pentoxide reacted with the melt producing a soluble species as the melt got gradually clear. It was suggested that the first step of the reaction was the conversion of vanadium pentoxide into metavanadate. The resulting metavanadate does not exist as such in the melt. Being a strong Lux-Flood acid, it directly attacks the base (nitrate ion) to yield pyrovanadate. The pyrovanadate was found to be stable and soluble at 350°C, but could be converted to orthovanadate on rendering the melt more basic by the addition of sodium peroxide.

Thermogravimetric studies have been done on sodium metavanadate and vanadium pentoxide in lithium nitrate-potassium nitrate eutectic. It was reported that the reaction of metavanadate commenced at 400°C yielding pyrovanadate as the first step. The second step started around 530°C producing orthovanadate. Whereas, vanadium pentoxide was found to react at a lower temperature (270°C) forming metavanadate. The later ion then reacted (410°C) to give a pyrovanadate, which at 500°C depolymerized into orthovanadate. A slower rate of reaction of these compounds in sodium nitrate-potassium nitrate eutectic, though forming the same products, was reported.(60)

In addition to the oxyanion melts, potassium thiocyanate melt has been used as a solvent in which the reaction mechanisms of vanadium compounds in oxidation state (III), (IV) and (V) have been studied. It was reported that orthovanadate and metavanadate were not reduced by the thiocyanate ion, but reacted to form a soluble thiovanadate species. The reaction of orthovanadate produced a series of intensely coloured solutions, i.e. yellow, orange, red and purple, which were attributed to the exchange of oxygen for sulphur in the orthovanadate ion.

$$VO_4^{3-} \rightarrow VSO_3^{3-} \rightarrow [VO_2S_2^{3-}] \rightarrow VS_3O^{3-} \rightarrow VS_4^{3-} \qquad \ldots \text{ II.1}$$

the final stage of reaction, i.e. $VS_3O^{3-} \rightarrow VS_4^{3-}$, was found to occur only in the absence of oxygen. Vanadium pentoxide and ammonium metavanadate were reported to be reduced in molten thiocyanate forming a black solid (VO_2) and a green solution (VO^{2+})

$$V_2O_5 \rightarrow VO_2 + VO^{2+} + O^{2-} + O \qquad \ldots \text{ II.2}$$

while vanadium (IV) oxide showed no reaction even at 350°C, but in the presence of oxide or sulphide it reacted at 200°C to yield red melts ($VO_2S_2^{3-}$). Vanadium (III) chloride was reported to be soluble in potassium thiocyanate melt and that a golden brown colour was formed which was suggested to be hexathiocyanatovanadate.(61)

Spectroscopic studies have been reported for vanadium compounds in molten sodium chloride-potassium chloride system. The spectrum of V^{3+} at 400°C has been interpreted as being due to the octahedral VCl_6^{3-} species. At a higher temperature a marked increase in the intensity of the spectrum was observed as well as a shift of the absorption bands to a longer wave length. This behaviour was interpreted as being due to the octahedral-tetrahedral transformation equilibrium.(62)

$$VCl_6^{3-} \rightarrow VCl_4^{-} + 2Cl^{-} \qquad \text{... II.3}$$

In lithium chloride-potassium chloride eutectic, the spectrum of V^{2+} was studied as a function of temperature in the range 400 - 1000°C. Marked intensity changes and shifts in band positions were noted in this temperature interval and were once again interpreted as being due to the octahedral-tetrahedral transformation equilibrium.(63)

In view of the observed reactions of many vanadium compounds in nitrate melt and the foregoing background, the objectives of the present work were formulated as follows. The reactions of potassium disulphatovanadate$^{(III)}$ vanadyl sulphate, vandium dioxide, vanadium pentoxide and metavanadates with sodium nitrite-potassium nitrite eutectic were studied and their stoichiometries were established.

The reduction behaviour of the nitrite melt and the formation of a lower oxidation state (vanadium (IV) oxide) by the reaction of vanadium pentoxide is reported. Finally, the catalytic effect of sodium orthovanadate on the thermal decomposition of the nitrite eutectic is also reported.

II.2 EXPERIMENTAL

II.2.1 Materials

The sodium nitrite-potassium nitrite eutectic was prepared as described in Chapter I. The materials used as reactants were B.D.H. reagent grade sodium orthovanadate, sodium metavanadata, ammonium metavanadate, vanadium pentoxide and vanadyl sulphate which had been dried at 250°C for two hours, 120°C for one hour, 100°C for one hour, 120°C for one hour and 300°C for six hours respectively. The vanadium content of the chemicals used was determined and the results are listed in the following table:

Table 1

Reagent	V% Found	V% Calc.
Na_3VO_4	34.8	36.9
$NaVO_3$	41.1	41.8
NH_4VO_3	36.7	38.9
V_2O_5	55.4	56.0
$VOSO_4$	30.2	31.3
VO_2	60.2	61.4
$KV(SO_4)_2$	16.6	17.4

II.2.2 Preparation of compounds

Vanadium (IV) oxide

Vanadium (IV) oxide was prepared using the procedure of Tandy as follows:(64) using a 500 ml conical flask, 20g of vanadium pentoxide were suspended in 250 ml of distilled water. The flask was placed on the hot plate of a magnetic stirrer. Sulphur dioxide was then passed through the suspension at 40°C for 12 hours with constant stirring. The solution formed was then decomposed by boiling under a stream of carbon dioxide. A precipitate was formed which on drying at 440°C under vacuum, gave pure V_2O_4.

Potassium disulphatovanadate

The $KV(SO_4)_2$ was prepared by evaporation of a mixture of 200 ml of NH_2SO_4, 10 g vanadyl sulphate, 21g of potassium sulphate and 10 ml of sulphurous acid on a water bath. Following the addition of 10 ml of concentrated sulphuric acid, the solution was heated until it fumed. The mixture was afterwards cooled to room temperature, 400 ml of distilled water were added, and the mixture was then boiled for 20 minutes on a hot plate. The green precipitate which was formed was filtered through a No. 3 sinter, washed with water, and finally dried under vacuum.(65)

II.2.3 Analytical procedures

Analyses of nitrate and oxide ion concentrations in the melt after reaction was carried out as mentioned in chapter I. The vanadium species were determined qualitatively and quantitatively as follows:

(a) Identification of Vanadium species

Qualitative analyses were applied to distinguish between orthovanadate and metavanadate using copper (II) sulphate solution as well as pH measurements.(66) Addition of copper (II) sulphate solution to an aqueous solution of sodium metavanadate gave a yellow precipitate, whereas an aqueous solution of sodium orthovanadate gave a green precipitate. The pH of the solution of orthovanadate was ≅ 11.0 while the pH of the solution of metavanadate was ≅ 7.5. As an example of the use of these methods the first reaction products of VO_2, $VOSO_4$, $KV(SO_4)_2$, V_2O_5 with nitrite melt, after dissolving in water, gave a yellow precipitate with copper (II) sulphate and a pH ranging between 7.5 - 7.9 which corresponded to the presence of metavanadate. The second stage reaction products solution gave a pH (10.5 - 11.0) and a green precipitate on the addition of copper (II) sulphate indicating the presence of orthovanadate.

(b) Determination of vanadium (IV) and (V)

Vanadium in solution as a vanadate ion was reduced to the vanadyl salt by the addition of sodium sulphite and the solution was then titrated with 0.1M potassium permanganate.(67) To the solution which contained the vanadate species dilute sulphuric acid (1:1) was added in excess followed by the addition of sodium sulphite. The solution was then boiled down to two-thirds of its volume to remove all the unreacted SO_2 which could be tested by its smell. After cooling, the solution was titrated with 0.1M potassium permanganate to a faint permanent pink colour. When the solution contained both vanadium (IV) and (V), vanadium (IV) was first determined directly and then all the vanadium was reduced to vanadium (IV) and titrated again with permanganate. Vanadium (V) concentration was then calculated from the differences between the first and the second titration figures.

II.2.4 Physical measurements

Ultraviolet spectroscopy of the melt solutions was carried out on a Unicam S.P.700 spectrometer modified for use up to 1000°C. The measurements of the soluble species of orthovanadate in the nitrite melt was carried out using a 1 cm pathlength spectrosil cell. The cell was filled, emptied and the measurement was then made on the thin film which remained. E.S.R. measurements were made using a Varian E-3 spectrometer operating at 9.20 GHz and the infra red spectra of the gases were obtained on a Unicam SP.200G as described in chapter III.

Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance with a heating rate of 2°Cper minute. The weight losses were reported as a percentage by weight of the vanadium contained in the starting material. (For details see Chapter III.)

X-Ray Diffractometer

A Philips X-ray powder diffractometer was used to identify some of the reaction products. The diffractometer consists of a goniometer for measuring the diffraction angles and a number of electronic circuits for determination of the intensity of diffraction at any angle. The goniometer employed a large flat sample combined with a parafocusing arrangement to increase the intensity of diffraction and an X-ray counter to detect the diffracted radiation. Glass slides were used for the preparation of the specimen. A sufficient amount of the finely ground powder, which was wetted to prevent the material from pouring out at steep angles, was placed on the glass and smoothed so that it was flat. In order to identify the unknown substance, the d spacing and the intensity values were matched with those in the A.S.T.M. diffraction tables.(68)

II.3 RESULTS

Sodium orthovanadate was found to be moderately soluble in sodium nitrite-potassium nitrite eutectic, approximately 1.3 m at 320°C. A thin film of this solution showed an absorption at 35000 cm^{-1} as a shoulder on the intense nitrite band (Figure 1). Thermogravimetric analysis indicated that the solutions were stable up to 360°C but that above this temperature a steady weight loss commenced (see Figure 2 curve A and Table 2). The rate of loss increased with the concentration of vanadate and with the temperature and showed some dependence on the quantity of melt in the standard 10 ml silica crucibles. Analysis of the quenched melt indicated an increased concentration of oxide and of nitrate, for example with experiment 1 of Table 2, after 19 hours the oxide and nitrate concentrations reached 0.88 m and 1.25 m respectively.

Sodium metavanadate was almost insoluble in the nitrate eutectic ($\sim 10^{-4}$ m at 250°) but commenced reacting at 310° with the evolution of a mixture of nitrogen dioxide and nitric oxide. The other product, a white solid, dissolved as the temperature increased and was shown to be orthovanadate after quenching and dissolving in

Fig . 1

U.V. specta of orthovanadate in molten nitrite

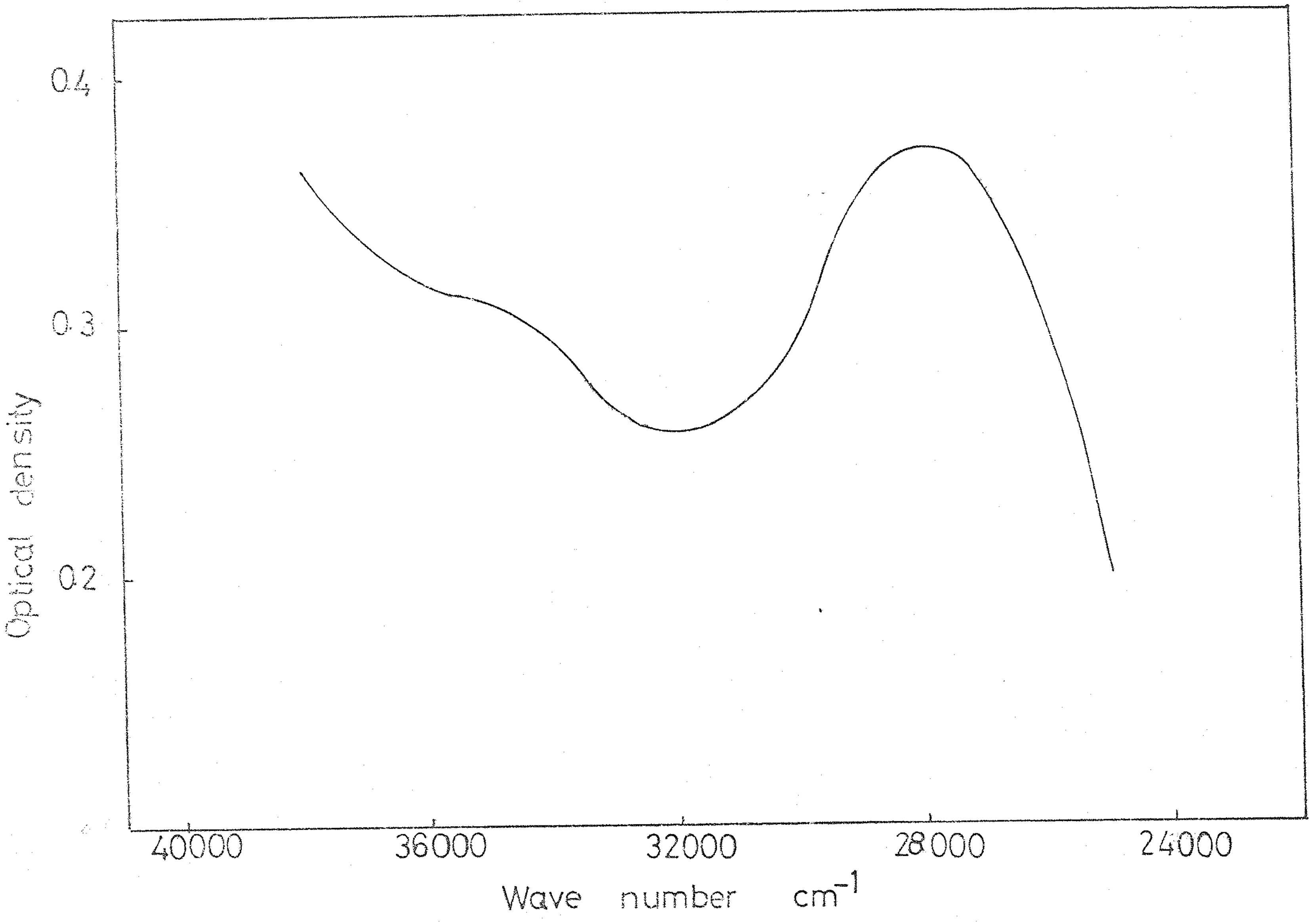
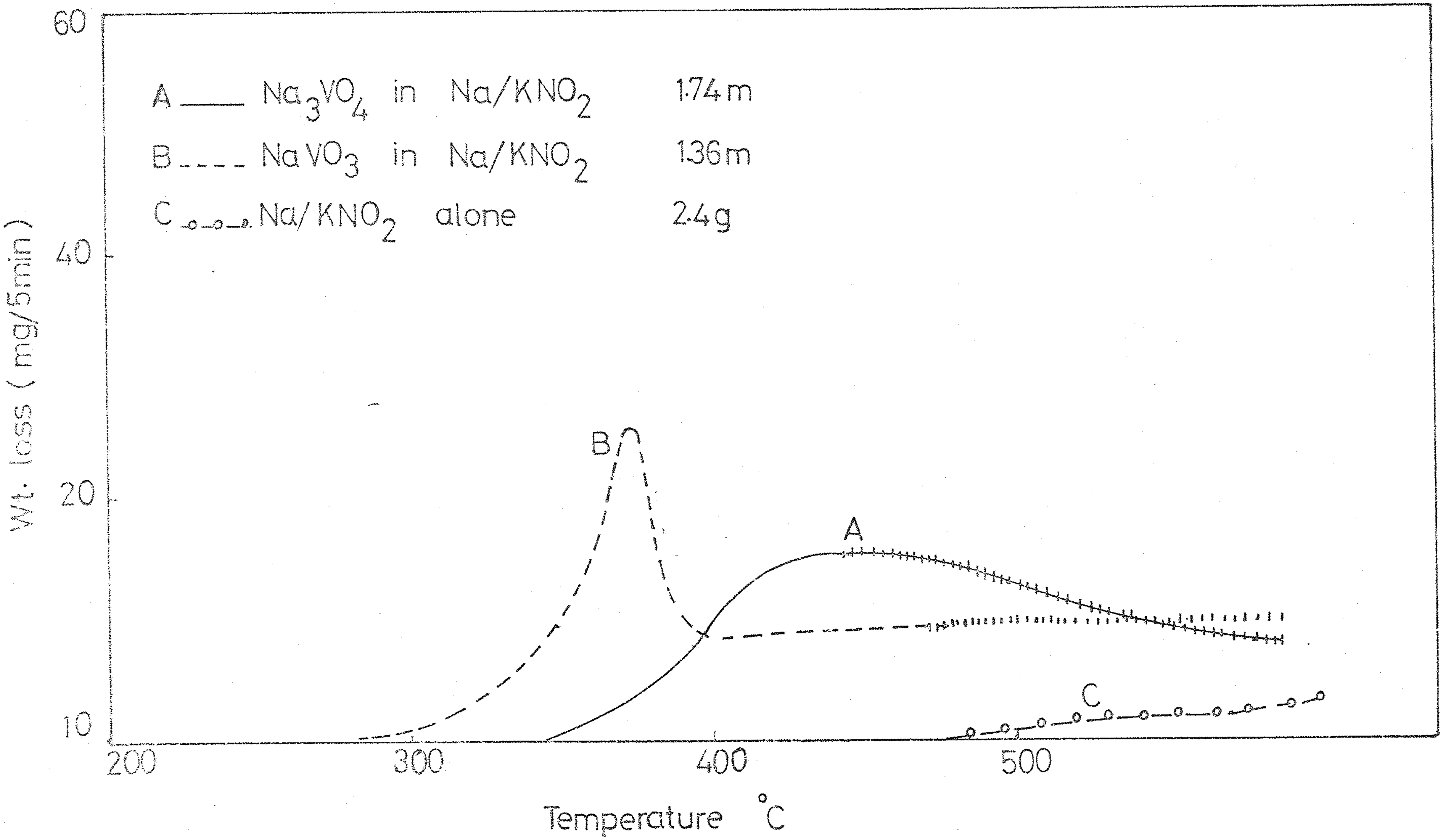


Fig. 2

T.G.A. of vanadium (v) compounds in nitrite eutectic



water. Thermogravimetric analysis showed a weight loss to begin at 280°C and to be continuous up to at least 480°C and for times of at least four hours. The total weight loss varied from 87 to 123%. (Calculated for loss of 2N + 30 per $NaVO_3$ 62.3%.) A typical experiment is represented in Figure 2 curve B with other results given in Table 2.

Ammonium metavanadate reacted, when added to a nitrite melt at 220°C, producing a white precipitate with the evolution of brown fumes. These gases were shown to be ammonia, nitrogen dioxide, nitric oxide and water. In order to follow the stages of the reaction, the mixture of the nitrite eutectic and ammonium metavanadate was slowly heated from room temperature up to 400°C and the visual changes were observed. At 160°C, a yellow colour was obtained, which changed to yellow-brown at 180°C. Around 200°C, brown fumes were evolved indicating the reaction of the vanadate ion with the nitrite eutectic. Above the melting point, a white precipitate of metavanadate occurred which reacted once again with the nitrite melt at elevated temperature forming a clear, yellow melt. The quenched melt was shown to contain orthovanadate.

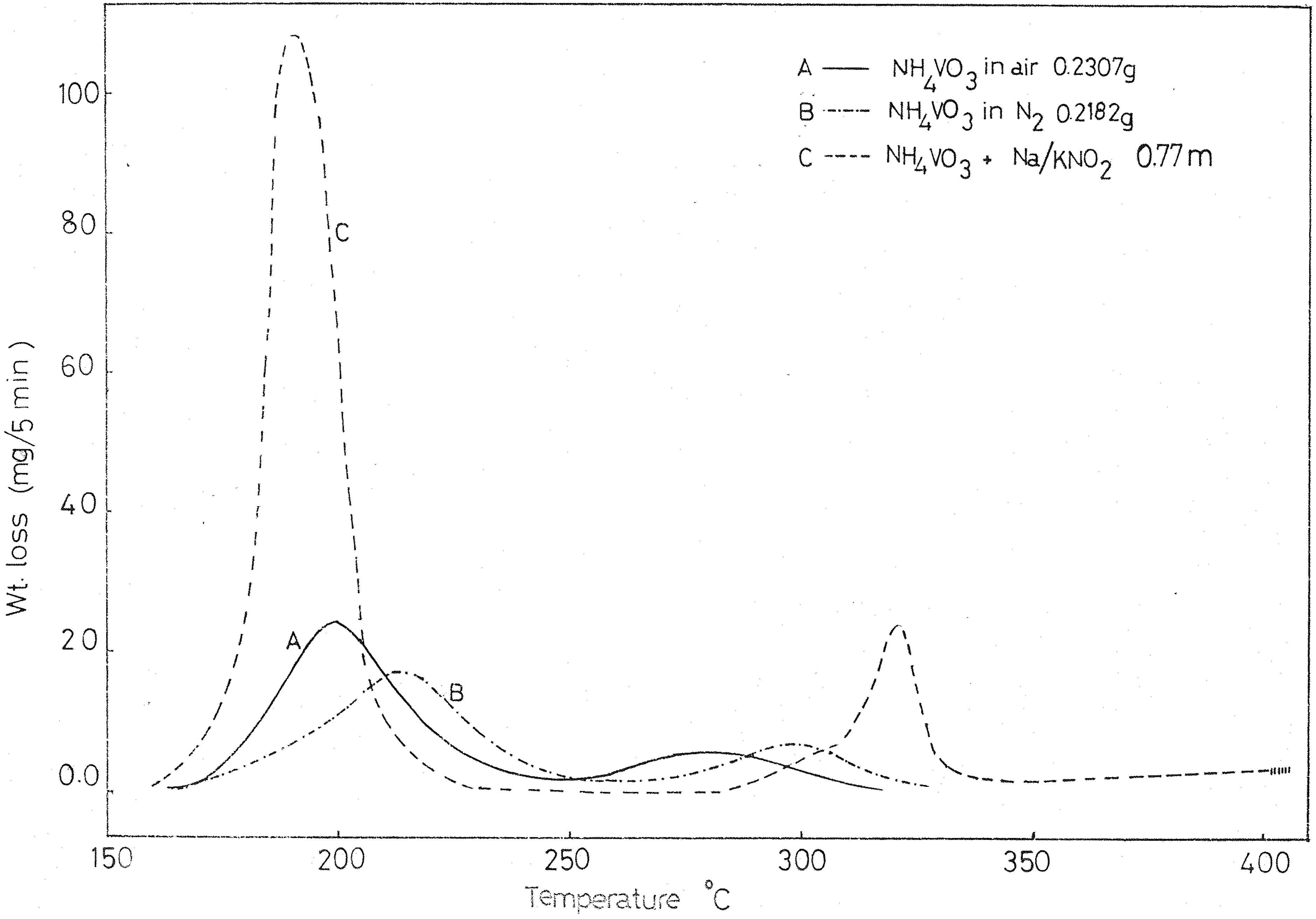
Thermogravimetric analysis (Figure 3 curve C) showed two stages of weight loss. The first commenced at 160°C followed by a rapid loss at 180°C. The weight loss varied from 44.2 to 46.0% which on correction for the formation of nitrate due to reaction of nitrogen dioxide and the nitrite melt

$$NO_2 + NO_2^- \rightarrow NO_3^- + NO \qquad \text{II.4}$$

became 51.4%. (Calculated for loss of 2N + 20 + 4H per NH_4VO_3

Fig. 3

T.G.A. of ammonium metavanadate in nitrite eutectic



52.1%.) The second weight loss started around 280°C with a steady loss in weight above 400°C.

For a better understanding of the reaction of ammonium metavanadate with the nitrite eutectic, the thermal decomposition of pure ammonium metavanadate was investigated. A change in colour to yellow was observed on heating the compound to 160°C; while at 180°C the colour became a yellow-brown and around 300°C the colour was orange. Analyses of the yellow-brown and the orange products shown the presence of ammonium hexametavanadate and vanadium pentoxide. Thermogravimetric analysis showed the weight loss to be in two stages. The first started at 160°C with a weight loss of 14.82% (Figure 3 curve A) and the second stage began at 250°C with a total weight loss of 21.8%.

Vanadium pentoxide commenced reacting below the melting point of the eutectic (Figure 4 curve A) with evolution of nitrogen dioxide and nitric oxide. On increasing the reaction temperature above the melting point of the eutectic, it was apparent that a white precipitate containing blue-black particles had formed. Rapid solution of the frozen melt in water allowed the extraction of the bulk of the white precipitate which was shown to be metavanadate. It did not prove possible to completely separate both precipitates as the blue-black particles tended to form a colloidal solution on continued washing. However, the particles remaining after thorough washing were dissolved in dilute sulphuric acid and formed a bright blue solution, shown to contain vanadium (IV) equivalent to 7% of the original vanadium. E.s.r. spectra on the reacted melt also indicated the presence of vanadium (IV) with a g. factor of 1.99 which

Figure 4

T.G.A. of V_2O_5 and Na_3VO_4 in nitrite eutectic

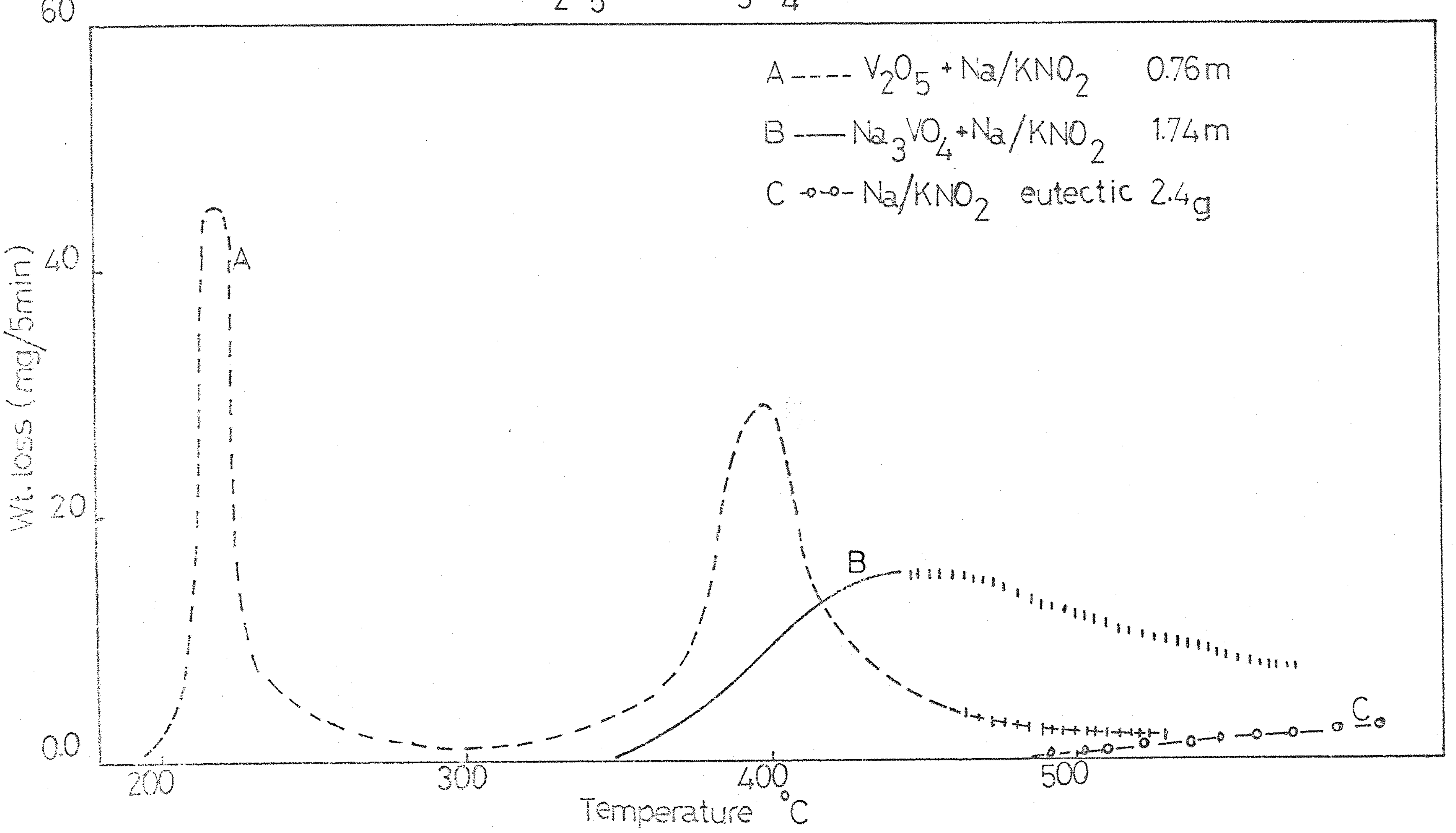


Table 2

Decomposition rates of sodium nitrite-potassium nitrite solutions of vanadium compounds

Expt	Initial solute	Solute concn.	Weight of melt	Temperature	Rate of weight loss
1	Na_3VO_4	1.17m	2.0g	380°	1.0mg/5 min.
2	Na_3VO_4	1.71	1.9	430°	15
3	$NaVO_3$	1.36	2.0	490°	7
4	$NaVO_3$	1.14	3.3	530°-650°	40
5	V_2O_5	0.48	2.2	390°	0.2
6	"	0.82	2.8	390°	0.7
7	"	0.76	1.9	450°	1.2
8	"	1.2	1.8	450°	2
9	$VOSO_4$	0.34	2.9	360°	0.7
10	$VOSO_4$	1.15	1.8	470°	1.5

may be compared to the value of 1.94 found for pure vanadium dioxide.(69) X-ray diffraction gave lines with 'd' values of 3.25 (100%), 2.41 (60%) and 1.65 (60%), corresponding to those of vanadium dioxide in the A.S.T.M. Index 3.20 (100%), 2.42 (60%), 1.65 (60%).

On further increasing the temperature or maintaining it at the melting point for some hours, the blue-black particles gradually reacted, at which stage all the vanadium was in the form of meta-vanadate. Isothermal thermogravimetric analysis showed that the weight loss after four hours at 220°C (m.p. of eutectic) was

31.6 - 32.6%. Assuming that all additional nitrate was formed by nitrogen dioxide reaction with nitrite eutectic, (equation II-4) the weight losses could be corrected to an average value of 41.4%. (Calculated for loss of 2N + 3O per V_2O_5 41.8%.)

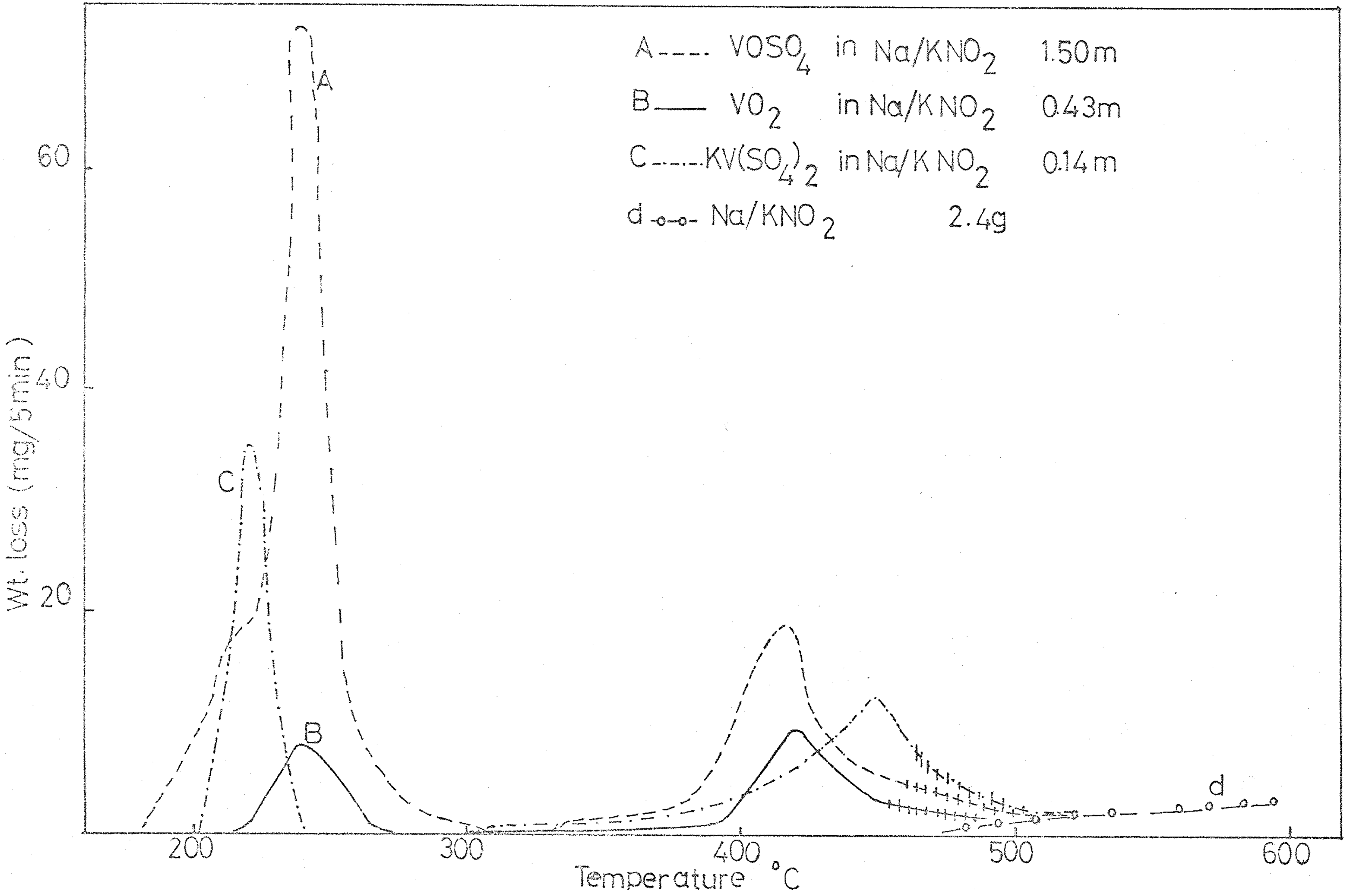
A further reaction commenced at about 310°C, resulting in further evolution of nitrogen dioxide and nitric oxide, and eventually in the formation of orthovanadate. Thermogravimetry indicated a steadily increasing weight loss with time, of more than 132%. (Calculated for loss of 6N + 9O per V_2O_5 125%.) The variation of the rate of weight loss with vanadium concentration and temperature (Table 2) was found to be similar to those of orthovanadate solutions.

Vanadyl (IV) sulphate also commenced to react in the solid state with evolution of a mixture of nitrogen dioxide and nitric oxide. On melting a cream coloured precipitate appeared, which after solidification and solution in water, was identified as metavanadate. Thermogravimetry (Figure 5 curve A) showed a weight loss of 55.5%. (Calculated for loss of 3N + 3O per $VOSO_4$ 55.2%.) Correction of the values for the nitrate formed via equation II.4 gave a loss of 62.9%. (Calculated for loss of 3N + 4O per $VOSO_4$ 65.0%.) On increasing the temperature of the melt, a second reaction commenced at 320°C with further evolution of nitrogen oxides and formation of orthovanadate. Weight losses ranged up to 160%. (Calculated for loss of 5N + 7O per $VOSO_4$ 112%.) The rates again varying with increasing vanadium concentration and temperature (see Table 2).

Vanadium dioxide commenced to react just below the melting point of the eutectic with evolution of nitric oxide, while formation of a white precipitate of metavanadate became evident on melting (Figure 5

Fig . 5

T.G.A. of vanadium(III) and (IV) in nitrite eutectic



curve B). Isothermal thermogravimetry gave a weight loss of 35.4%. (Calculated for loss of N + O per VO_2 36.2%.) When the temperature rose to 300°C a further reaction commenced with considerable evolution of nitrogen dioxide and nitric oxide and formation of orthovanadate.

Potassium disulphatovanadate (III) reacted below the melting point with the evolution of a mixture of nitrogen dioxide and nitric oxide. On raising the temperature above the melting point, a white creamy precipitate appeared. Analysis of the quenched melt, after dissolving in water, showed the presence of metavanadate. Thermogravimetric analysis showed two stages of reaction (Figure 5 curve C). The first stage began at 205°C with a weight loss 41.1% which became 47.1% on correction for the formation of nitrate according to equation II.4 . (Calculated for loss of 4N + 5O per $KV(SO_4)_2$ 47%.) The second stage of weight loss commenced at 300°C, resulting in a further evolution of nitrogen dioxide and nitric oxide with a total weight loss of 114%. (Calculated for loss of 6N + 8O per $KV(SO_4)_2$ 110%.) Analysis of the final product showed the presence of orthovanadate.

II.4 DISCUSSION

Orthovanadate was itself stable in nitrite melts, showing an absorption shoulder not far from that found for the charge transfer band in aqueous solution (36900 cm^{-1}),(70) but had an unexpected catalytic effect on the thermal decomposition of the nitrite, lowering the temperature of the onset of decomposition from 500° to 360°C. The involatile products, oxide and nitrate, were also identified as the products of the uncatalysed decomposition,(55,56,71) while the dependence of the decomposition rate on the silica/melt interface, as well as on the orthovanadate concentration and temperature suggests a heterogeneous mechanism as has been postulated for the uncatalysed decomposition.(55,71) Catalysis by dissolved anions has not hitherto been observed in nitrite melts, though the catalytic decomposition of nitrate melts by chloride and bromide anions has been reported.(72)

The reaction of sodium metavanadate followed that expected of a Lux-Flood acid and was in accord with the equation

$$VO_3^- + 2NO_2^- \rightarrow VO_4^{3-} + NO_2 + NO \qquad \text{II.5}$$

though the overall weight losses were much higher than could be expected from equation II.5 and were attributed to catalytic decomposition of the melt by the orthovanadate formed.

Ammonium metavanadate, as shown previously, undergoes thermal decomposition yielding an intermediate stable ammonium hexavanadate according to the equation

$$3NH_4VO_3 \rightarrow NH_4V_3O_8 + 2NH_3 + H_2O \qquad \text{II.6}$$

The formation of the intermediate ammonium hexavanadate has been reported in several investigations.(73,74,75) Ingraham(76) had studed the process of heating ammonium metavanadate using a thermal balance and stated that the first stage weight loss was 14.85% which is very close to our thermogravimetric losses (14.82%). Therefore, the second stage weight loss should be due to the decomposition of ammonium hexavanadate (Figure 3) forming vanadium pentoxide according to the equation

$$2NH_4V_3O_8 \rightarrow 3V_2O_5 + 2NH_3 + H_2O \qquad \text{II.7}$$

In the presence of nitrite eutectic, the first stage weight loss is due to a mixture of two reactions; the thermal decomposition of ammonium metavanadate, and the reaction of the decomposition products (hexavanadate) with the nitrite eutectic. The overall weight loss agreed with the following equation

$$2NH_4VO_3 + 2NO_2^- \rightarrow 2VO_3^- + 2NH_3 + H_2O + NO + NO_2 \tag{II.8}$$

in which the reaction of the intermediate product is represented by the equation:

$$2NH_4V_3O_8 + 6NO_2^- \rightarrow 6VO_3^- + 2NH_3 + H_2O + 3NO + 3NO_2 \tag{II.9}$$

The metavanadate formed then reacts with the nitrite ion as did the sodium metavanadate above 300°C, forming the orthovanadate ion (equation II.5).

Similarly the overall reaction of the vanadium pentoxide as a Lux-Flood acid followed the equation

$$V_2O_5 + 6NO_2^- \rightarrow 2VO_4^{3-} + 3NO_2 + 3NO \tag{II.10}$$

with the higher observed weight loss again attributed to catalysis. The intermediate complete conversion to metavanadate likewise conformed to the expected equation

$$V_2O_5 + 2NO_2^- \rightarrow 2VO_3^- + NO_2 + NO \tag{II.11}$$

The initial reaction which produced vanadium dioxide as well as metavanadate, illustrated the much less commonly found reducing character of the nitrite melts and may be expressed as

$$V_2O_5 + NO_2^- \rightarrow VO_3^- + VO_2 + NO_2 \tag{II.12}$$

though the proportions of the vanadium products could not be determined exactly.

The vanadium dioxide formed then reacted further, as did vanadium dioxide added as such, with a weight loss in agreement with the equation

$$VO_2 + NO_2^- \rightarrow VO_3^- + NO \qquad II.13$$

with the metavanadate product reacting further above 300°C to form orthovanadate (equation II.5). The two equations II.12 and II.13 do, of course, sum to equation II.11.

Confirmation that vanadium (IV) was not the stable oxidation state in the nitrite melt was given by the reaction of vanadyl (IV) sulphate solutions with the melt which were both oxidized and partially neutralized, conforming fairly closely with the equation

$$VOSO_4 + 4NO_2^- \rightarrow VO_3^- + NO_3^- + 3NO + SO_4^{2-} \qquad II.14$$

while after correction for the nitrate formed by equation II.4 the weight loss corresponded to

$$VOSO_4 + 3NO_2^- \rightarrow VO_3^- + SO_4^{2-} + NO_2 + 2NO \qquad II.15$$

The metavanadate formed reacted at a higher temperature to give orthovanadate, which in turn catalysed the melt decomposition and led to a larger weight loss than that calculated from the overall equation

$$VOSO_4 + 5NO_2^- \rightarrow VO_4^{3-} + SO_4^{2-} + 2NO_2 + 3NO \qquad II.16$$

Potassium disulphatovanadate (III) was also found to be oxidized to vanadium (V). The reaction took place in the solid state according to the equation

$$KV(SO_4)_2 + 4NO_2^- \rightarrow KVO_3 + 3NO + NO_2 + 2SO_4^{2-} \qquad \text{II.17}$$

The metavanadate produced from the above reaction reacted at a higher temperature yielding the orthovanadate which catalysed the decomposition of the melt. The overall reaction is in accordance with the equation

$$KV(SO_4)_2 + 6NO_2^- \rightarrow VO_4^{3-} + 4NO + 2NO_2 + 2SO_4^{2-} + K^+ \qquad \text{II.18}$$

The only previously known instance of the intermediate formation of a lower oxidation state of a transition metal solute in a nitrite melt before subsequent reoxidation to the original higher oxidation state, was found when both chromium (VI) oxide and trichromate ions were partially reduced to chromium (III).(29) The relative proportions of chromium (III) and the other product, chromate anions, depended on the initial concentrations of the reactants. The sole final product was chromium (VI) as chromate. With both chromium solutes and also in the case of vanadium pentoxide described above, the reactant is a metal-oxygen polymer and it may be postulated that the unsymmetrical rupture of the oxygen bonds surrounding any one metal could take place to form more fully neutralized anions (CrO_4^{2-} and VO_3^- polymers respectively) together with less highly coordinated ions, which would necessarily be oxocations (possibly CrO_2^{2+} and VO_2^+ respectively). Such oxocations would be expected to form ion pairs with the nitrite and to behave as powerful oxidizing agents, rapid reduction of the transition metal and evolution of nitrogen dioxide therefore ensuing. It may be noted that such unsymmetrical rupture of a metal-oxygen bond could not take place with dichromate anions, which have indeed been found not to form any chromium (III) as an intermediate.(29) Since the lower oxidation states were not stable in nitrite melt and were subsequently oxidised, e.g. as equation II.13, the overall reactions appear to be of a simple Lux-Flood acid-base type.

Essentially the correlation is one of oxidation state with acidity, a lower oxidation state being one of the products of a more acidic environment (i.e. with a relative deficiency of oxide ions) while the higher oxidation state was reformed in the presence of nitrite where oxide ions are more readily available. Stabilisation of higher oxidation states in more basic melt solutions has already been observed fairly widely in melt chemistry. For example, in molten nitrates, neptunium (VII) is formed in hydroxide solutions,(77) and the manganese (II)/manganese (IV) equilibrium is displaced as acidity decreases.(78) In borates, chromium (III) is formed in acidic glasses and chromium (VI) in more basic solution.(79) In this light the apparently anomalous behaviour of vanadium and chromium-oxygen polymers thus becomes explicable.

CHAPTER III

COBALT (III) COMPOUNDS IN NITRITE MELT

III.1 INTRODUCTION

The properties of some inorganic cobalt (III) compounds in molten salts have been the subject of investigation. These investigations included electronic spectral measurements as well as the reaction processes. Molten nitrate was one of the oxyanion eutectics which have already been used as reaction media for the study of sodium cobaltinitrite and hexaamminecobalt (III) chloride. The two compounds exhibited very similar behaviour, dissolving slightly to give an initially stable brown solution which slowly decomposed forming a blue solution of cobalt (II) ion and an insoluble black precipitate. The addition of potassium pyrosulphate to the brown solution caused the formation of a blue clear solution of cobalt (II) ions containing no oxide precipitate.(80) Cobalt (II) ions have been found stable and soluble in nitrate melt. In lithium nitrate-potassium nitrate eutectic the spectrum of cobalt (II) ion has been measured and was attributed to the octahedral complex with four nitrate ions surrounding the metal ion.(81) This postulate was criticised by Johnson and Piper who proposed that three nitrate groups acting as bidentate ligands surrounded the central metal ion.(82) In a more recent spectroscopic investigation, it has been stated that the cobalt (II) ions in nitrate melt are dodecahedrally coordinated.(83)

In molten nitrite, the cobalt (II) ion has been found unstable since it reacts immediately with the melt at 220°C with the evolution of brown fumes of nitrogen oxides and producing a black precipitate of Co_3O_4, while thermogravimetric analysis has shown the reaction to commence below the melting point of the eutectic.(31) Where the same compound has been studied in both melts, nitrite melt has been shown to be more reactive than nitrate.

The object of the present investigation was to study the behaviour of sodium cobaltinitrite and hexamminecobalt (III) chloride in nitrite eutectics. The thermal behaviour of these cobalt (III) compounds, which have been studied by several workers, are very important in the interpretation of the results of this investigation because of the possible occurrence simultaneously of both thermal decomposition and a reaction with the melt. Sodium cobaltinitrite has been thermally studied by Wendlandt and also by Duval using thermogravimetric analysis; there is some disagreement about the exact nature of the products, since Wendlandt has reported the final products of the decomposition to be Co_3O_4 and nitrite but Duval has reported Co O and nitrate.(84,85) Davies, in an attempt to reconcile the differences between these workers' results suggested that the thermal decomposition temperature as well as the final products were dependent on the particle size of compound being investigated.(86)

The thermal stability of hexa-ammine-cobalt chloride has been studied by Wendlandt who showed that the decomposition took place in two stages with cobalt (II) chloride as an intermediate and Co_3O_4 as the final product.(87)

The present work includes, in addition to the behaviour of sodium cobaltinitrite and hexa-ammine-cobalt (III) chloride in nitrite eutectics, studies of the thermal decomposition of the pure compounds.

In an attempt to obtain a soluble species of cobalt (III) ion in nitrite eutectic, the lower melting lithium nitrite-potassium nitrite (in comparison with Na/KNO_2) was used. The stoichiometries of the decomposition and reactions of these compounds were established using the weight loss on the thermograms and the analysis of the solid products, which was shown to be Co_3O_4 in both cases.

III.2 EXPERIMENTAL SECTION

III.2.1 Materials

Three different nitrite eutectics were used in the present studies, the sodium nitrite-potassium nitrite, lithium nitrite-potassium nitrite and sodium nitrite-potassium nitrite-barium nitrite eutectics, prepared as described in Chapter I. Analar sodium cobaltinitrite (B.D.H.) and Analar hexamminecobalt chloride (B.D.H.) were dried at 110°C for two hours before use.

(a) Cobalt (II) chloride

B.D.H. Analar $CoCl_2.6H_2O$ was dehydrated by refluxing with B.D.H. reagent grade thionyl chloride for two hours.(88) The residual traces of thionyl chloride, not removed by pumping and gentle heating of the cobaltous chloride in vacuo, were removed by heating to 200°C in a current of dry oxygen-free nitrogen. The purity of the compound was determined using E.D.T.A., and the cobalt content was found Co = 45.28%. (Calculated for $CoCl_2$ Co = 45.39%.) The analysis procedure is reported later in this section.

(b) Potassium pyrosulphate

Since Analar potassium pyrosulphate was contaminated with a hygroscopic impurity, believed to be potassium bisulphate, potassium pyrosulphate was prepared by the thermal decomposition of Analar potassium persulphate(85) according to the equation

$$2K_2S_2O_8 \rightarrow 2K_2S_2O_7 + O_2 \qquad \text{... III.1}$$

This method involved the heating of Analar potassium persulphate at 250°C for ten hours, as thermogravimetric analysis showed that potassium persulphate maintained at 250°C stopped losing weight after four hours. A sample dissolved in water gave no blue colour with starch-iodide paper, indicating the absence of persulphate ion.

III.2.2 Analysis

Qualitative and quantitative analysis were carried out for the cobalt in both the reactants and the products. The X-ray diffractometer was used for the identification of the cobalt compounds according to their intensities and d-spacings. The procedure for the diffractometer was described in Chapter II. Quantitatively, the cobalt was determined by first dissolving the compounds in dilute hydrochloric acid and then titrating with a standard E.D.T.A. solution after buffering the prepared solution to pH6 with dilute ammonia solution. Murexide was used as indicator (yellow to violet).

The cobalt was also determined colourmetrically on a Unicam S.P.800 spectrometer by measuring the absorption maxima after treating the cobalt solution with ammonanium thiocynate and acetone. Calibration was carried using standard solutions of analysed cobalt (II) chloride.

The nitrate was determined according to the procedure of

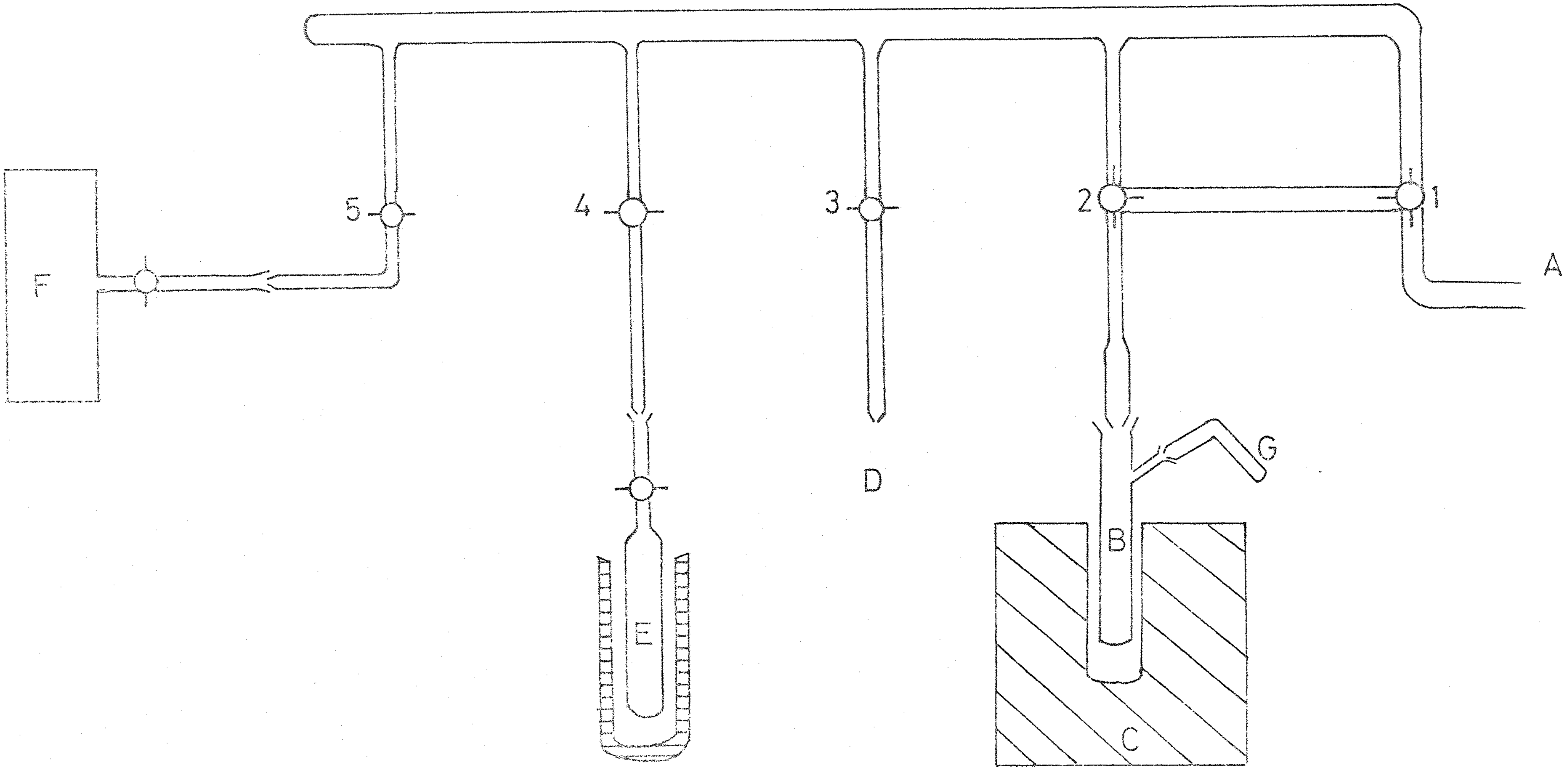
Leithe discussed in Chapter I. The oxide ion was titrated with standard sulphuric acid using phenolphthalein as indicator.

III.2.3 Gas analysis

The gases produced in reactions, nitric oxide and nitrogen dioxide, were identified using a Unicam 200G infra red spectrometer. The gases were collected in a gas cell with either potassium bromide or silicon windows. The cell with silicon windows was preferable because the windows were fused into the glass, thus avoiding the leaks that sometimes occurred with the potassium bromide windows. Silicon has a wide absorption peak (at $1100 cm^{-1}$), but this peak does not interefere with those for nitrogen dioxide and nitric oxide. The gases evolved from the reaction were collected in the cell using a vacuum line (Figure 1) as follows: The reaction tube (B) fitted with a side arm adaptor (G), was connected to the vacuum line. About 15 grams of the eutectic were placed in the reaction tube while the chemical reagents placed in the side arm tube. To bring the apparatus to the required condition, it was evacuated to about 10^{-2} torr, which was directly measured by a Pirani gauge (D). While the system was being evacuated, the temperature of the furnace was raised to the desired level. Before adding the chemicals from the side arm, the three way valve (1) and the two way valves (3) and (4) were closed. The side arm was then rotated to add the reagents and the gases evolved from the reaction were collected in the gas cell (F) for later analysis. In some cases, a mass spectrometer (AEI - MS12) was used for the identification of the gaseous products, in which case the system was evacuated to 10^{-2} torr as described above but the valves (1),

Fig. 1

Vacuum line



(3) and (5) were closed and the gases trapped in a gas collection flask (E) cooled in liquid nitrogen.

III2.4 Thermogravimetric Analysis

The weight loss due to gaseous reaction products, the temperature at which the reaction began and the presence of multi-stage reactions were followed on a Stanton TR-1 self recording thermoblance. The balance was adjusted so that a change in weight loss up to one gram, at one mg sensitivity,could be followed and recorded automatically. The balance was equipped with a vertical tube furnace suitable for use to 1000°C. Recent developments have been made on the Stanton balance which render it more suitable to use under different circumstances. These developments include an automatic control for isothermal operation as well as the possibility of passing two different gases in which one (nitrogen) acts as a sealing gas, protecting the balance and the atmosphere from diffusion of the other gas, which is often corrosive or poisonous, by carrying it to the fume cupboard through an outlet line. Cooling water tube was attached to the immovable part of the furnace so that the sealing rubber ring could be protected when the temperature reached 1000°C. Two flow meters as well as two drying towers (containing sulphuric acid and chromous chloride solutions) were connected to the flow gas tubes. These developments make it possible to run the thermobalance in air, nitrogen or most other gas as required.

(a) Interpretation of the thermogravimetric results

In thermogravimetric analysis, the continuous traces of the thermobalance recorded the weight change of the contents with respect to time and temperature. The experimental weight loss was determined directly from the trace and then expressed as a percentage of the initial weight of solute as will be found reported under Results. The reaction rate was recorded as a function of temperature by use of a differential thermogram method. This was done by plotting weight loss during five minute intervals against temperature. By this method the temperature of the maximum rate of reaction i.e. (rate of weight loss) could easily be determined.

(b) Isothermal operation of thermobalance

In a multi-stage reaction, the weight loss from the first stage reaction tended to merge into the loss from the second when the temperature range separating the two stages was small. In such cases the Stanton thermobalance was operated at constant temperature, thus the thermogram was stopped in the weight loss level between the two reactions and the two reactions separated. In addition, the species produced by the first reaction could be analysed from the quenched melt. Several reactions in molten nitrites, in the present investigation were found to have two or more stages of reaction which merged to some extent with each other or with the decomposition of the nitrite melt.

In these cases, the first reaction might be completed by holding the furnace at a constant temperature corresponding to the maximum rate of the first reaction while the second reaction was still proceeding at a negligible rate. On the other hand, if two reactions were separated by a wide temperature range, during which a negligible weight loss occurred, an accurate determination of the separate losses was practicable.

(c) Precautions in the use of thermobalance

In using the Stanton thermobalance, many factors should be considered such as the balance, rate of gas flow etc., in order to avoid variable results. It was found that the weight losses recorded were usually reproducible, within the limits of experimental error, but that the temperature range of a reaction was not always reproducible unless a number of precautions were taken. The factors that effect the decomposition or reaction temperature are summarised below:(85)

(1) Different types of thermocouple and crucible material have an effect on reaction temperature. These effects were eliminated by using the same type of thermocouple and size of vitrosil crucible throughout the present work.

(2) The effect of the heating on reaction temperature is very important, particularly when the reaction is taking place in several stages. A low heating rate lowers the temperature of the thermal reactions and brings out the individual stages clearly whereas at a high rate the stages tend to merge with loss of detail. In most of the present studies, a heating rate of 2°C per minute, was used as most of the reactions took place in more than one stage.

(3) The crystalline nature of the substance being heated is also important since the grain size of a single substance has an effect on the decomposition temperature and the smaller the size the lower the decomposition temperature.

In some reactions in the present work it was found that a very vigorous reaction could proceed with explosion and thus loss of non-volatile matter resulting in an incorrectly high weight loss. This could be avoided by placing an inverted funnel on the crucible before heating.

(4) The thoroughness with which two or more reactants were mixed was found to have an effect on the reaction temperature range. Well mixed reactants have a lower temperature range of reaction than unmixed. To prevent these variations, the reactants were ground very well and mixed together thoroughly before using.

(5) The mass of reactants affects the reaction temperature as well by causing a temperature lag between the furnace and reactants; on heating, a large weight obviously increases the lag. To allow for this approximately the same total weight of reactants was used for each thermogram. In addition, the heat of the reaction, which may be positive or negative, will alter the temperature lag and the Stanton thermobalance does not make allowance for this factor, but it is not considered to have a serious effect.

In general, all the factors affecting the thermogravimetric results were taken in account whenever the thermobalance was used. As a result of these precautions a reproducible result was obtained in most of the thermograms.

III.3 RESULTS

III.3.1 Sodium cobaltinitrite

Sodium cobaltinitrite was found to be thermally unstable when added to molten sodium nitrite-potassium nitrite eutectic at 230°C.

When first added, no reaction was observed, but within five minutes thermal decomposition was visible with the production of brown fumes and the formation of a black precipitate. The gases evolved were shown by infra red spectroscopy to consist of nitrogen dioxide and nitric oxide. After separating the black precipitate from the quenched nitrite melt by dissolving in water, filtering and drying, X-ray diffraction showed the diffraction lines 2.87(m), 2.44(s) and 1.44(w) which corresponded with those of Co_3O_4 [A.S.T.M. index 2.86(40), 2.44(100), 1.43(45)]. Quantitative colourimetric analysis for the black oxide showed a cobalt content of 73.87%. The percentage of cobalt obtained from E.D.T.A. compleximetric titration was 73.2%. (Calculated for Co_3O_4. Co = 73.4%, Co_2O_3. Co = 71.06%, CoO. Co = 78.64%.)

An attempt was made to obtain a soluble species of sodium cobaltinitrite in molten sodium nitrite - potassium nitrite at 230°C using potassium pyrosulphate as a Lux-Flood acid. The addition of pyrosulphate to the melt (which reacted immediately evolving brown fumes) did not appreciably alter the course of reaction and a black precipitate was again produced which when examined with X-rays, gave lines similar to those of Co_3O_4.

Lower melting nitrite eutectics were tried in an effort to get a soluble cobalt (III) ion in solution. No reaction was observed on the addition of sodium cobaltinitrite to either molten lithium nitrite-potassium nitrite (m.p.110°) or the ternary sodium nitrite-potassium nitrite-barium nitrite (m.p.170°) and no visible solution of cobalt (III) ion was noticed even in the presence of pyrosulphate ion. On raising the temperature gradually to around

220°C, brown fumes started to come off and black particles which, when separated from the melt, washed and dried, gave the X-ray powder pattern characteristics of Co_3O_4.

Thermogravimetric analyses were carried out for pure sodium cobaltinitrite and for sodium cobaltinitrite in nitrite eutectics. The thermogram of the pure compound showed that the thermal decomposition commenced at 170° ± 5 (Figure 2) with a maximum rate of weight loss around 205°. The weight loss was found to vary between 18.3% and 22.1%. No significant change in weight loss between samples heated in air and in nitrogen was noted. The mass loss obtained from the thermogravimetric analysis of sodium cobaltinitrite in a sodium nitrite-potassium nitrite eutectic (Figure 2) showed that a thermal decomposition took place in two stages. The first stage started at 170° ± 5, the second stage around 225°C and the reaction was complete at 260°C. The overall weight loss was found to vary from 21.5% to 24.2% which became 29.9% and 30.2% when corrected for the formation of nitrate due to the reaction of nitrogen dioxide with nitrite according to the equation II.4. (Calculated for loss of $3N + 4\frac{2}{3}\,O$ per $Na_3\left[Co(NO_2)_6\right]$ 30.6%). (See equation III.2.) It was found that a lower weight loss for the second stage was associated with an increase in the melting point of the sodium nitrite-potassium nitrite melt as shown in Table 1. (See Figure 3.) The higher melting point was obtained by increasing the sodium nitrite content.

Table 1

m.p. °C	Molality	$Na_3Co(NO_2)_6$ g	Total wt loss %	Second stage wt loss %
220	0.472	0.3428	24.3	4.0
240	0.295	0.3238	23.5	1.5

Fig. 2

T.G.A. of sodium cobaltinitrite in Na/KNO$_2$ eutectic

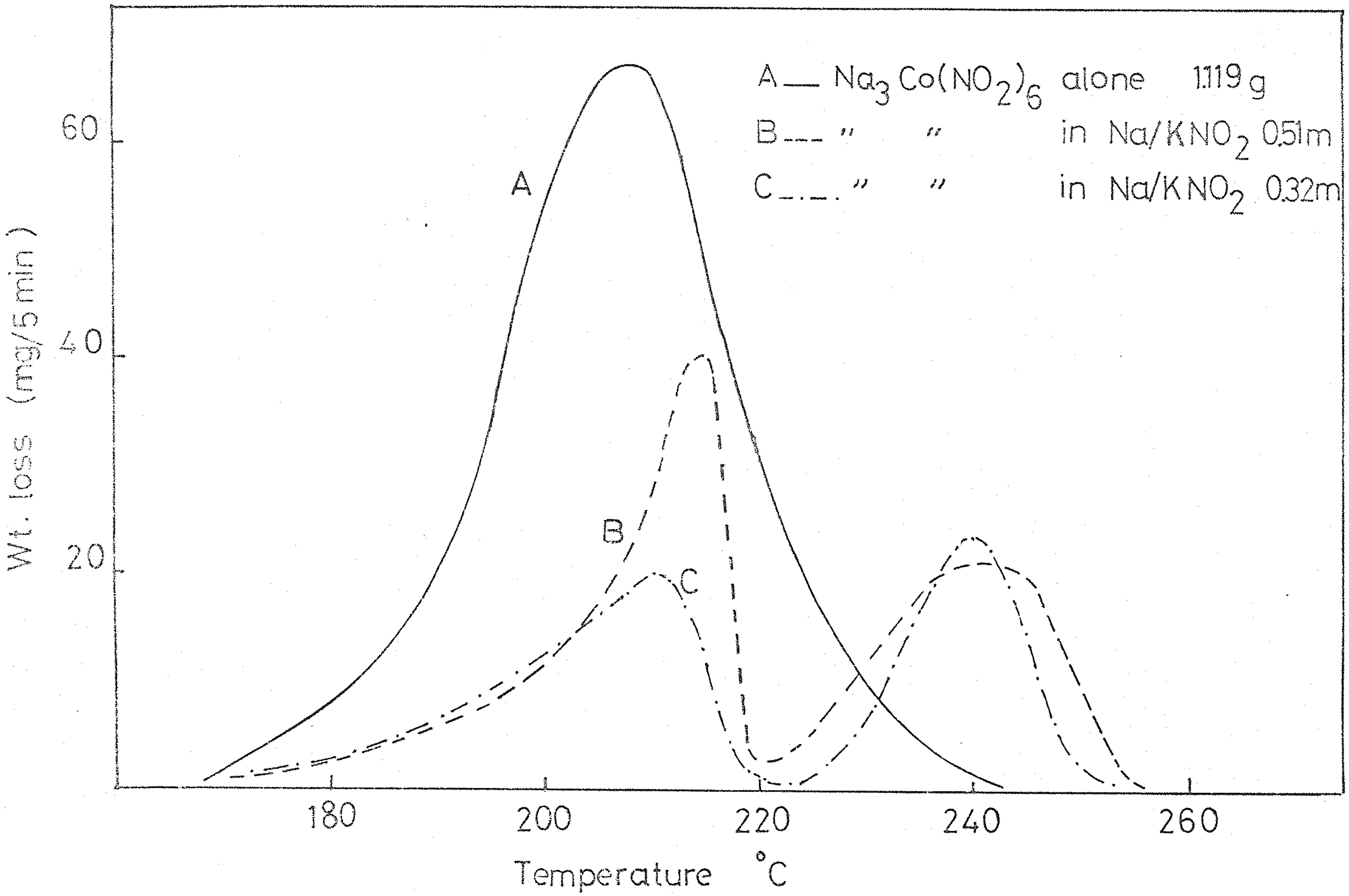
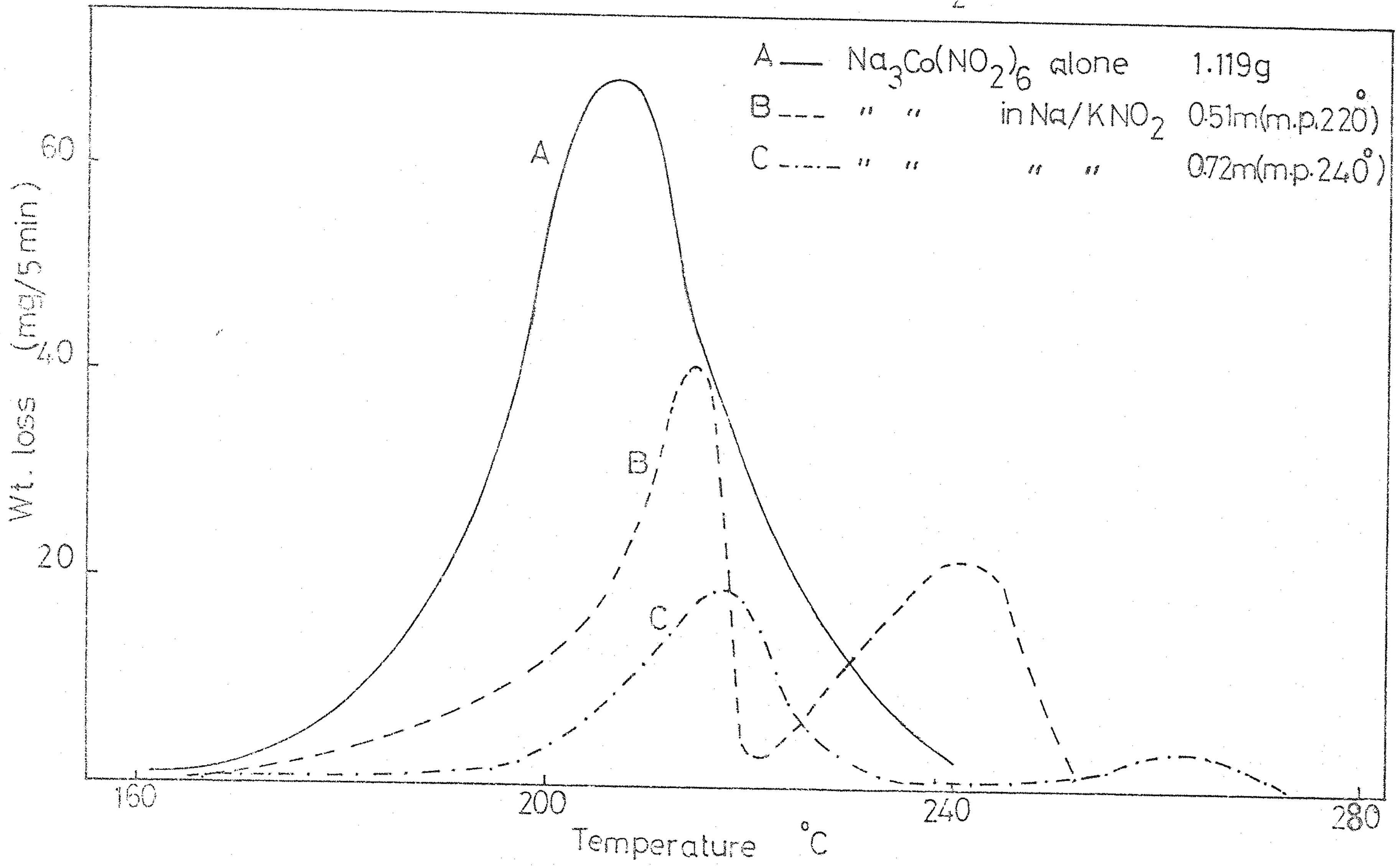


Fig. 3

T.G.A. of sodium cobaltinitrite in Na/KNO$_2$ eutectic



Isothermal thermogravimetric analysis at 220°C showed that a greenish-yellow precipitate resulted from the decomposition of sodium cobaltinitrite in sodium nitrite-potassium nitrite melt. As this compound was insoluble in water, it was separated by dissolving the quenched melt in distilled water. The infra red spectra of the greenish-yellow compound, after filtering and drying, showed peaks similar to those of potassium cobaltinitrite.

Thermogravimetric analysis of sodium cobaltinitrite with the ternary sodium nitrite-potassium nitrite-barium nitrite eutectic (m.p.170°C) showed only one stage of thermal decomposition (Figure 4). Decomposition started at 225° ± 5 with a maximum rate of weight loss at about 260°. The total weight loss varied from 23.5% to 26.5% which on correcting for the formation of nitrate due to the reaction II.4 became 30.1%.

In the lithium nitrite-potassium nitrite eutectic (m.p.110°) (Figure 5), sodium cobaltinitrite decomposed at 225° ± 5 in one stage and the total weight loss varied from 24.2% to 29.7% which became 29.9% on correcting for nitrate formation.

III.3.2 Hexa⁄ammine⁄cobalt (III) chloride

Hexa⁄ammine⁄cobalt (III) chloride reacted immediately when added to a molten sodium nitrite-potassium nitrite eutectic at 220°C with the evolution of brown fumes and the formation of a black precipitate. The black precipitate after washing and drying was examined by X-ray diffration and found to be Co_3O_4. (2.85(m), 2.43(s), 1.43(w)). A.S.T.M. index for Co_3O_4 (2.86(40), 2.44(100), 143(45)).

Fig. 4

T.G.A. of sodium cobaltinitrite in $Na/K/Ba(NO_2)_2$ eutectic

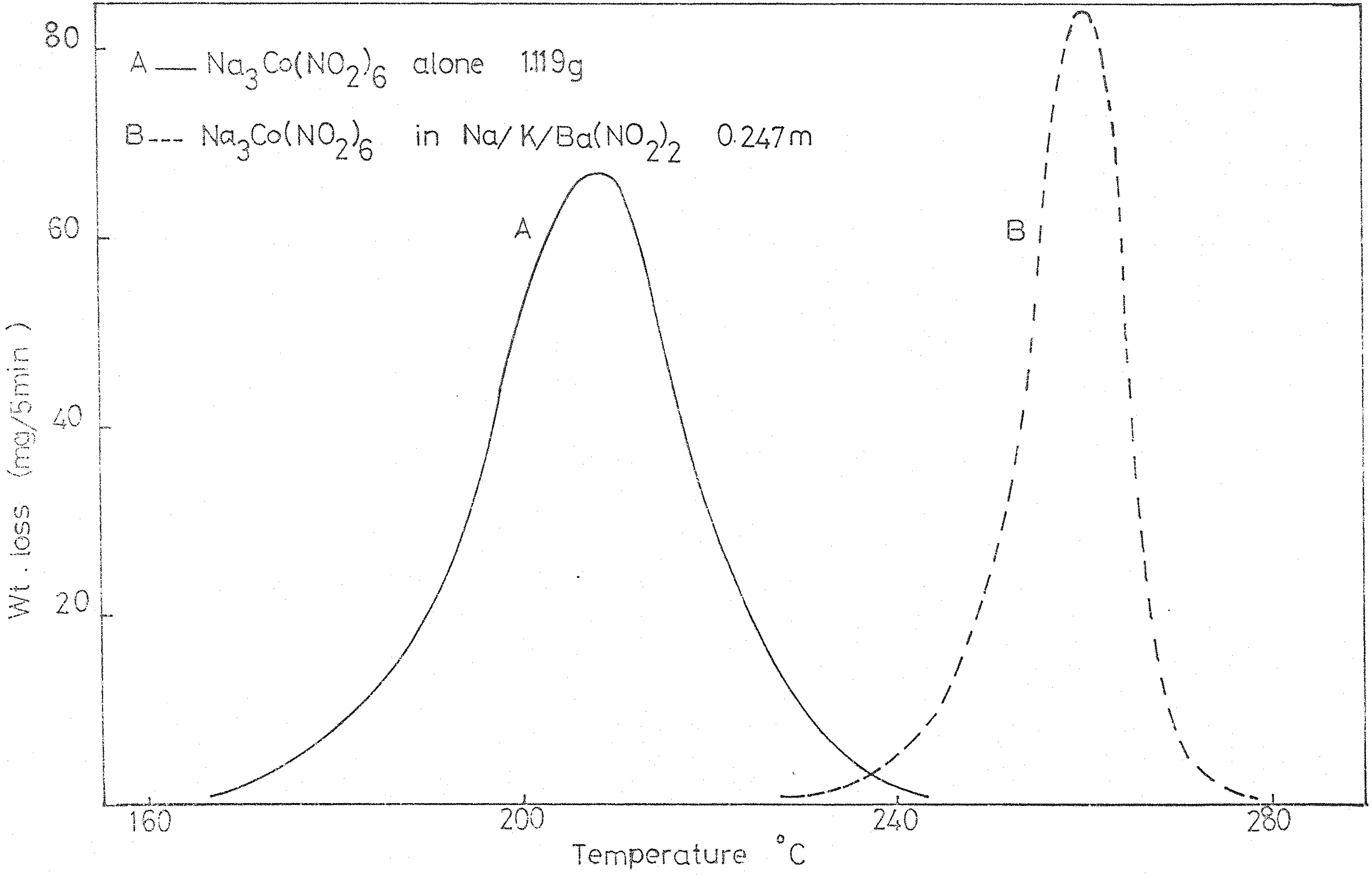
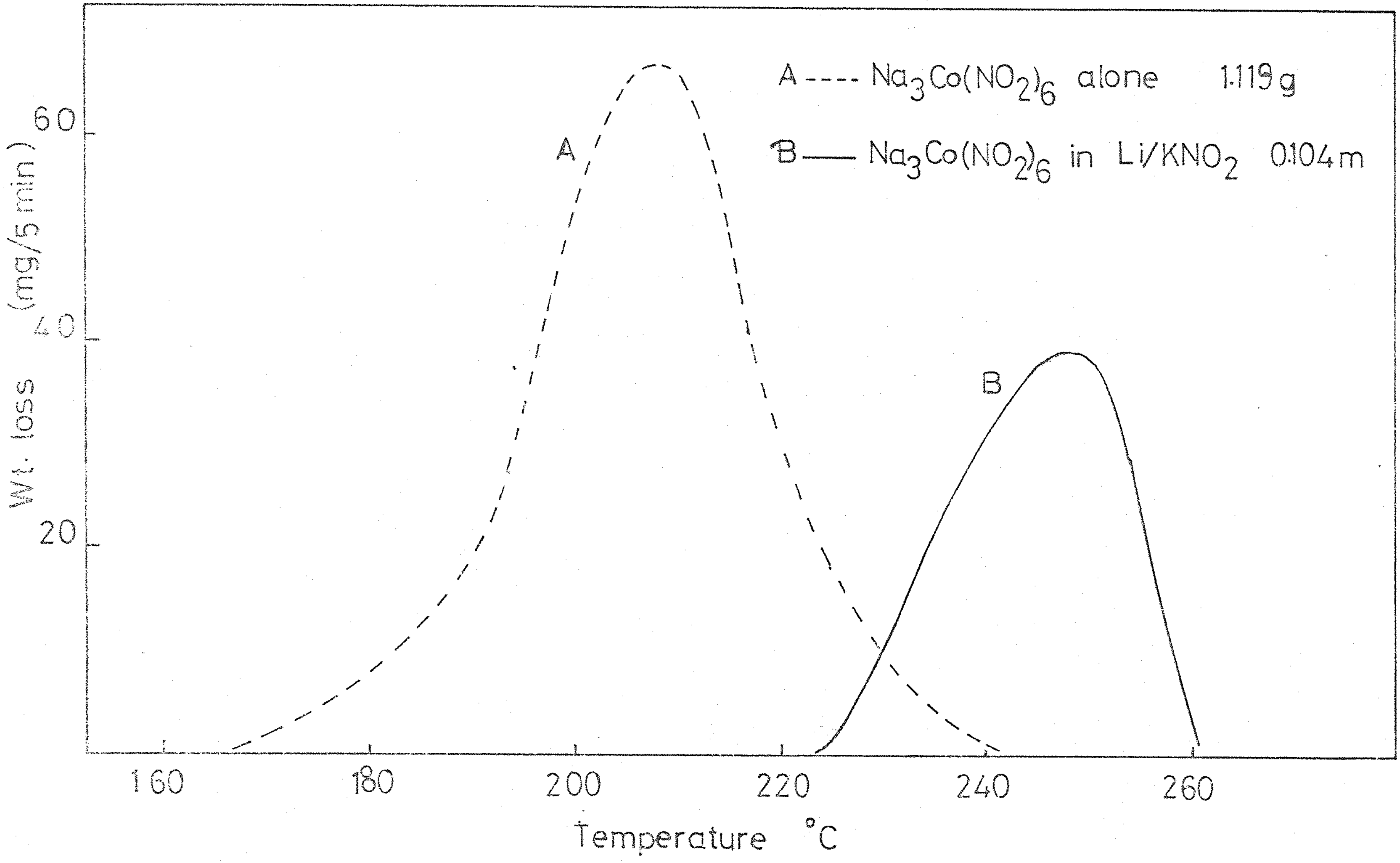


Fig. 5

T.G.A. of sodium cobaltinitrite in Li/KNO$_2$ eutectic



It was of interest to study the decomposition of pure hexa⁄ammine⁄cobalt (III) chloride in order to better understand its behaviour in molten nitrite eutectic. Thermogravimetric analyses were therefore carried out on pure hexa⁄ammine⁄cobalt (III) chloride up to 400°C. These showed that the decomposition started at 165 ± 10°C in two stages. The first stage, with a maximum rate of weight loss around 230°C while the second with a maximum at 280°C and finished at 325°C. The solid remaining was blue in colour, and was shown by quantitative analysis to contain 45.15% cobalt (calculated for $CoCl_2$, Co = 45.39%). The infra red spectrum of the blue residue confirmed the presence of cobaltous chloride when compared with the infra red spectrum of pure prepared cobalt (II) chloride. The overall weight loss was found to vary from 50.3% to 50.5%. Isothermal thermogravimetric analysis at 230°C was carried out in an attempt to separate the intermediate product for analysis. This failed since the second reaction also took place at the same temperature.

Thermogravimetric analysis of hexa⁄ammine⁄cobalt (III) chloride in the sodium nitrite-potassium nitrite eutectic (Figure 6) showed a one stage weight loss to commence at 170 ± 10°C with the production of blue coloured particles. The reaction became rather rapid around 220°C and finished at 280°C with an overall weight loss varying from 74.9% to 75%, which on correction for the formation of nitrate due to equation II.4 became 77.6%. (Calculated for $8N + 2\frac{1}{4}O + 1Cl + 16H$ 77.8% per $Co(NH_3)_6Cl_3$.) In sodium nitrite-potassium nitrite-barium nitrite eutectic the decomposition reaction, as shown by the thermogram (Figure 7), took place in two stages, the first started at 165 ± 10°C and the second stage at 245 ± 10C

Fig. 6

T.G.A. of hexamminecobalt(III) chloride in Na/KNO$_2$ eutectic

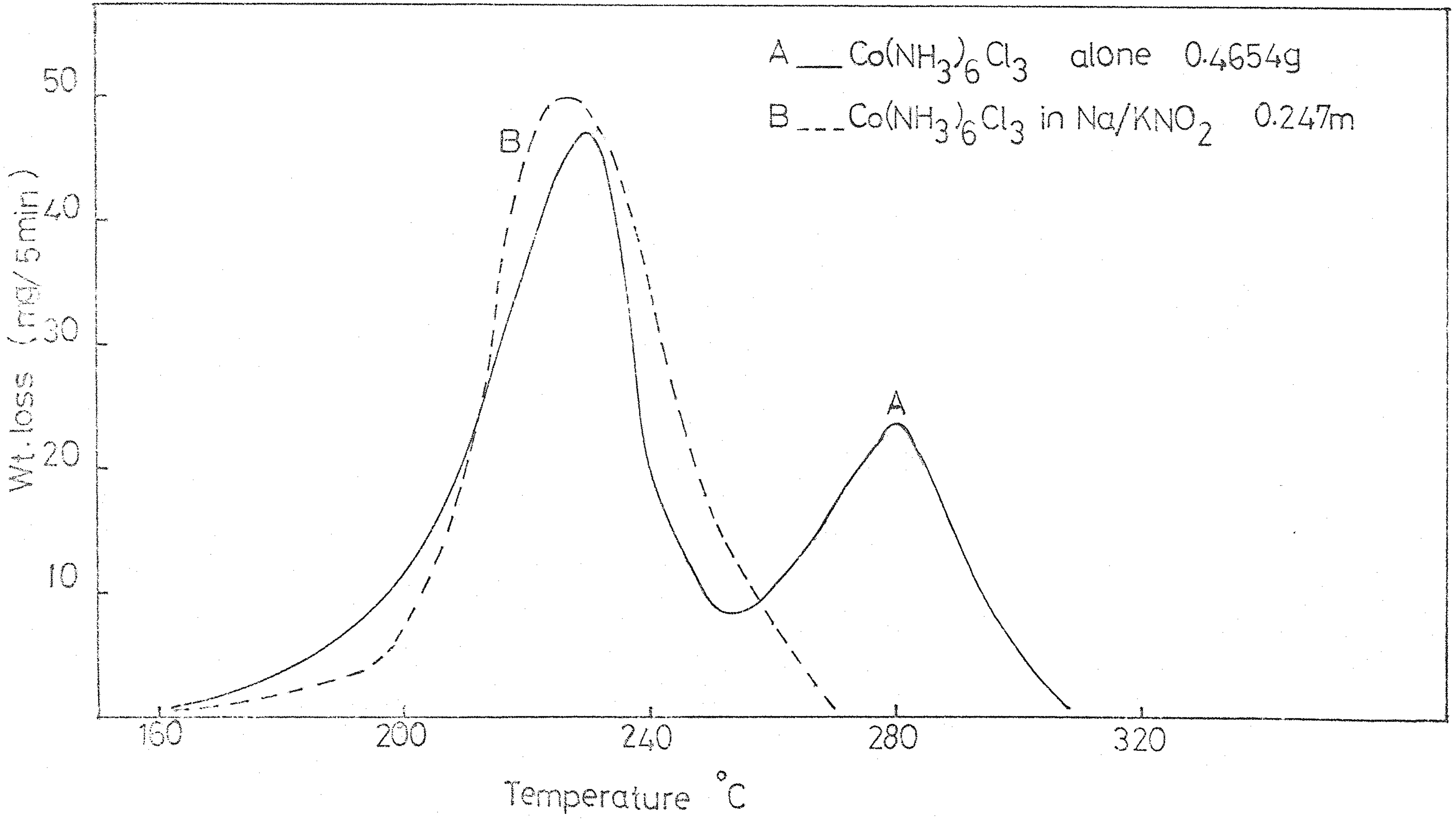
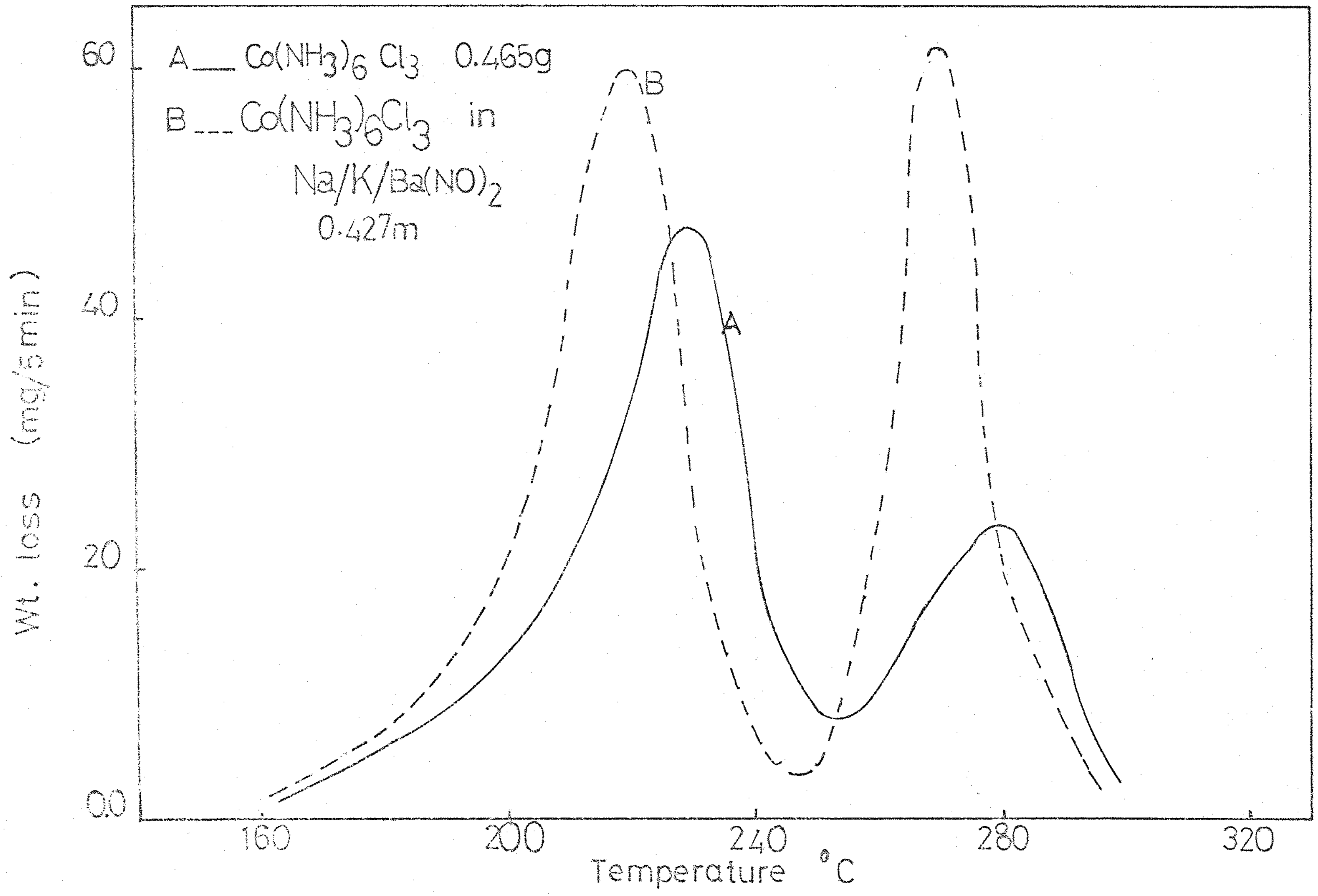


Figure 7
T.G.A. of hexamminecobalt(III)chloride in Na/k/Ba(NO)$_2$



with an overall weight loss varying from 70.8% - 71.1% and which became 78.2% after correction for nitrate formation. Isothermal thermogravimetric analysis at 220°C showed the formation of a green-yellow substance, insoluble in water, and which on examination with X-rays gave the same diffraction lines as $K_3[Co(NO_2)_6]$. The d-spacing are listed in the following table:

Table 2

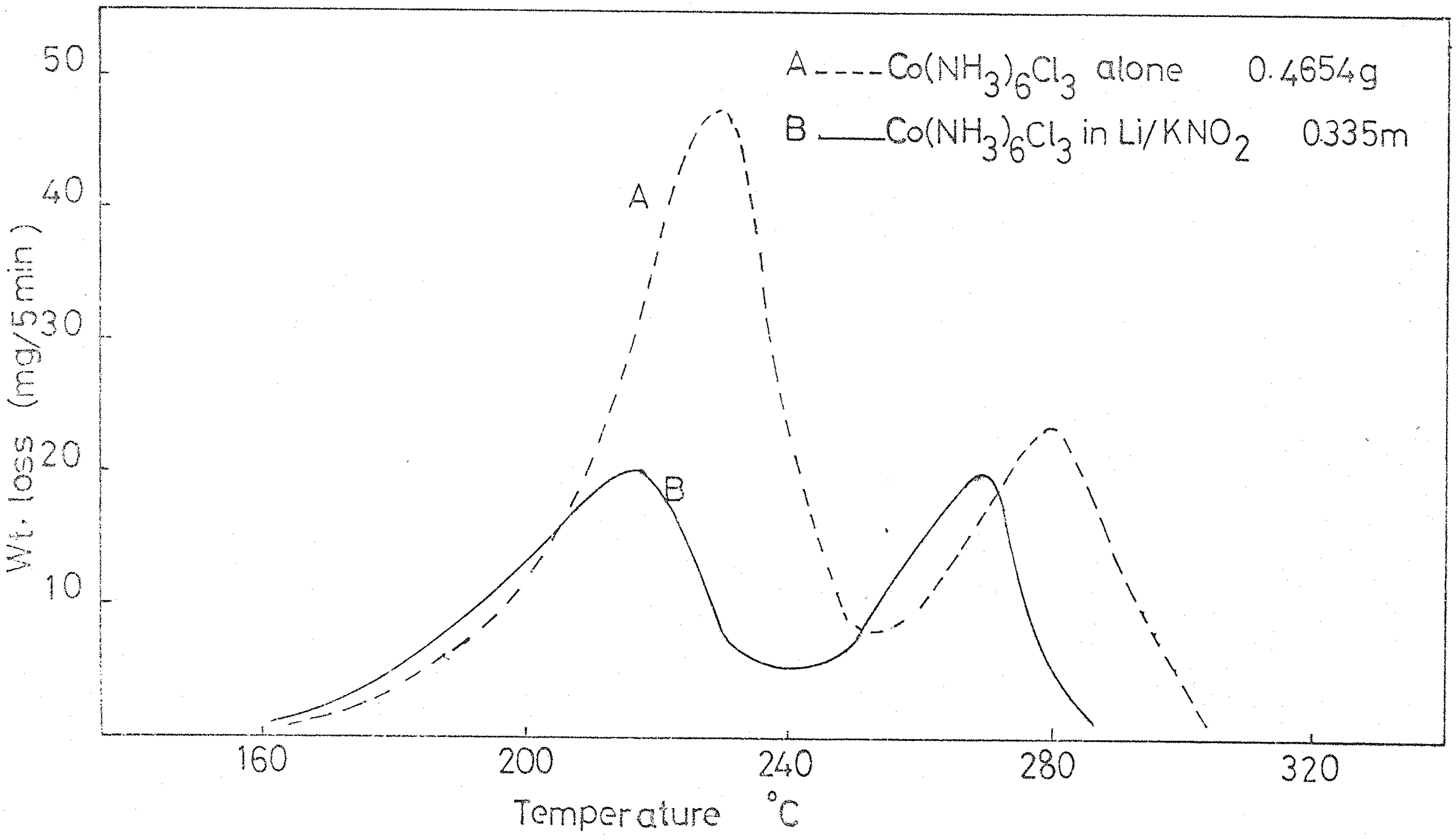
unknown compound d-spacing	intensities relative to the strongest line as 100	B.D.H. $K_3[Co(NO_2)_6]$ d-spacing	intensities of the known compound
6.020	50	5.98	50
5.211	28	5.181	25
3.683	55	3.658	50
3.003	30	3.001	30
2.598	100	2.590	100
2.320	40	2.318	40
2.122	75	2.115	70

Qualitative analysis for the intermediate green-yellow substance produced after the first stage weight loss confirmed the presence of potassium (flame test) and cobalt (borax bead test).

The thermogram of hexaammine cobalt (III) chloride in lithium nitrite-potassium nitrite showed two stages of the thermal decomposition reaction (Figure 8). The first stage began at 165 ± 10°C and the second stage at 240°C with a total weight loss 74.4%. On

Fig. 8

T.G.A. of hexamminecobalt(III)chloride in Li/KNO_2 eutectic



correcting for the formation of nitrate, the total weight loss became 78.4%. As with the ternary nitrite eutectic, the isothermal thermogram with lithium nitrite-potassium nitrite eutectic carried out at 220°C, a green-yellow substance was formed. The X-ray analysis showed diffraction lines similar to those of $K_3[Co(NO_2)_6]$ (Table 2). The final black product was determined to be Co_3O_4 from the X-ray diffraction lines.

III.4 DISCUSSION

As a result of thermogravimetric analyses of the sodium cobaltinitrite alone and in the presence of nitrite eutectics, in which a small difference in the weight loss between both of them was observed, sodium cobaltinitrite in the presence of nitrite melt probably undergoes a thermal decomposition rather than a chemical reaction. The overall experimental weight loss of sodium cobaltinitrite in sodium nitrite-potassium nitrite eutectic led to the conclusion that the decomposition took place in accordance with the equation

$$3Na_3[Co(NO_2)_6] \rightarrow 9NaNO_2 + Co_3O_4 + 5NO_2 + 4NO \qquad \text{... III.2}$$

after correcting for the formation of nitrate according to reaction II.4.

The second stage decomposition reaction of sodium cobaltinitrite in sodium nitrite-potassium nitrite is probably due to the formation of a compound with a higher decomposition temperature which was shown by analysis to be $K_3[Co(NO_2)_6]$. Potassium cobaltinitrite, as reported by Davies,(86) commenced thermal decomposition at 216°C which is in close agreement with the second stage decomposition temperature (220 ± 5°C) of sodium cobaltinitrite in sodium nitrite-potassium nitrite reported earlier. The formation of potassium cobaltinitrite is probably due to cation exchange between the sodium and potassium in sodium cobaltinitrite and sodium nitrite-potassium nitrite eutectic respectively. The cation exchange has probably taken place in the molten state, as the second horizontal line on the thermogram was around the melting point of the eutectic (Figure 2). The decrease in the second stage weight loss associated with an increase in the melting point of the sodium nitrite-potassium nitrite mixture was attributed to the decomposition of greater amounts of the sodium cobaltinitrite below the melting point and before the formation of potassium cobaltinitrite.

In both lithium nitrite-potassium nitrite and sodium nitrite-potassium nitrite-barium nitrite eutectics, the one stage weight loss at 220°C was probably due to the decomposition of potassium cobaltinitrite produced from the cation exchange in the molten eutectics which took place at temperatures lower than the decomposition temperature of sodium cobaltinitrite.

The thermal properties of sodium cobaltinitrite have also been investigated by other workers. Wendlandt(84) and Southern, using thermogravimetric analysis, differential thermal analysis and mass spectroscopy, found that the cobalt (III) complex was thermally stable up to 200°C, whereas Duval(85) reported on the basis of thermogravimetric analysis that sodium cobaltinitrite started decomposition at 160°C. In recent study of the thermal behaviour of sodium cobaltinitrite, Davies(86) attributed the difference between the results found by Wendlandt and Duval to the particle size and the amount of sodium cobaltinitrite used for investigation. Davies reported decomposition temperatures varying between 160°C and 177°C, (the latter is in close agreement with the decomposition temperature reported in the present work), for a random sized sample and a sample with particle size 0.178 mm respectively.

The mass spectral analysis data obtained by Wendlandt(84) revealed the presence of nitrogen dioxide, nitric oxide and a small amount of nitrogen and oxygen which led to the suggestion that the decomposition reaction is in accordance with the following stoichiometry

$$6Na_3[Co(NO_2)_6] \rightarrow 18NaNO_2 + 2Co_3O_4 + 10NO_2 + 6NO + N_2 + O_2 \quad \text{...III.3}$$

but, if the nitrogen and oxygen were the products of a hot tube dissociation of nitrogen (II) oxide, as proposed by Wendlandt, the actual decomposition stoichiometry would be as given in equation III.2.

The final residual products were reported to be Co_3O_4 and a high proportion of nitrate as well as nitrite. The formation of nitrate in the decomposition procedure, as assumed by Duval,(85) was at least in part due to the oxidation of the nitrite by cobalt (III) leading to the postulation of cobaltous oxide in the reaction products. The examination of the water insoluble black products by X-ray diffration showed the presence of Co_3O_4. Since no CoO was found, the probability of oxidation of nitrite to nitrate by cobalt (III) seems almost negligible.

Hexa/ammine/cobalt (III) chloride has been studied by Wendlandt using thermogravimetric analysis which showed that the thermal decomposition started at 160°C producing cobaltous chloride. This result agrees with that found in the present work, since the decomposition, reported here, started at 165 ± 5°C. From the weight loss and the products obtained, the decomposition of pure hexa-ammine⁄cobalt (III) chloride has taken place according to the equation;

$$6[Co(NH_3)_6]Cl_3 \rightarrow 6CoCl_2 + 6NH_4Cl + 28NH_3 + N_2 \qquad ...III.4$$

In nitrite eutectics, hexa⁄ammine⁄cobalt (III) chloride acted as a Lux-Flood acid abstracting oxide ion from the nitrite melt. The overall experimental weight loss in any one eutectic agreed with the following stoichiometry when allowance was made for the formation of nitrate

$$6[Co(NH_3)_6]Cl_3 + 12NO_2^- \rightarrow 2Co_3O_4 + 6NH_4Cl + 28NH_3 + N_2 + 4NO_2 + 8NO + 12Cl^- \qquad ...III.5$$

In sodium nitrite-potassium nitrite eutectic, the one stage weight loss was attributed to a mixture of several reactions. These reaction included (a) the decomposition of hexa⁄ammine⁄cobalt (III) chloride at 180 ± 5°C, (b) the reaction of cobalt (II) chloride, produced from the decomposition according to equation III.4, with nitrite eutectic in the solid state producing nitrogen oxides and black precipitate of Co_3O_4 according to the following equation,(31)

$$3CoCl_2 + 6NO_2^- \rightarrow Co_3O_4 + 2NO_2 + 4NO + 6Cl^- \qquad ...III.6$$

(c) the reaction of the remaining hexa⁄ammine⁄cobalt (III) chloride with nitrite eutectic at melting temperature 220°C. These three reactions probably overlap each other, appearing as one stage of weight loss as shown in Figure 6.

The reaction of hexa⁄ammine⁄cobalt (III) chloride in both lithium nitrite-potassium nitrite and the ternary eutectic sodium nitrite-potassium nitrite-barium nitrite showed two stages of weight loss. The first weight loss is probably due to the thermal decomposition of hexa/ammine/cobalt (III) chloride (equation III.4) plus the reaction of cobalt (II) chloride, produced from the above decomposition, with nitrite eutectic. The second weight loss was attributed to the decomposition of the cobaltinitrite complex produced from the reaction of cobalt (II) chloride in molten nitrite below 180°C.

The formation of a potassium cobaltinitrite complex as an intermediate product was confirmed by the addition of cobalt (II) chloride to lithium nitrite-potassium nitrite eutectic at 120°C which produced a green-yellow precipitate, insoluble in water as well as in melt and gave the diffraction lines 5.99 (50), 5.22 (25), 3.666 (54), 3.002 (30), 2.598 (100), 2.316 (40), 2.119 (65) which on comparison, were almost identical to the d-spacing of $K_3[Co(NO_2)_6]$.

CHAPTER IV

SPECTROSCOPIC STUDIES OF SOME TRANSITION METAL IONS IN NITRITE MELTS

IV.1 INTRODUCTION

In recent years, electronic spectra measurements in molten salts have been employed to characterize new compounds and to provide information about the bonding and structure of complexes. Such spectroscopic investigations may produce information on the electronic transition within the ligand, the charge transfer process and the d-d transition spectra of the transition metal ion.

The inorganic molecules which occur as ligands in transition metal complexes possess a characteristic absorption spectra called the ligand spectra which is generally located in the ultraviolet region as a result of allowed $\pi \rightarrow \pi^*$ transitions. Thus nitrates, nitrites and many other poly atomic ions commonly possess very intense bands in the ultraviolet region as well as weaker bands at lower energy. As an example, spectroscopic observation on molten sodium nitrite showed a weak absorption band at 28000 cm^{-1} which has been attributed to a transition within the nitrite ion. This band has been used to interpret the mechanism of melting, since a change in the position of the band maximum is associated with the phase change from solid to liquid.(89,90)

Because of the close proximity of the metal atom and the ligands and the bonding between them, transition of an electron can occur from an orbital lying principally on the ligand to one lying principally on the metal ion and vice versa. This kind of transition is called a charge transfer transition; an example is the band located in the visible region of the chromate ion(91) in which no d-d transition is expected as the metal has a d^o electronic configuration.

Whereas both pure ligand and charge-transfer transitions are usually observed as intense absorption bands, the opposite is true for d-d spectra in which the absorption bands are expected to be very weak or not observable. In the d-d transition spectra of transition metals, the spectrum obtained is realted not just to the metal ion but also to the geometry of the whole complex. These spectra are dependent on the ligand field acting on the incomplete d shell. The ligand field is determined by the nature and spatial arrangement of the nearest anions, so that measurements of the spectrum should provide quantitative information on the coordination of the transition metal ions. In molten nitrites there are further complications in determining the geometry and nature of coordination of the nitrite ion to the central metal ion, because the nitrite ion has the ability not only to coordinate either through the nitrogen (such complexes being referred to as nitro complexes) or through the oxygen (nitrito complexes) but also can act as a bidentate oxygen ligand. Indeed in some compounds a mixed bonding of both nitro and nitrito ligands has been observed. A further possibility is that the nitrite ion can bridge two metal ions either through the nitrogen and oxygen or through two oxygen atoms only.(92)

In general, transition metal complexes in molten salts have been found to be either octahedrally or tetrahedrally coordinated, assignments being made according to their d-d spectra, the complexes being classified either by comparison with the spectrum of a compound of known structure or by calculations of the crystal field splitting energies from predictions of the ligands that might coordinate to the transition metal ion. To distinguish between an octahedral and tetrahedral complexes, a general rule is often applied which states that the crystal field splitting energy of a tetrahedral complexes is about $^4/_9$ the magnitude of that in an octahedral complexes with the same ligands. The intensity of the absorption bonds can also be used for distinguishing between the two symmetries, as the intensity of a tetrahedral complex is much greater than that of a regular octahedral complex.

In the present investigation, the electronic spectra of three transition metal ions, nickel (II), copper (II) and chromium (VI) have been studied. All these three ions have earlier been studied intensively in different melts. The spectrum of nickel (II) in molten alkali metal chlorides was found to be affected by the by the alkali metal cation, as in the presence of a large metal cation, i.e. Cs (I), the nickel (II) was shown to prefer a tetrahedral environment, whereas when lithium was the cation, an octahedral nickel environment was preferred. Thus in the lithium chloride-potassium chloride melts, a solvent composition effect on the spectra was found in the range 20 - 55% potassium chloride. The variation in spectra due to an increase in potassium chloride concentration was attributed to the increase in the proportion of tetrahedral nickel (II) chloride complexes largely surrounded by potassium ions and a decrease in the proportion of octahedral complexes surrounded by lithium ions. The temperature also had an effect on the coordination geometry of the nickel (II) in chloride melts, the tetrahedral species being favoured by an increase in temperature.(93)

The absorption spectrum of nickel (II) ions in nitrate melts has been founds to be similar to that in aqueous solution. Since the nickel (II) ions are hexa-coordinated in aqueous solution, a similar coordination was suggested in the nitrate melt.(81) The spectrum in molten nitrate was thought to be due to nickel (II) ions surrounded by three nitrate ions acting as bidentate ligands thus giving an octahedral environment. On the addition of chloride ions to the nitrate melt, a change in the spectrum of nickel (II) ion was observed and interpreted as due to the successive replacement of nitrate groups by chloride ions resulting, at a high chloride concentration, in the formation of tetrahedral $(NiCl_4)^{2-}$ ion. The coordination of nickel (II) ion has also been studied in sulphate melts. In the ternary lithium sulphate-potassium sulphate-sodium sulphate eutectic at 550°C, the nickel (II) spectrum was interpreted as distorted octahedral with three sulphate ions coordinated to the metal ion as bidentate ligands.(82)

In contrast with the above mentioned studies, the study of nickel (II) complexes with nitrite ligands has been made spectroscopically hitherto in the solid state only. An early X-ray diffraction investigation suggested that the nickel (II) nitrite complex $[K_4Ni(NO_2)_6]$ had six nitrite groups coordinated to the metal ion through the nitrogen.(94) In more recent studies, this hexanitrite nickel (II) compound was shown by spectroscopic methods to be monohydrated. On dehydration a change in the nature of the coordination was found and the formula suggested for the anhydrous compound was $K_4(NO_2)_4(ONO)_2$.(92)

Copper (II) complexes, which have also been studied in the present work, have a d^9 configuration and are thus subject to a considerable distortion which render their absorption spectra more complex. The distortion is due to the Jahn-Teller effect in which any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some kind of distortion that will lower its symmetry and split the degeneracy. The spectrum of copper (II) ion in molten chlorides has been studied, showing a single band in the visible region which was attributed to a d-d transition of the $Cu\,Cl_4^{2-}$ ion and interpreted as due to a strong distortion from tetrahedral symmetry.(95) In molten sulphate, the copper (II) ion has been reported to be surrounded by two bidentate sulphate ligands with a possibility of two monodentate sulphate ligands at a greater distance.

Spectroscopic studies on the hexanitro copper (II) complex have been limited to reflectance spectra on the powdered samples. These have shown that the copper (II) ion is octahedrally coordinated by six nitro groups. The coordination through the nitrogen has been confirmed by both infra red and X-ray diffration measurements.(96)

Chromium compounds have been studied in molten salts. In a nitrate melt, chromate ion has been investigated and the spectroscopic measurements showed an absorption maxima at 27000 cm^{-1} which was attributed to a change transfer transition.(91) Whereas in nitrite melt the absorption maxima occurred at 24000 cm^{-1}. The large shift in position of the absorption maxima was attributed to absorption by nitrite and the asymmetry of the chromate band strengthened this suggestion. The reactions of other chromium compounds in nitrite melt have been reported, for example, potassium tri-chromate and chromium (VI) oxide for which reduction reactions were found to occur with the formation of chromium (III). The spectrum of the green-yellow solution of chromium (III) in nitrite melt was shown to have an absorption maxima at 17000 cm^{-1}.(29) In chloride melt, chromium (III) showed two bands with maxima at 12500 cm^{-1} and 18500 cm^{-1}, which were interpreted as due to the octahedral $CrCl_6^{3-}$ complex.(97)

Like many other transition metals, iron compounds have been studied in molten salts. In chloride melt, spectral measurements showed that the iron (II) is tetrahedrally coordinated to four chloride ions $FeCl_4^{2-}$(63), while in sodium nitrite-potassium nitrite eutectic the iron (II) and iron (III) were found to be unstable and reacted below the melting point producing Fe_2O_3.(31)

It is evident from the above introduction that no spectral measurements have been made on positive transition metal ions in nitrite melts. The object of the present investigation was therefore to measure the spectra of the nickel (II), copper (II) and iron (III) ions in a nitrite melt as well as to investigate the effect of the oxidation-reduction behaviour of the melt on chromyl (VI) chloride.

IV.2 EXPERIMENTAL

IV.2.1 MATERIALS

Lithium nitrite-potassium nitrite and sodium nitrite-potassium nitrite eutectics were used in the present investigation. The preparation, purification and dehydration of both melts and the preparation of lithium nitrite have already been described in Chapter I. The melts were analysed for nitrate before and after the reactions by the methods mentioned in Chapter I. Other chemical reagents were dehydrated and analysed as follows:

Nickel (II) chloride

B.D.H. Analar $NiCl_2 \cdot 6H_2O$ was dehydrated by refluxing with B.D.H. reagent grade thionyl chloride.(88) Residual traces of thionyl chloride which could not be removed from the nickel chloride by pumping and gentle heating in vacuo, were removed by heating to 200°C in a current of dry, oxygen-free nitrogen. The purity of nickel chloride was determined by the analysis procedure described later in this chapter.

Analysis Ni = 44.79% (Calc. for $NiCl_2$ 46.29%)

Cl = 54.13% (Calc. for $NiCl_2$ 54.71%)

Copper (II) sulphate

The dehydration of $CuSO_4 \cdot 5H_2O$ has been the subject of several studies. Duval(85) has found that the hydrated copper sulphate started to lose four molecules of water from 47°C to 153°C, the residual monohydrated salt then commenced losing the remained water molecule around 250°C. However other workers have reported that the transition from five to three molecules of water occurs from 30°C to 38°C, from $3H_2O$ to $1H_2O$ between 68°C and 74°C and from the monohydrated to the anhydrous salt at 200°C to 220°C.(98)

The dehydration of B.D.H. Analar $CuSO_4.5H_2O$ was carried out in vacuo at 200°C for three hours. Thermogravimetric analysis showed no further weight loss up to 300°C.

Analysis	Cu = 39.35%	(Calc. for $CuSO_4$ Cu = 39.82%)
	SO_4 = 59.7%	(Calc. for $CuSO_4$ SO_4 = 60.18%)

The analysis procedure is described later in the analysis section.

Chromyl (VI) chloride

B.D.H. reagent grade CrO_2Cl_2 was used without further purification.

Iron (III) chloride

Reagent grade iron (III) chloride B.D.H. sublimed in chlorine at 110°C.(99)

Analysis	Found Fe = 34.3%	(Calc. for $FeCl_3$ 34.4%)
	Cl = 64.4%	(Calc. for $FeCl_3$ 65.6%)

IV.2.2 CHEMICAL ANALYSIS

Chemical analysis was carried out on the solid pure solutes as well as when dissolved in the melt. For molten solutions, the melts were solidified by cooling, dissolved in water and diluted to the required volume.

The nickel was precipitated by the addition of an alcoholic solution of dimethylglyoxime $[CH_3C(NOH)C(NOH)CH_3]$ to a hot, faintly acid aqueous solution of the nickel salt, followed by the addition of a slight excess of aqueous ammonia solution. The resulting red precipitate was digested, filtered and washed with cold water, then weighed as nickel dimethylglyoximate after drying at 110°C. The chloride was precipitated as silver chloride by the addition of silver nitrite to the solution of chloride slightly acidified with dilute nitric acid and estimated gravimetrically.

The copper was determined gravimetrically by the addition of freshly ammonium thiocyanate to a hot solution of copper (II) ions which was acidified with a few drops of hydrochloric acid and a slight excess of sulphurous acid solution. The white precipitate of copper (I) thiocyanate was dried at 110°C.

The sulphate ion was determined by the addition of barium chloride to hot acid sulphate solution. The precipitate was weighed as barium sulphate after ignition at 900°C.

Chromium was estimated gravimetrically by precipitation as barium chromate. Barium chloride solution was added to a chromate solution which contained a few grams of ammonium chloride and was acidified with dilute acetic acid. The precipitate after filtering and washing was dried at 120°C.

IV.2.3 PHYSICAL MEASUREMENTS

Infra red spectra of the solid were recorded as mulls using KBr discs on Perkin Elmer 157 G.I.R. spectrometer. Precautions were taken in the preparation of the specimen of the solute in lithium nitrite-potassium nitrite melt to avoid complication due to the hygroscopic nature of lithium nitrite, as the presence of water molecules causes a change in the coordination system of the complex.

The melt solution containing nickel (II) or copper (II) ions were poured into an evaporating basin in a small desiccator, which was evacuated and placed in a dry box. The solid melt was ground to fine particles and the specimen prepared using a few drops of mulling hexachlorobutadiene. A small portion was placed on the KBr discs and then sealed up with Sellotape avoiding as far as possible any contact with the atmosphere. As a result of these precautions good spectra were obtained since no peak due to water molecules appeared.

Infra red spectra of gases were carried out on a S.P. 200 I.R spectrometer similar to the procedure described in Chapter III. Thermogravimetric analysis was carried out on a Stanton T.R-1 thermobalance at a heating rate of 2°C per minute, the weight losses being reported as percentages by weight of the solute. Details of the procedure for using the balance and the precautions taken are given in Chapter II. A Unicam S.P. 800 spectrometer was used to measure the reflectance spectra of the solid samples.

High temperature spectra

The high temperature spectroscopic measurements were made using a Unicam S.P. 700 spectrometer modified for use up to 700°C. The spectral range of the instrument was from 54,000 cm^{-1} to 2800 cm^{-1}. From 54,000 cm^{-1} to 13000 cm^{-1}, detection was by a photomultiplier, while a lead sulphide photocell was used over the range 13000 cm^{-1} to 2800 cm^{-1}. Quartz spectroscopic cells of 1 mm pathlength were used for both reference and sample solution in the present work. Since the nitrite melt expanded on cooling to room temperature, cracking was avoided by removing the melt before solidification.

IV.3 RESULTS

IV.3.1 Nickel (II) chloride

The solution of nickel (II) chloride in molten lithium nitrite-potassium nitrite at 120°C was slow, since observation showed no change in the colour of the melt immediately after the addition of the nickel compound. However, in three hours, the compound dissolved forming a green solution. A few black particles formed on the surface of the melt, a few minutes after the time of addition. On analysis these were shown to be nickel (II) oxide. The green melt, after filtering off the black particles, was found to be stable for 24 hours but eventually started to form a black precipitate again but very slowly. The absorption spectra of the green filtered melt was measured within the range 27000 cm^{-1} - 4000 cm^{-1} at 120°C. The absorption bands found, with their extinction coefficients, are listed in Table 1 and the spectral curve is shown in Figure 1. The extinction coefficient was calculated after determining the nickel content in the quenched melt gravimetrically with dimethyglyoxime.

The colour of the melt changed on solidification from green to orange-red. Reflectance spectra measurements of the orange-red powdered melt showed an absorption band at 20500 cm^{-1}. (Figure 2).

In order to indicate whether the coordination of the ligands was through the nitrogen (nitro) or through the oxygen (nitrito), infra red spectral measurements were obtained for both the anhydrous and the hydrated nickel (II) complexes. The infra-red spectrum of the anhydrous nickel (II) complex showed bands at 1386 cm^{-1}, 1350 cm^{-1}, 1325 cm^{-1} and 1208 cm^{-1}, whereas for the hydrated complex the spectrum showed bands at 1350 cm^{-1} and 1325 cm^{-1} only.

Fig . I

Spectrum of Nickle (II) chloride in Li / KNO_2

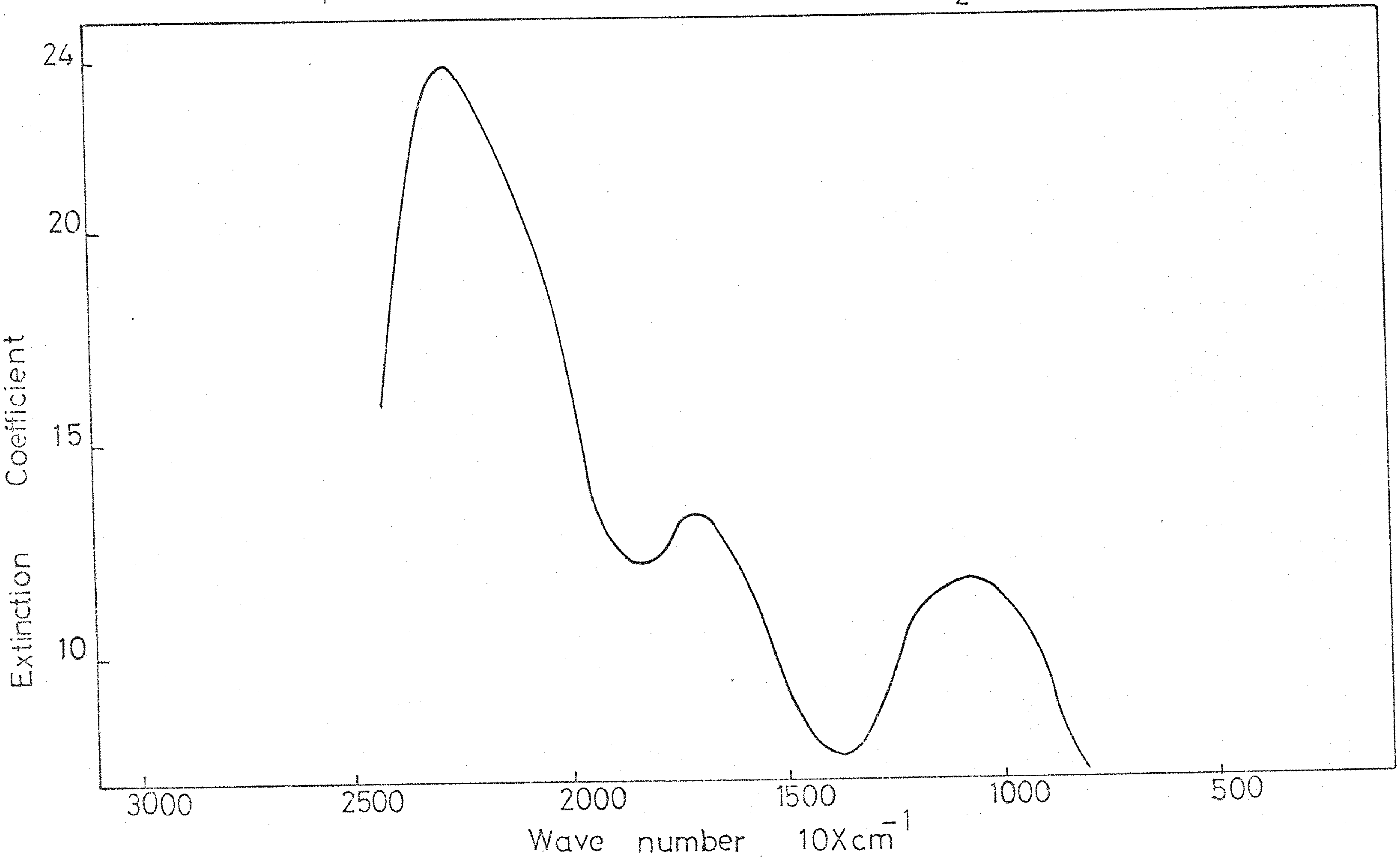


Fig. 2

Electronic reflectance of Nickel(II) chloride in nitrite eutectic

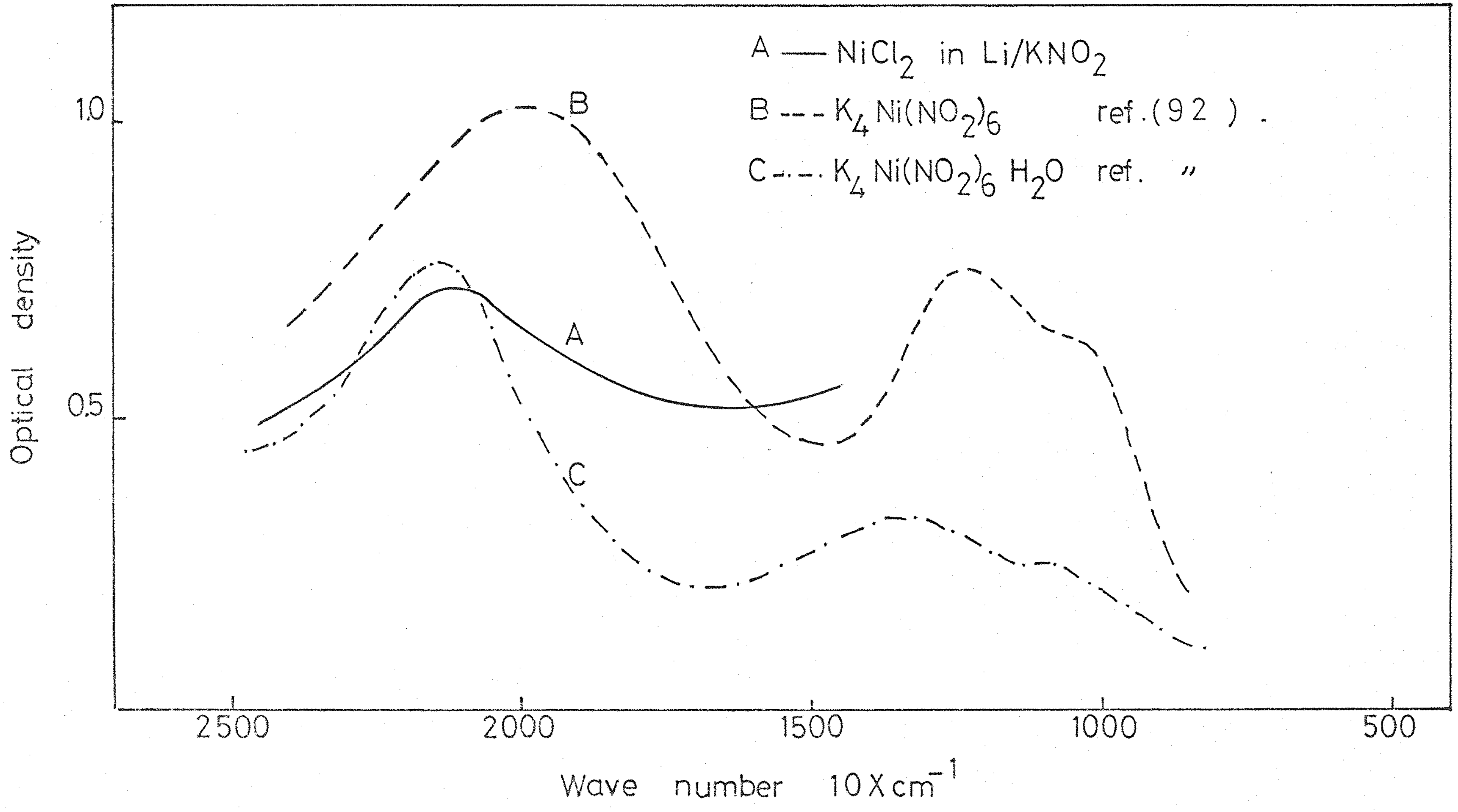


Table 1

Electronic spectra of octahedral nickel (II) nitrite complexes

in melt at 120°C absorption bands	εmax	solid reflectance spectra at 20°C	solid reflectance spectra at 25°C*
10800 cm^{-1}	11.7	-	11000 cm^{-1}
17000 cm^{-1}	13.4	-	13200 cm^{-1}
22600 cm^{-1}	23.4	20500 cm^{-1}	20700 cm^{-1}

* spectra measured by Goodgame ref (92).

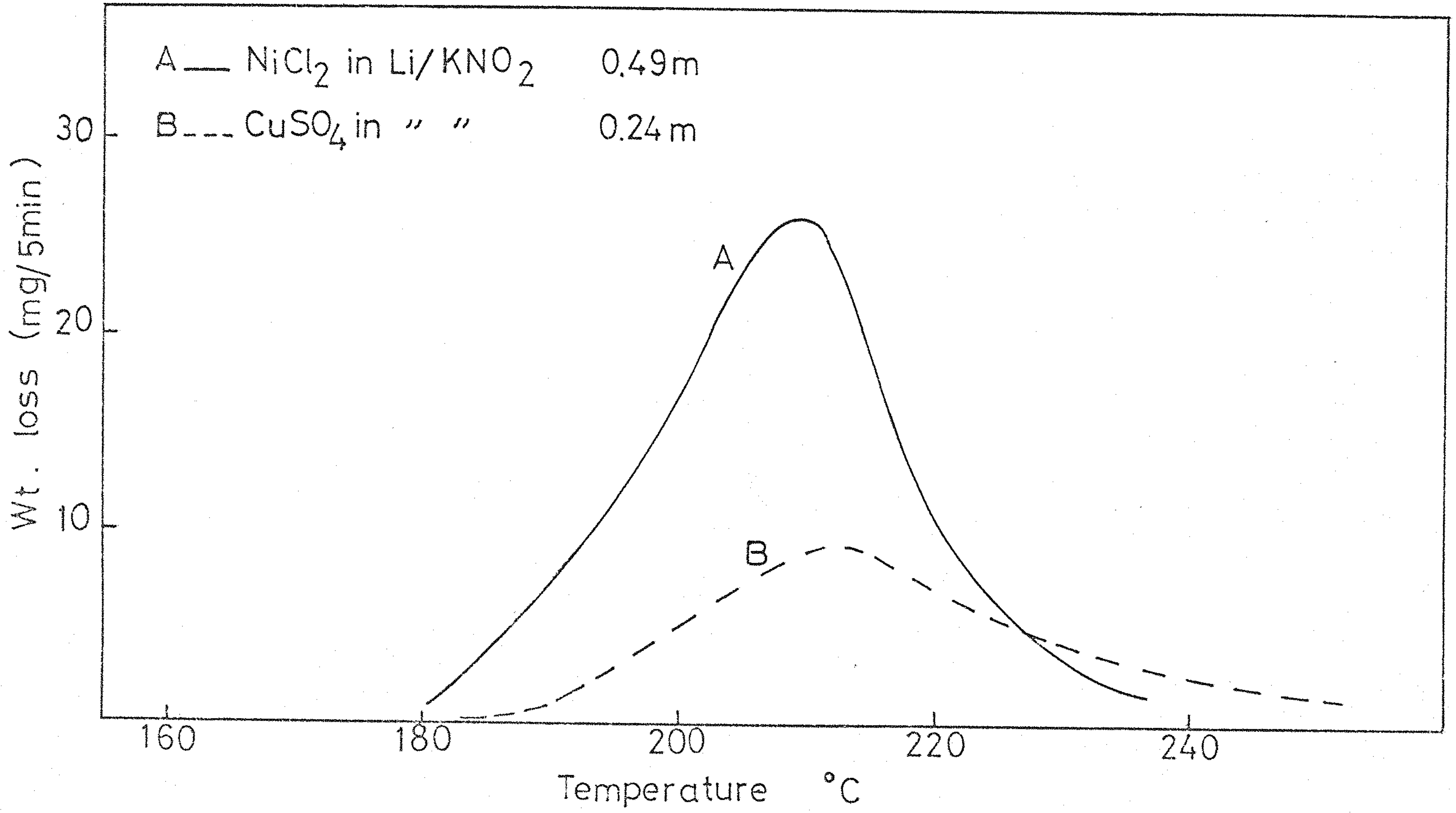
Thermogravimetric analysis showed the reaction to commence at 180°C with a maximum weight loss occurring around 210°C (Figure 3). The total weight loss was found to average 51.4% but became 57.9% after correction for the formation of nitrate due to the reaction of nitrogen dioxide and nitrite melt (equation II.4). (Calculated for loss of 2N + 3O per $NiCl_2$ 58.6%). The X-ray powder pattern of the black precipitate after washing and drying gave the lines (2.42, 2.09, 1.48) corresponding well with that of NiO [A.S.T.M. index 2.41 (91), 2.09 (100), 1.48 (57)].

IV.3.2 Copper (II) sulphate

A green coloured melt was obtained immediately after the addition of copper (II) sulphate to the lithium nitrite-potassium nitrite melt. A few black particles formed on the surface of the melt, which, after dissolving the quenched melt in water, filtering and drying, were examined by X-ray diffraction and gave the lines 2.50, 2.32 and 2.52 which correspond to those of CuO. [A.S.T.M.

Fig ..3

TGA of Nickle(II) and Copper(II) compounds in Li/KNO_2



2.52 (100), 2.32 (96), 2.53 (49)].

The electronic spectra of the filtered green melt was determined over the range of 27000 cm^{-1} - 4000 cm^{-1} (Figure 4) and the energy of the band maxima with their extinction coefficients, calculated after the determination of the copper (II) content in the melt, are listed in Table 2.

In order to have a better understanding of the coordination of the ligands, infra red spectral measurements were carried out on the solid powder of both the hydrated and the anhydrous copper (II) complexes. The anhydrous copper (II) complex showed a vibrational band at 1380 cm^{-1}, 1350 cm^{-1} and a shoulder at 1208 cm^{-1}. Whereas the hydrous complex showed a band at 1350 cm^{-1} and 1325 cm^{-1} only.

Table 2

Electronic spectra of octahedral copper (II) complex

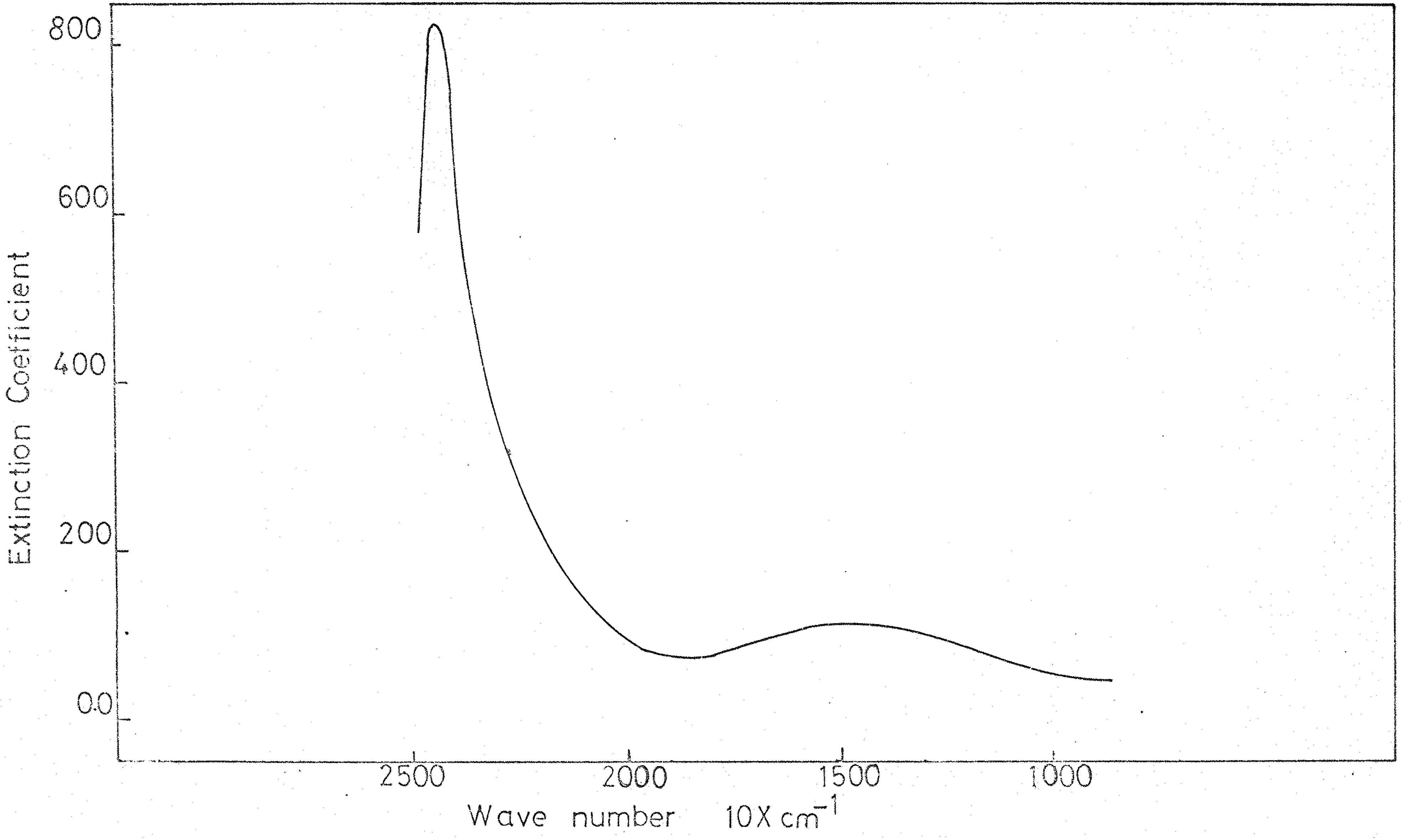
Absorption bands in melt at 120°C	εmax	Solid reflectance spectra of K_2Ba [$Cu(NO_2)_6$] *
-	-	7880 cm^{-1}
14400 cm^{-1}	107	16530 cm^{-1}
24500 cm^{-1}	860	24800 cm^{-1}

* Elliott ref (96).

Thermogravimetric analysis showed the reaction between copper (II) sulphate and nitrite eutectic to have commenced at 185 ± 5° with a maximum weight loss around 210°C (Figure 3 curve B). The experimental weight loss was found to be 41.3% which when

Fig. 4

Spectrum of Copper(II) sulphate in Li/KNO_2



corrected for the formation of nitrate due to the reaction (II.4) became 44.1%. (Calculated for loss of 2N + 3O per $CuSO_4$ 44.7%).

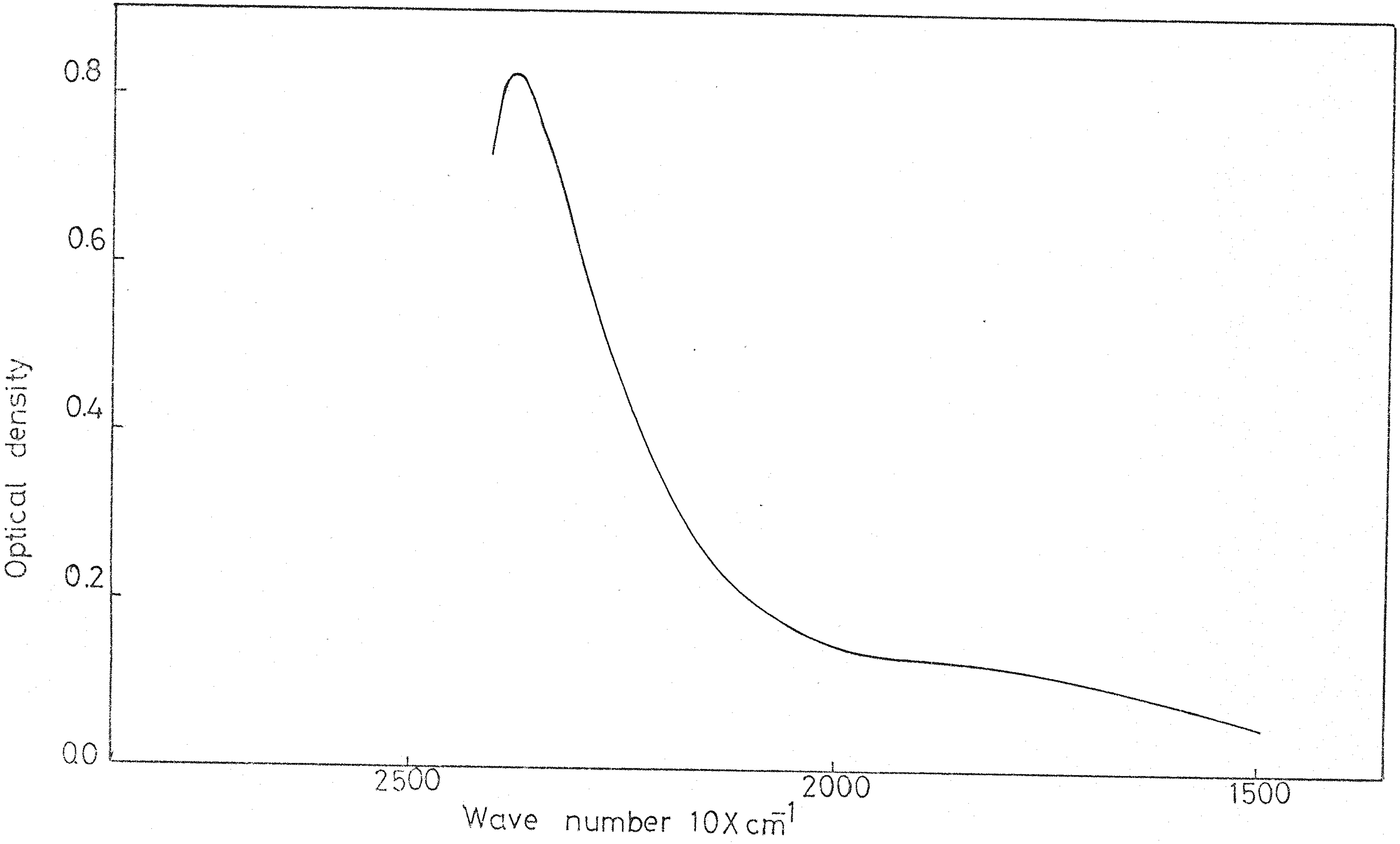
IV.3.3 Chromyl(VI) chloride

Chromyl(VI) chloride reacted immediately on contact with molten nitrite. The addition of a drop of the compound to a molten lithium nitrite-potassium nitrite caused a violent reaction with the evolution of brown fumes and the formation of a black-brown melt. The black-brown melt underwent no further change on heating at 120°C for ten hours, but after that time, the colour started to change until it became completely yellow. A similar yellow colour melt was obtained more rapidly on raising the temperature to 230°C. On addition of more lithium nitrite-potassium nitrite eutectic, the black-brown colour dispersed forming a green-yellow melt which slowly reacted producing a yellow solution after eight to ten hours. In the sodium nitrite-potassium nitrite melt at 220°C, the chromyl (VI) chloride reacted more vigorously with the evolution of brown fumes and the formation of black-brown melt which was stable for about three hours before the yellow colour was produced.

Spectral measurements were made on the black-brown, green-yellow and the yellow melts at different temperatures over the range of 27000 cm^{-1} - 4000 cm^{-1}. In the case of the black-brown melt, an absorption band at 24200 cm^{-1} was obtained at 120°C which on raising the temperature to 230°C shifted to 23800 cm^{-1}. A similar absorption band and shift was obtained in molten sodium nitrite-potassium nitrite. The green-yellow melt as well as the yellow melt showed absorption bands at 24200 cm^{-1} and 23800 cm^{-1} respectively (Figure 5).

Fig . 5

Spectrum of Chromyl chloride in nitrite eutectic



Analysis carried out on a solution of the yellow melt in water showed the presence of chromate ion.

IV.3.4 Iron (III) chloride

An orange-coloured melt was formed when iron (III) chloride was added to lithium nitrite-potassium nitrite at 120°C with the formation of a red brown precipitate at the surface of the melt. The precipitate after washing and drying was analysed and found to be Fe_2O_3. The orange colour of the melt was unstable and started to disappear within four minutes forming more of the red-brown precipitate and a clear yellow melt.

IV.4 DISCUSSION

IV.4.1 Nickel (II) chloride

Nickel (II) ion, $3d^8$, has been studied in various melts in which it has showed a tetrahedral and octahedral coordination. In molten lithium nitrite-potassium nitrite the absorption spectrum does not resemble either the aqueous octahedral complex $[Ni(H_2O)_6]^{2+}$, (as does nitrate melt) or the solid reflectance spectra of the nitro complex $[Ni(NO_2)_6]^{4-}$. However, the molar extinction coefficient ($\varepsilon = 23$) of the absorption band at 22600 cm^{-1} of nickel (II) in nitrite melt is similar to that found in the nitrate melt(81) ($\varepsilon = 28$) and lower than that of the tetrahedral complex in chloride melt(100) ($\varepsilon = 62$), suggesting that the nickel (II) ions in nitrite melt are octahedrally coordinated through either the oxygen (nitrito) or the nitrogen (nitro). The distinction between nitro and nitrito complexes by means of their electronic spectra rests upon the fact that the two groups occupy quite different positions in the spectrochemical series. The nitro group exhibits large Δ values and lies between O-phenanthroline and the cyanide ion in the spectrochemical series, whereas the nitrito groups exert a much weaker ligand field which is closer to urea in the series as shown(101)

$$I^- < Br^- < Cl^- \sim \underline{S}CN^- < F^- \sim \text{Urea} \sim OH \sim \underline{N}O_2^-$$
$$< OX^{2-} < H_2O < SC\underline{N}^- < gly < py \sim NH_3 < en \sim \underline{S}O_3^-$$
$$< dip < phen < \underline{N}O_2^- << \underline{C}N^-$$

In order to determine whether the nitrite ions are coordinated to nickel (II) ion through the nitrogen or the oxygen, it is useful to make a comparison between the complex formed by these type of ligands with the others formed from ligands which are very close to them in the spectrochemical series, i.e. with urea which has almost the same strength as a nitrito group and O-phenanthroline which is close to the nitro group. If the six ligands are assumed to coordinate to the nickel (II) ion through the oxygen (-ONO), then the splitting energy Δ for the octahedral nitrito complex should be similar to that of the octahedral urea complex. Since the Δ values of the nickel (II) $(\text{Urea})_6$ complex could be worked out approximately as a product of a function f of the ligands and g of the central ion from the equation(101)

$$\Delta = f(\text{ligand}) \cdot g(\text{central ion}) \qquad \text{... IV.1}$$

and since both f for the 6 urea and g for nickel (II) ion have been derived, it was thus possible to calculate

$$\Delta_{Ni(\text{Urea})_6^{2+}} = (0.91)(8900\ cm^{-1}) = 8200\ cm^{-1}$$

Hence, the octahedral nickel (II) nitrito complex should have a Δ value close to 8200 cm^{-1}. As the Δ value of the green melt, containing nickel (II) complex, was found to be 10,800 cm^{-1}, the proposal of six nitrito ligands coordinated to the central nickel (II) ion is not in agreement with the calculated value for Δ (8200 cm^{-1}).

On the other hand, the Δ value for nitro groups octahedrally coordinated to the nickel (II) ion has been determined from the visible reflectance spectra of $K_2Ba[Ni(NO_2)_6]$ and was reported to be Δ = 13400 cm^{-1}. The Δ value for the octahedral nickel (II) complex in nitrite melt (10800 cm^{-1}) is thus neither close to the Δ value of the urea complex nor to that of the nitro complex. This result leads to the suggestion that the species coordinated to the nickel (II) ion is a mixture of nitro groups and nitrito groups. For better understanding the nature of this species, it is useful to make a comparison between its Δ value and that of nickel (II) ion coordinated to ligands which lie in the middle of the spectrochemical series between the nitro and the nitrito groups i.e. $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$, in which the H_2O ligands are close to the nitrito groups and the ammonia is nearer to the nitro group.(101)

Table 3

Δ values of nickel (II) complexes

Ni (II) complex	Δ cm^{-}
$[Ni(H_2O)_6]^{2+}$	8500
$[Ni(gly)_3]^{2+}$	10100
$[Ni(NH_3)_6]^{2+}$	10800
$[Ni(em)_3]^{2+}$	11500
$[Ni(phen)_3]^{2+}$	12200

Since the Δ value of nitrite complex is approximately half the summation of Δ values for three nitro and three nitrito groups (Jorgenson rule of average environment), the nickel (II) ion in nitrite melt is probably octahedrally coordinated to three nitrito groups and three nitro groups i.e. $[Ni(NO_2)_3(ONO)_3]^{4-}$.

The Δ values of $[Ni(NH_3)_6]^{2+}$ is similar to the Δ value obtained from the nickel (II) spectrum in nitrite melt, and the absorption spectra of the octahedral nickel (II) nitro-nitrito complex (Figure 1) showed three absorption band similar to those for ammonia complex which may be attributed to the three spin-allowed transitions

$10800\ cm^{-1}$	$^3A_{2g} \rightarrow {}^3T_{2g}$
$17000\ cm^{-1}$	$^3A_{2g} \rightarrow {}^3T_{1g(F)}$
$22800\ cm^{-1}$	$^3A_{2g} \rightarrow {}^3T_{1g(P)}$

The absorption maxima ($22800\ cm^{-1}$) was expected to occur at a higher wave number, as the spectrum of hexamminonickel (II) shows this absorption band at $28200\ cm^{-1}$.(102) The explanation is probably that this band is shifted to a lower energy due to the presence of the very strong charge transfer band of nitrite at $27800\ cm^{-1}$. A similar phenomena has been observed in the electronic spectrum of chromate in nitrite melt in which both the position of the absorption maximum and its intensity were changed.(29)

Solidification of the green melt resulted in a change in the colour to red-orange. Since the reflectance spectra of the solidified melt showed different absorption spectra than those obtained in the molten state, a change might have taken in the manner of coordination of some of the nitrite groups on solidification. A band maximum at $20500 cm^{-1}$ was obtained from the reflectance spectra of the hydrated compound which was in close agreement with the band found by Goodgame at 20700 cm^{-1}.(92) The other two bands found by Goodgame at 13200 cm^{-1} and 11,000 cm^{-1} could not be detected because this region was outside the range of the reflectance spectrometer. Both the present spectrum and that of Goodgame showed no indication of any band at 17000 cm^{-1} such as that found in the molten state.

On the other hand, the infra red spectrum obtained on the red-orange solidified melt was in agreement with that obtained by Goodgame, showing the infra red bands 1386 cm^{-1}, 1350 cm^{-1}, 1325 cm^{-1} and 1208 cm^{-1}. Thus by similar argument this is considered to indicate the presence of the nitrito group as well as the nitro. However, the infra red spectrum for the hydrated complex showed only peaks due to nitro groups. The band maxima of the reflectance spectra of both the anhydrous and the hydrated nickel (II) nitrite complexes were similar (Figure 2) although a slight decrease towards a lower wave number could be noticed for the anhydrous compound. This weakening of the ligand field about the nickel (II) ion on dehydration was attributed to the conversion of some nitro groups to nitrito groups. From the extent of the reduction in the ligand field, the anhydrous compound probably has the structure $K_4Ni(NO_2)_4(ONO)_2$.(92)

The nickel (II) chloride was found to be reasonably stable in lithium nitrite-potassium nitrite, since the thermogravimetric analysis showed that the reaction commenced at 180° ± 5, in contrast to sodium nitrite-potassium nitrite eutectic where the reaction started at 130°C, in the solid state.(31) This additional stability in molten lithium nitrite-potassium nitrite may be attributed to the formation of the nickel (II) nitro-nitrito complex which seems to be stable up to 180°C. The weight loss on the thermogram, after correction for the formation of nitrate due to reaction (II.4), fitted the following stoichiometry

$$NiCl_2 + 2NO_2^- \rightarrow NiO + NO + NO_2 + 2Cl^- \qquad \text{... IV.2}$$

The metal ion, acted as a Lux-Flood acid, abstracted oxide ions from nitrite forming nickel (II) oxide similar to that of nickel (II) in nitrate melts.

IV.4.2 Copper (II) sulphate

Nitrite ion, as shown previously, may bond either through the nitrogen or through the oxygen. For the copper (II) complex in nitrite melt, it is useful to use the infra red and electronic spectra of copper (II) nitro and nitrito complex in order to identify the nature of the coordination of nitrite to the central metal ion. The infra red spectrum of the copper (II) complex in the solid melt showed an absorption band at 1380 cm^{-1} which is similar to the infra red band at 1372 cm^{-1} of the compounds o-cat$[(Cu(ONO_2)_4]$(103) as shown in Table 4, whereas the absorption band at 1350 cm^{-1} is close to 1340 cm^{-1} of the compound $K_2Ca[Cu(NO_2)_6]$.

Table 4

Infra red spectra of copper (II) nitro and nitrito complex

compound	state	absorption bands			
O-cat$[Cu(ONO)_4]$	mull MeCN	1372 *	- -	- -	1195(103) 1188
$K_2Ca[Cu(NO_2)_6]$	mull	-	1340	1294	- (96)
$[Cu(NO_2)_n(ONO)_{6-n}]^{4-}$(a)	mull	1380	1350	-	1208

(O-cat) = [O-Xylyenebis (triphenyl-phosphonium)].

(a) Suggested formula of the copper (II) complex in nitrite melt.

The most important conclusion obtained from the infra red bands is that the nitrite groups of the copper (II) complex in the solidified melt appears to be bonding both through the nitrogen ($-NO_2$) and throught the oxygen (-ONO). The manner of coordination of nitrite groups to the copper (II) ion in molten nitrite is probably similar to that in the solidified melt, since the complex has the same green colour in both cases.

Besides the infra red spectra, the electronic spectra can be used to identify the manner of coordination of the nitrite groups to the central metal ion as well as the possibility of determining the geometry of the copper (II) complex. The value of the extinction coefficient obtained from the spectra ($\varepsilon = 107$) for the absorption band 14400 cm^{-1} might suggest that the copper (II) ion is tetrahedrally coordinated, since most of the centrosymmetrical octahedral copper (II) complexes have an ε value between 20 - 50. In order to find out whether the copper (II) complex is tetrahedrally or octahedrally coordinated the Δ values of these complexes were worked out using equation (IV.1) and the results are listed in Table (5). The calculation of these values for Δ were based on the f values for urea and o-phenanthroline.

The calculated Δ values for the tetrahedral copper (II) complex of both the nitro and nitrito as shown in Table (5) do not agree with the Δ value of copper (II) in nitrite melts. In spite of the difference in the Δ values, tetrahedral copper (II) derivatives, if approximately regular are generally expected to give a single broad

Table 5

Δ values for Oh and Th copper (II) nitrite complexes

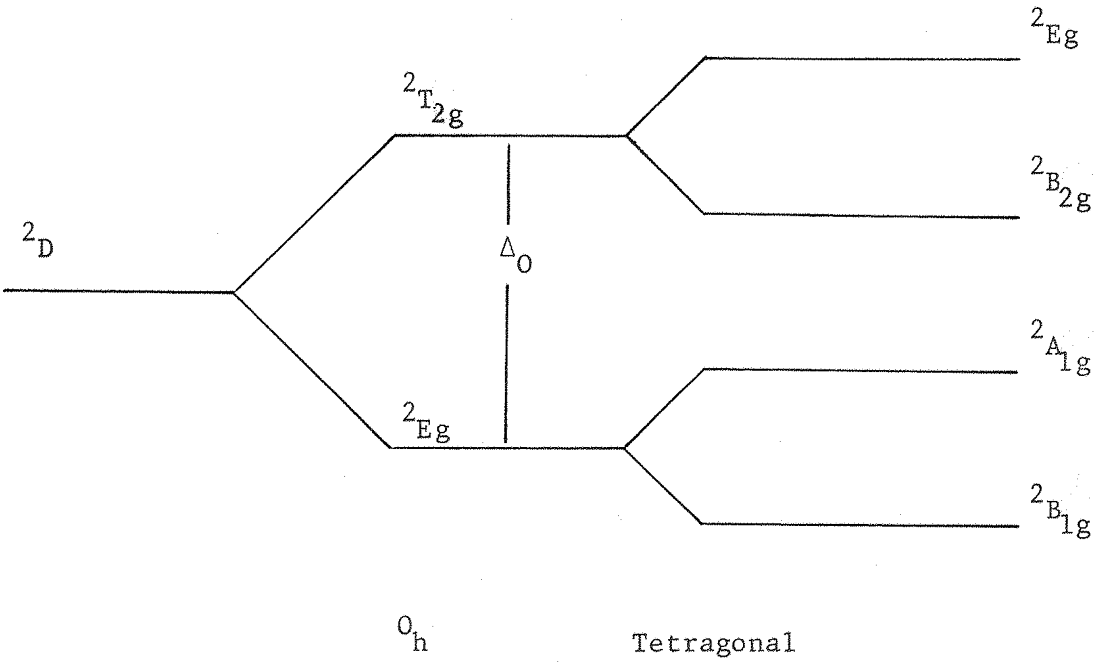
Compound	Δ_O cm^{-1}	Δ_T cm^{-1}
$[Cu(ONO)_4]^{2-}$	-	∿ 4650
$[Cu(NO_2)_4]^{2-}$	-	∿ 7045
$[Cu(ONO)_6]^{4-}$	∿ 10465	-
$[Cu(NO_2)_6]^{4-}$	15855	-
$[Cu(NO_2)_n(ONO)_{6-n}]^{4-*}$	14400	-

* Suggested formula for copper (II) complex in nitrite melt.

band at room temperature of about 10^2 molar intensity in the near infra red and not to absorb between 10000 cm^{-1} and 20000 cm^{-1}.(104) An alternative explanation for the high value of the extinction coefficient is that the copper (II) complex has a distorted octahedral structure in which the distortion might be due to the Jahn-Teller effect. On the other hand the calculated Δ_0 values for the pure octahedral nitro or octahedral nitrito complexes (Table 5) are not completely in agreement with the value of Δ obtained from the spectrum, thus again the ligands coordinated to the metal ion are probably a mixture of nitro and nitrito. The calculated Δ_0 value for copper (II) complex with four nitro ligands and two nitrito ligands was very close to the Δ value obtained from the molten spectrum. Hence, the copper (II) complex in nitrite melt might have the structure $[Cu(NO_2)_4(ONO)_2]^{4-}$.

In the case of an octahedral copper (II) complex, the electronic ground state is $^2Eg(^2D)$. If the complex was perfectly octahedral, only a single band due to the transition $^2Eg \rightarrow {}^2T_{2g}$ would be occur (Figure 6)(96)

Figure 6



The copper (II) ion is probably subjected to a considerable Jahn-Teller effect, which gives rise to a tetragonal distorted complex with four short metal ligand bonds in one plane (xy) and two longer metal-ligand bonds lying along the z axis. The hexanitrocopper (II) complex spectrum shows two absorption bands, a relatively strong band at 16000 cm^{-1} and a less intense band at 7500 cm^{-1} considered to be due to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ respectively. But it is unusual to observe such a clear separation of these two bands in the spectra of copper (II) complexes, as they usually tend to overlap to produce a single broad band.(96)

The observed transition (14400 cm^{-1}) of copper (II) ion in molten nitrite is probably to be assigned to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$, whereas the second expected transition, $^2B_{1g} \rightarrow {}^2A_{1g}$, was not observed probably due to the overlapping with the first band.

The other absorption band observed at 24450 cm^{-1} for the copper (II) ion in molten nitrite is probably due to a charge transfer transition, since this band is much more intense than the band at 14400 cm^{-1} and its energy is rather high for a d-d transition.

The copper (II) complex showed considerable stability in lithium nitrite-potassium nitrite melt, as no black precipitate of copper (II) oxide due to the reaction of copper (II) ions with nitrite ions was observed for several hours. The stability of the complex was confirmed using thermogravimetric analysis (Figure 3) which showed that the reaction commenced at 185 ± 5°C. The weight loss after correction for nitrate formation is in agreement with the equation

$$CuSO_4 + 2NO_2^- \rightarrow CuO + NO + NO_2 + SO_4^{2-} \qquad \text{IV.3}$$

IV.4.3 Chromyl (VI) Chloride

In molten lithium nitrite-potassium nitrite chromyl chloride produced several coloured solutions due to the formation of different chemical species, depending on solute concentration and melt temperature. At 120°C the black-brown melt was probably due to the formation of a compound which is possibly similar to the brown compound, prepared from an aqueous solution of chromium (III) chloride and excess of silver chromate, described as $Cr[Cr(CrO_4)_3].3H_2O$.(105) It has been found, as well, that aqueous solutions of chromate and chromium (III) form brown solutions providing the former is in excess and will give a black-brown precipitate which has been found to be $Cr_2(CrO_4)_3$ (if the ratio Cr VI/Cr III is greater than 3). In molten nitrite the black-brown precipitate was obtained only when the ratio was greater than 9.(29)

The spectrum of the black-brown melt showed an absorption maxima at 23800 cm^{-1}, whereas the yellow melt obtained by raising the temperature to 220°C showed an absorption band at 24000 cm^{-1} which is similar to the absorption maximum of the yellow solution of potassium chromate in nitrite melt (24000 ± 60 cm^{-1}). Since no d-d transitions are possible for the d^0 electronic configuration of chromium (VI), this absorption was due to a charge transfer transition. By comparison with the charge transfer spectra obtained for potassium chromate in nitrate melt(91) and aqueous solutions(106) with absorption bands 27000 cm^{-1} and 26900 cm^{-1} respectively, the large shift in position of the absorption maximum in nitrite melt is due to the absorption of nitrite. The asymmetry of the chromate band strengthened the above suggestion.

The green-yellow melt was expected to contain a chromium (III) species, since nitrite melt can act as a reducing agent, as well as an oxidizing agent, reducing chromium (VI) oxide to chromium (III).(29) But the band expected between 16000 cm^{-1} and 17000 cm^{-1}, due to the presence of chromium (III), did not occur. The failure to find this band in the green-yellow lithium nitrite-potassium nitrite melt might be due to the high dilution of the melt. The presence of chromium (III) species in green-yellow nitrite melt was also found on the addition of chromium (III) chloride to the nitrite melt which gave two absorption bands at 17000 cm^{-1} and 23400 cm^{-1}.(29)

Chromyl (VI) chloride behaved as expected, i.e. as a Lux-Flood acid, removing oxide ion from nitrite melt with the formation of chromate. The reaction occurring according to the following equation.

$$CrO_2Cl_2 + 4NO_2^- \rightarrow CrO_4^{2-} + 2NO_2 + 2NO + 2Cl^- \qquad IV.4$$

IV.4.4 Iron (III) chloride

The soluble iron (III) species in lithium nitrite-potassium nitrite melt was unstable, as its orange colour disappeared in four minutes making it impossible to run a spectrum. In previous work,(31) it had been found that iron (III) chloride reacted very rapidly when added to molten sodium nitrite-potassium nitrite at 220°C with the production of a red brown precipitate which has been found to be Fe_2O_3 and a thermogram had shown the reaction to commence in the solid state at 130°C. The stoichiometry of the reaction has been reported to be in accordance with the equation

$$2FeCl_3 + 6NO_2^- \rightarrow Fe_2O_3 + 3NO + 3NO_2 + 6Cl^- \qquad IV.5$$

CHAPTER V

REACTIONS OF LEAD COMPOUNDS

V.1. INTRODUCTION

In earlier investigations the thermal behaviour of metallic lead and lead compounds have been studied in an air atmosphere. In these studies it has been shown that when metallic lead is heated in air lead monoxide is obtained as a yellow powder which on fusion turns red.(107) Lead monoxide has been found to be more thermally stable than the other lead oxides, as it was reported by Faivre and Weiss(108) that lead dioxide decomposed completely below 600°C in a nitrogen atmosphere to form lead monoxide. The thermal behaviour of lead dioxide has also been investigated by Perrault and Brenet.(109) These workers found that on the slow heating of lead dioxide to 510°C decomposition to Pb_3O_4 occurred, whereas between 540°C and 575°C the decomposition of lead dioxide yielded lead monoxide PbO.

In an investigation, which included both thermal analysis and thermogravimetric analysis, Spinedi and Gauzzi(110) heated PbO_2, Pb_2O_3 and Pb_3O_4 at 5°C per minute in a stream of oxygen and found the following reaction temperatures:

$PbO_2 \rightarrow Pb_2O_3$ between 375°C and 460°C

$Pb_2O_3 \rightarrow Pb_3O_4$ between 460°C and 495°C

$Pb_3O_4 \rightarrow PbO$ between 585°C and 675°C

In addition to the lead oxides, lead nitrate has been studied thermogravimetrically by Duval(111) who found the compound to be thermally stable up to 280°C whereupon decomposition proceeded slowly up to 500°C. The decomposition then accelerated with complete conversion to lead monoxide at 648°C.

Wendlandt(87) and Nicol(112) have also studied lead nitrate and the latter, through successive quenchings guided by the thermolysis curve, has isolated the following compounds.

(1) $Pb(NO_3)_2 . PbO$ up to 445°C

(2) $Pb(NO_3)_2 . 4PbO$ from 445°C to 455°C

(3) $Pb(NO_3)_2 . 5PbO$ from 455°C to 470°C

the latter compound then decomposed yielding lead monoxide which in turn was oxidized by the atmospheric oxygen to form Pb_3O_4.

Besides the thermally unstable lead compounds, lead chloride has been found to be stable since no weight loss is observed on the thermogram up to 500°C. Above 550°C the weight loss was attributed to the volatility of the salt, while at 946°C the residue consists of lead chloride contaminated with a trace of lead monoxide produced by incipient decomposition.(85)

In addition to the thermal properties of pure lead compounds, investigation of their behaviour in molten salts has been studied to a small extent. Reports indicate that lead carbonate decomposes to white lead in potassium nitrate at 350 - 415°C(113) according to the equation

$$2PbCO_3 \rightarrow PbCO_3 . PbO + CO_2 \qquad V.1$$

while in lithium nitrate-potassium nitrate the pure metal surface is oxidized at 143°C.(114)

The present work is the first extensive investigation of the behaviour of lead compounds in molten nitrite. The behaviour of the compounds PbO, PbO_2,Pb_3O_4 $Pb(NO_2)_2$, $Pb(NO_3)_2$ and $PbCl_2$ as well as metallic lead were studied in a sodium nitrite-potassium nitrite eutectic. The probable stoichiometries of these reactions were established from the weight losses obtained on the thermograms and analyses of the products.

V.2 EXPERIMENTAL

V.2.1 Materials

The sodium nitrite-potassium nitrite eutectic used in the present investigation (melting point 220°C) was prepared and dehydrated as previously described in chapter I. The temperatures at which the lead compounds were dried are listed in Table 1.

Table 1

Reagent	Grade	Purity (Bottles)	Drying Temp.*
Lead metal	AR	99.9%	100°C
PbO	AR	99%	120°C
PbO_2	AR	97%	120°C
Pb_3O_4	RG	85%	120°C
$PbCl_2$	RG	99%	120°C
$PbNO_3$	AR	99.5%	120°C

* The compounds were dried for one hour.

Lead nitrite was used without further treatment and the purity was found to be 86.1% from the gravimetric analysis of the lead content (found Pb = 59.6%. Calculated for $Pb(NO_2)_2$ Pb = 69.2%) which is in agreement with the purity found by thermogravimetric analysis (see result section). The analytical procedures are described in the analysis section below.

V.2.2 Analysis

The melts were quenched, dissolved in distilled water and filtered. The nitrate in the filtrate, after decomposition of the excess nitrite with sulphamic acid, was reduced by iron (II) and the excess titrated against dichromate. The nitrite was titrated against permanganate. (For details see chapter I.) The lead was estimated gravimetrically by precipitation as lead chromate as follows:

The lead compounds were dissolved in dilute nitric acid and then heated on a water bath to dryness. The residue was dissolved in distilled water to which equal volumes of 3% chromium nitrate and 2% potassium bromate were then added and the mixture was heated to boiling. After precipitation was complete, i.e. when the supernatant liquid was clear, the solution was cooled to room temperature, filtered through a No. 4 sinter, dried at 120°C, and weighed.(67)

V.2.3 Instrumentation

Thermal analyses were carried out on a Stanton TR.1 thermobalance as described in chapter III. The Philips X-ray diffractometer was used for the identification of the lead compounds produced in the reaction. The gases evolved from the reaction were identified using a

Unicam S.P.200 infrared spectrometer. The procedure for gas collection was described in chapter III.

V.3 RESULTS

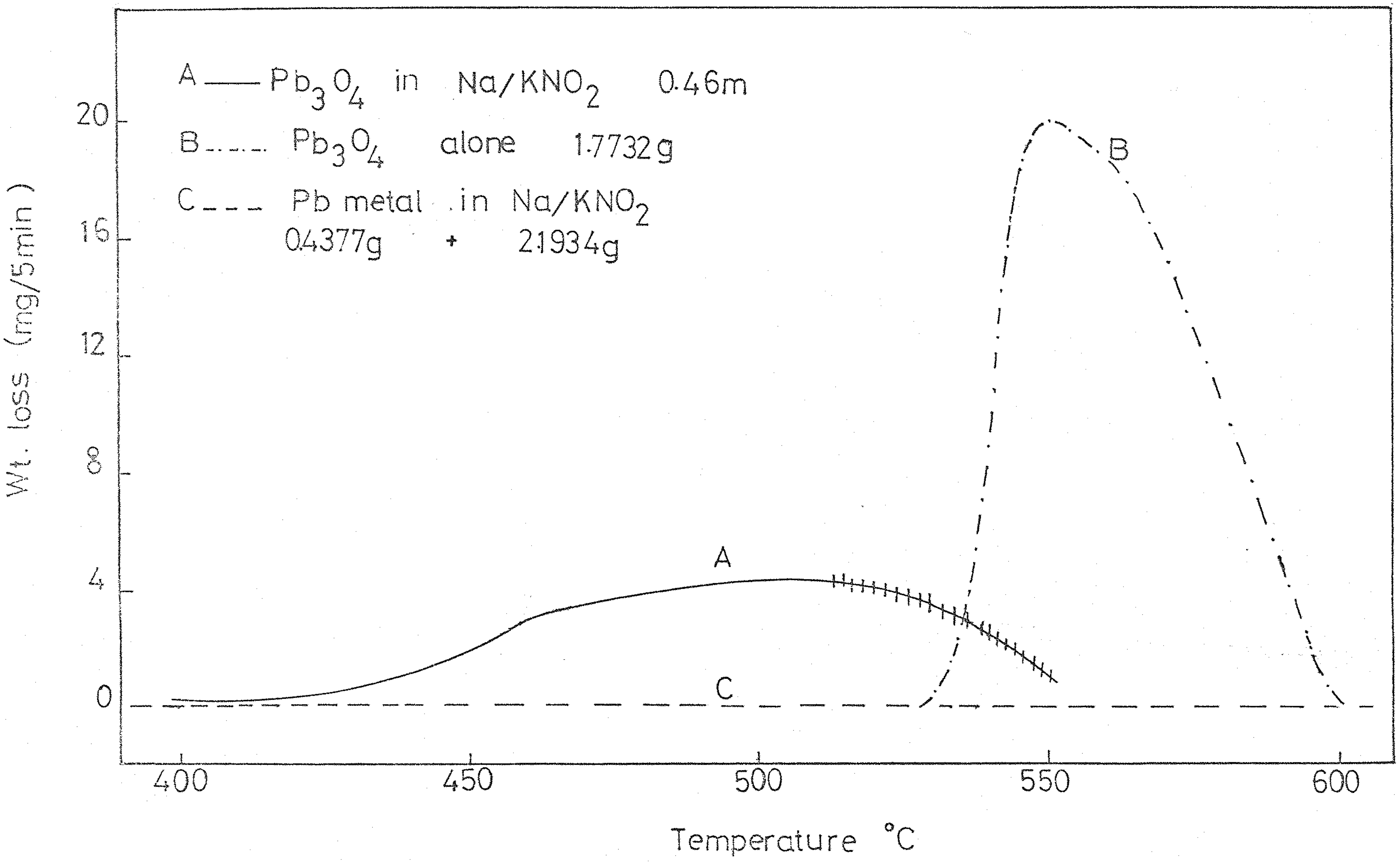
Neither lead metal nor the red coloured lead monoxide were found to react with the sodium nitrite-potassium nitrite eutectic at 230°C. Nor was any evolution of gases observed when the temperature of the melt was raised to 400°C. Similarly, thermogravimetric analyses of the metallic lead (Figure 1 curve C) and lead monoxide (Figure 3 curve C) in the nitrite melt showed no weight loss up to 400°C. However the metallic lead, after separation from the quenched melt by dissolving in water, was found to be covered with a greyish-black film of lead oxide.

When red lead, Pb_3O_4, was heated alone in a test tube from room temperature to 600°C the colour was observed to change to orange-red. This colour was similar to the colour of the red lead monoxide. On cooling to room temperature the colour changed once again to yellow. The lead content of the yellow particles, determined after dissolving in dilute nitric acid by precipitation as lead chromate, was found to be 92.11%. (Calculated for PbO, Pb = 92.8%; Pb_3O_4, Pb = 90.3% and PbO_2, Pb = 86.6%.)

Thermogravimetric analysis of pure Pb_3O_4 (Figure 1 curve B) showed that the decomposition started at 530°C with a total weight loss of 2.1%. (Calculated for loss of 1 O per Pb_3O_4 2.3%.) In sodium nitrite-potassium nitrite eutectic the weight loss commenced at a lower temperature (400°C) a typical thermogram being illustrated (Figure 1 curve A). The total weight loss varied between 14.4 and

Fig. 1

T.G.A. of Pb_3O_4 in nitrite eutectic



17.4% but after correction for the formation of nitrate due to the reaction of nitrogen dioxide with nitrite melt according to equation II.4 the average loss was 19.2%. (Calculated for loss of 3N + 5½O per Pb_3O_4 18.9%.) After dissolving the quenched melt in water, filtering and drying, the red precipitate was examined by the X-ray diffratometer and gave a d-spacing and intensities as shown in Table 2.

Table 2

X-ray diffraction lines of PbO (A.S.T.M.) and the unknown red precipitate

Red product of the reaction of Pb_3O_4 in nitrite melt		PbO (red) A.S.T.M. index	
Intensity	d-spacing	Intensity	d-spacing
100	3.11	100	3.115
50	2.80	62	2.809
28	2.49	18	2.51
10	1.97	8	1.988
35	1.86	37	1.872
18	1.66	24	1.675
14	1.54	11	1.542

The black lead dioxide was found to be stable in sodium nitrite-potassium nitrite eutectic at 230°C since no change in the colour of the particles was observed and no evolved gases were detected. However the colour of the particles did change to red on raising the temperature to 400°C.

Thermogravimetric analysis (Figure 2 curve A) showed that pure lead dioxide commenced decomposition at 340 ± 5°C with a total weight loss of 6.5%. (Calculated for loss of1 O per PbO_2 6.6%.) On the other hand, in the nitrite melt thermogravimetric analysis of a mixture of lead dioxide and sodium nitrite-potassium nitrite eutectic (Figure 2 Curve B) showed no weight losses up to 400°C, but reaction did occur to form an orange-red coloured precipitate. This precipitate, after dissolving the nitrite melt in water, filtering and drying, was examined by X-ray diffraction and found to have the following d-spacings 3.11 (100), 2.80 (50), 2.49 (15), 1.979 (10), 1.868 (32), 1.67 (24), 1.541 (20), which on comparison with the A.S.T.M. index (Table 2) corresponded to PbO.

Nitrate ions were also found to be produced in the nitrite melt and analysis showed the molar ratio of nitrate ions: lead dioxide was 0.98 ± 0.02 : 1.

Lead nitrite decomposed on heating evolving brown fumes and forming orange-red particles. Thermogravimetric analysis of the pure compound (Figure 3 Curve A) showed three stages of decomposition. The first stage commenced at 100 ± 10°C with a maximum rate of weight loss at 130°C; the second stage began at 310 ± 10°C with a maximum rate in weight loss of 490°C; and the third stage started around 410°C with a maximum rate at 460°C. Decomposition was completed at 480°C. The total weight loss was found to be 21.8%. (Calculated for loss of 2N + 3O per $Pb(NO_2)_2$ 25.4%). The final product was shown by gravimetric analysis to contain 92.2% lead. (For PbO, Pb = 92.8%.)

Fig. 2

T.G.A. of PbO_2 in nitrite eutectic

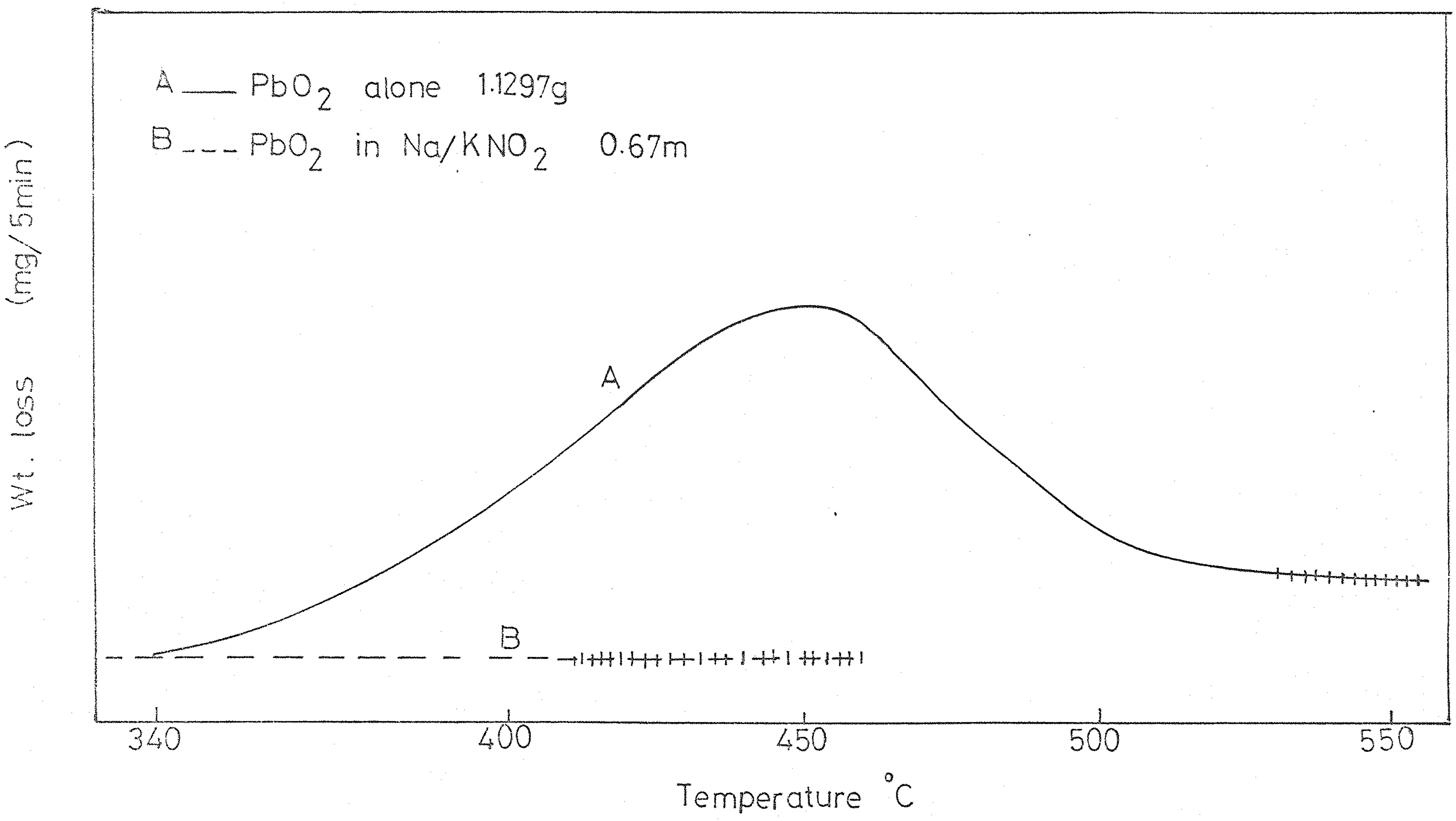
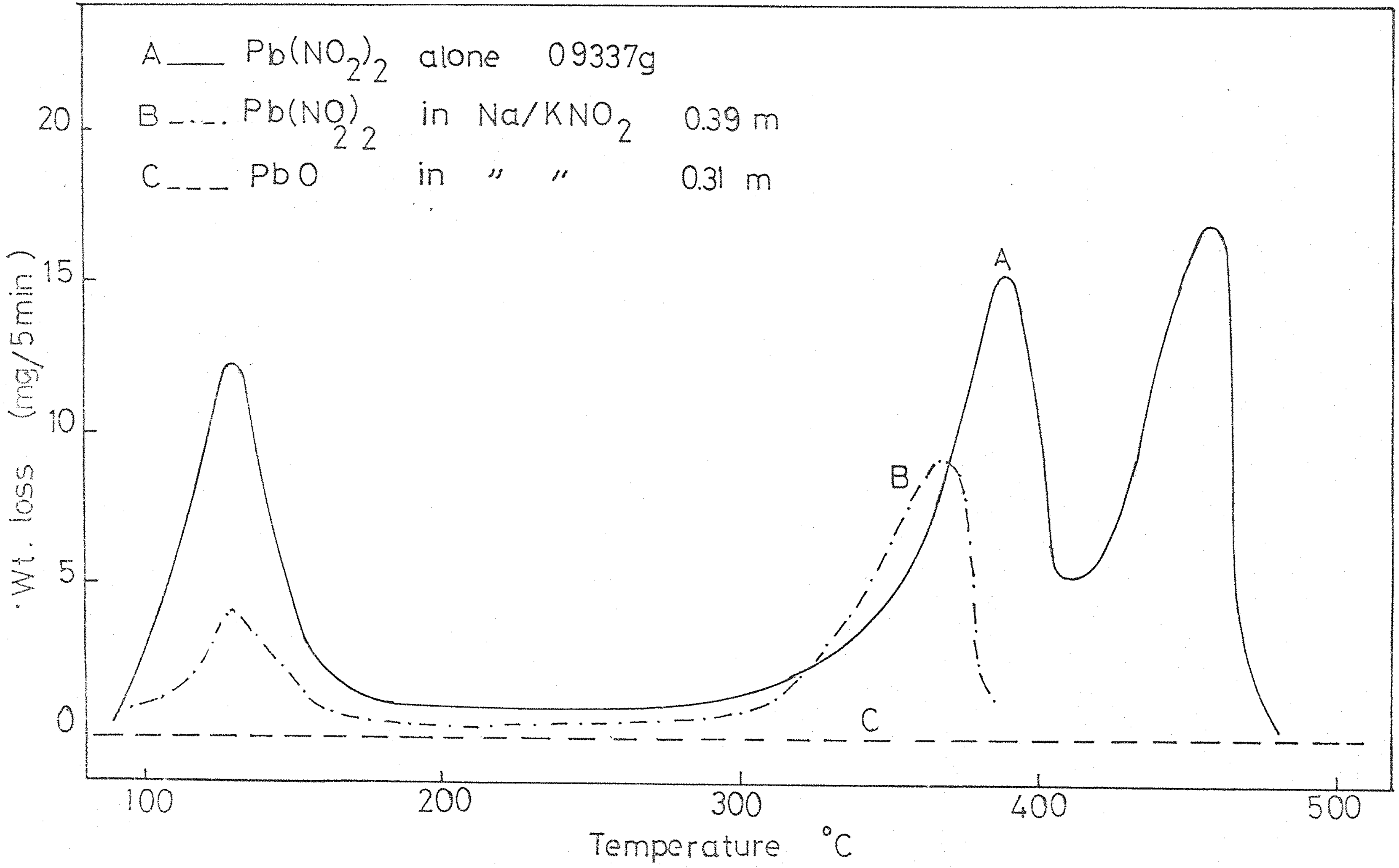


Fig . 3

T.G.A. of $Pb(NO_2)_2$ in nitrite eutectic



A yellow product was isolated from the isothermal thermogravimetric analysis at 130°C and it was analysed gravimetrically. It was found to have a lead content of 78.5%. (Calculated for $2Pb(NO_2)_2 \cdot PbO$, Pb = 75.6%.)

In the nitrite eutectic, lead nitrite decomposed when added to the melt at 230°C with the evolution of brown fumes of a mixture of nitrogen dioxide and nitric oxide forming a yellow precipitate.

Thermogravimetric analysis of lead nitrite in sodium nitrite-potassium nitrite eutectic showed two stages of weight loss. (Figure 3 curve B). The first stage of decomposition commenced at 110 ± 10°C with a maximum rate of weight loss at 130°C. A yellow precipitate with a lead content of 78.1% was formed together with the nitrate ion. The second reaction commenced at 310° ± 10°C with a total weight loss of 11.5% which, when corrected for the formation of nitrate ions due to reaction II.4, became 21.4%. (Calculated for loss of $2N + 3O$ per $Pb(NO_2)_2$ 25.4%.) The final solid orange-red particles were analysed and found to contain 92.3% lead. (PbO, Pb = 92.8%.)

Lead nitrate, dissolved in a sodium nitrite-potassium nitrite melt at 230°C, formed a clear orange solution which started forming a yellow precipitate and evolving brown fumes of a mixture of nitrogen dioxide and nitric oxide within five minutes. On heating the mixture of lead nitrate and nitrite eutectic from room temperature to its melting point, an orange liquid layer was formed on the nitrite eutectic particles at 120°C. Around the melting point, brown gases were evolved and a yellow precipitate was formed. On raising the temperature to 400°C another reaction occurred with the formation of an orange-red precipitate. The orange-red particles were examined using an X-ray diffractometer and showed the diffraction lines: 3.10 (100), 2.79 (55), 2.49 (40), 1.98 (12), 1.89 (50) and 1.67 (30) which correspond to PbO (see Table 2).

Thermogravimetric analyses were carried out both on pure lead nitrate and a mixture of lead nitrate and nitrite eutectic. Pure lead nitrate commenced decomposition at 380 ± 5°C with a maximum weight loss around 470°C (Figure 4 Curve A) which was followed by two additional small weight losses with maximum rates of weight loss at 490°C and 530°C respectively. The total weight loss was found to be 32.9%. (Calculated for loss of 2N + 5O per $Pb(NO_3)_2$ 33.6%.)

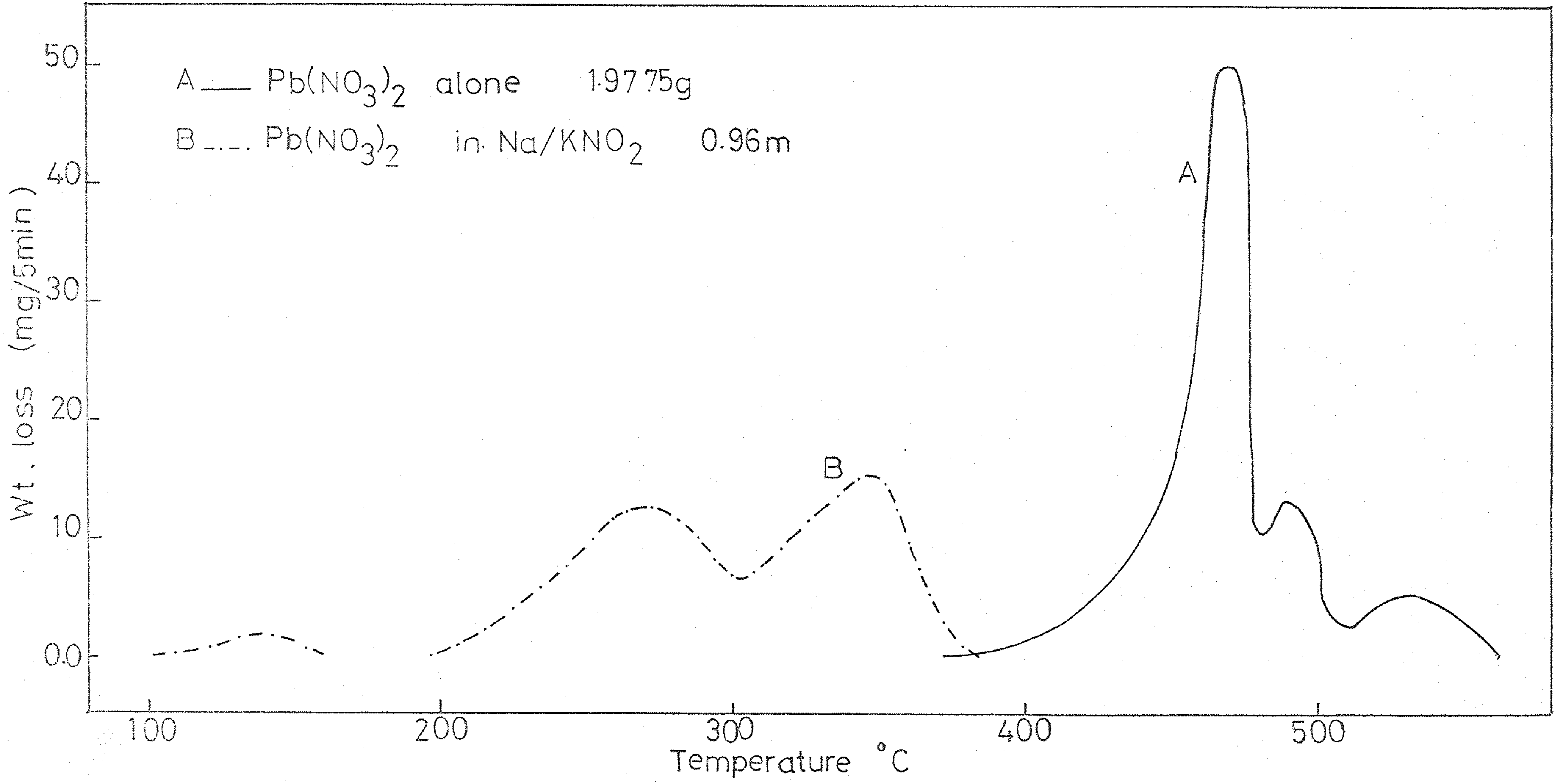
Thermogravimetric analysis of lead nitrate in a nitrite eutectic showed the weight losses to occur in three stages (Figure 4 Curve B). The first stage, which exhibited a small loss in weight, in comparison with the others, commenced at 110 ± 5°C and ceased at 160°C. The second stage started at 200 ± 5°C with a maximum rate of weight loss at 270°C. While the third stage started around 300 ± 5°C with a maximum rate of weight loss at 350°C and was complete at 380°C. The total weight loss varied from 18.5 to 19.6%. The high nitrate concentration found in the product was due to nitrate ion added as lead nitrate as well as reaction II.4.

The final orange red precipitate, after dissolving the melt in water filtering, washing and drying gave an X-ray diffration pattern similar to that of lead monoxide PbO. 3.11 (100), 2.79 (55), 2.50 (35), 1.89 (50), 1.67 (30). (See table 2.)

Isothermal thermogravimetric analysis of lead nitrate in nitrite eutectic was carried out at 250°C. The water insoluble yellow

Fig. 4

T.G.A. of $Pb(NO_3)_2$ in nitrite eutectic



product was analysed and the lead content was found to be 78.7%. (Calculated for $2Pb(NO_2)_2 \cdot PbO$, Pb = 75.6%.) The X-ray diffraction powder pattern of the yellow precipitate gave the d-spacings and intensities shown in Table 3.

Table 3

d-spacing	intensities
4.036	49
3.127	45
3.088	46
3.082	47
2.884	100
2.712	30.5
2.488	43
2.259	20
2.135	20.5
2.024	19.5
1.843	26
1.815	38
1.581	24.5
1.547	18.5

Lead (II) chloride reacted immediately with sodium nitrite-potassium nitrite eutectic at 230°C with the formation of a yellow precipitate and the evolution of brown fumes of a mixture of nitrogen dioxide and nitric oxide. On raising the temperature to 400°C brown fumes of a mixture of nitrogen dioxide and nitric oxide were evolved and an orange red precipitate was formed. The orange red precipitate, after separation from the quenched melt by dissolving in water, filtering, washing and drying gave the diffraction lines 3.109 (100), 2.804 (50), 2.506 (30), 1.985 (10), 1.871 (30) and 1.67 (20) which correspond to those of PbO (Table 2).

Thermogravimetric analysis showed the reaction to take place in two stages. The first stage reaction commenced at 190°C with a rapid loss in weight reaching the maximum rate at 200°C. The second stage weight loss started at 310 ± 5°C with a maximum rate of weight loss around 360°C. The total weight loss was found to be 20.3% which after correction for the formation of the nitrate ions due to reaction II.4 became 26.1%. (Calculated for loss of 2N + 3O per $PbCl_2$ 27.3%.)

All the above thermograms of the lead compounds were done under a flow of nitrogen. In addition, other thermograms were obtained for the same compounds with nitrite eutectic under atmospheric conditions and these showed a behaviour similar to the thermograms under nitrogen up to 400°C. Above this temperature a gain in weight was observed, e.g., with lead nitrate in nitrite eutectic (Figure 6). The total gain in weight, which started around 410°C, occurred in three stages. The steady gain in weight of the first stage finished at 500°C whereupon the second stage started. The third stage commenced at 525°C and completed at 625°C when a loss in weight recommenced.

Fig. 5

T.G.A. of $PbCl_2$ in nitrite eutectic

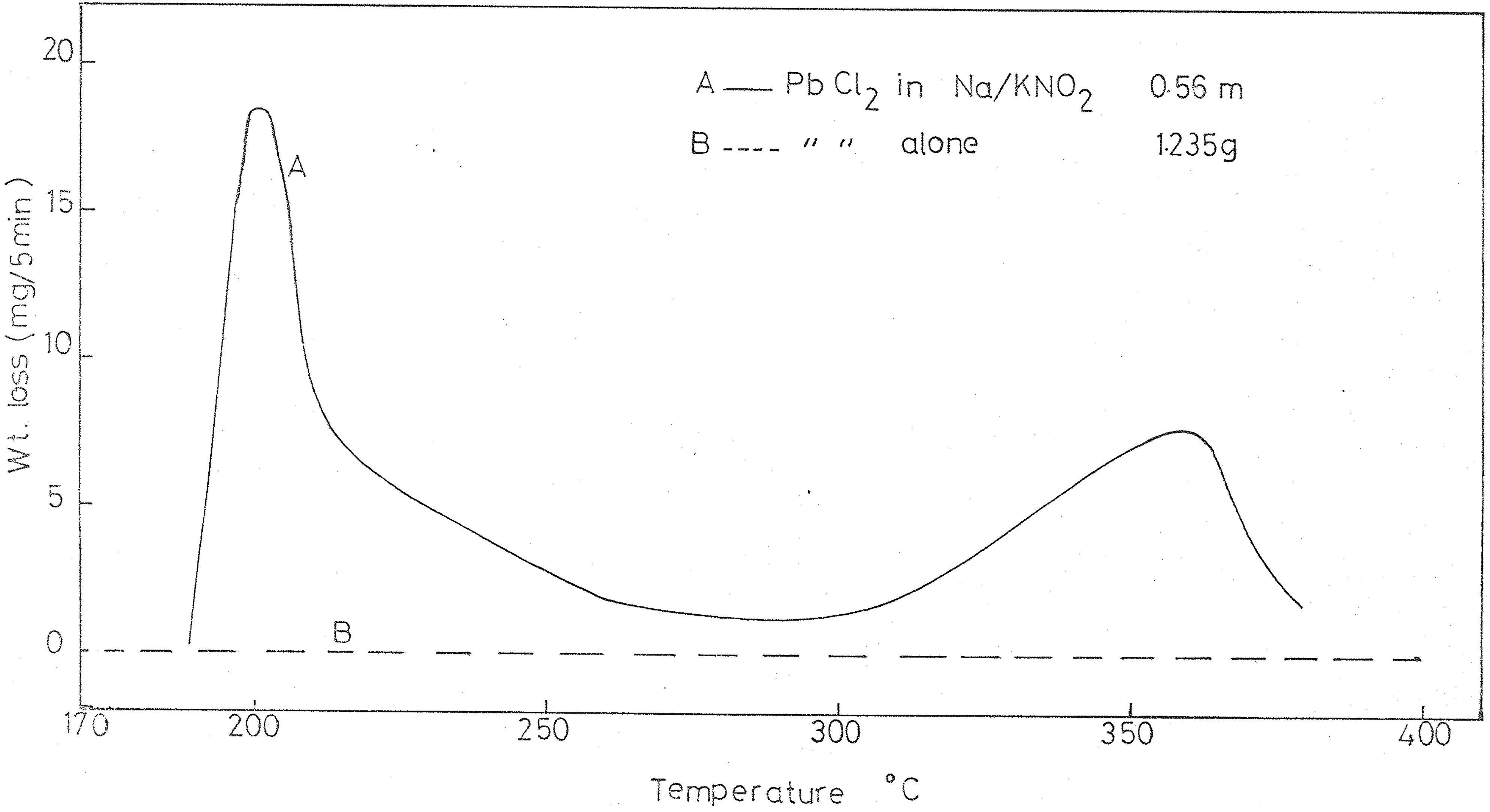
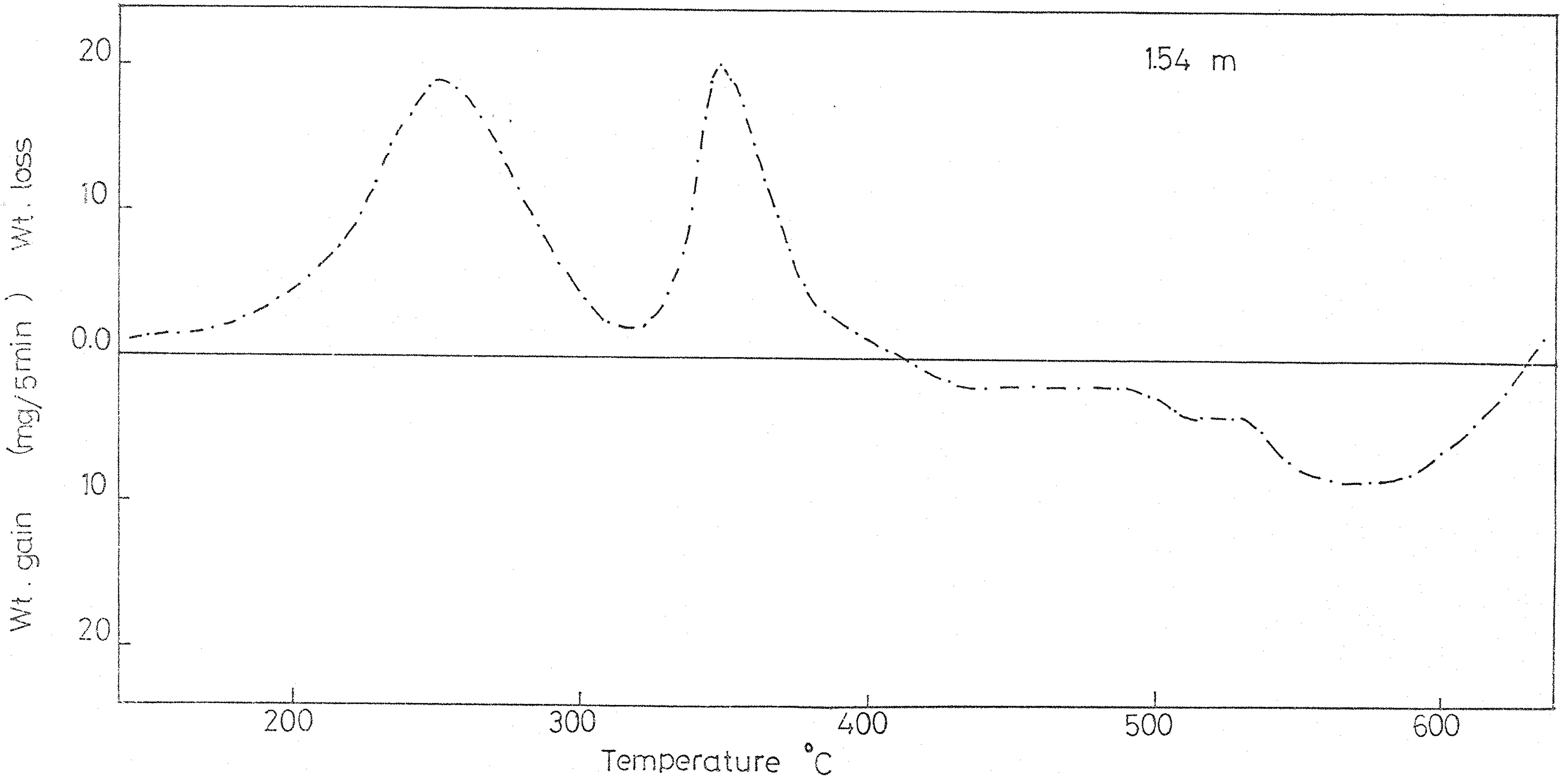


Fig. 6

T.G.A. of $Pb(NO_3)_2$ in Na/KNO_2 eutectic



V.4 DISCUSSION

Metallic lead and lead monoxide were stable in the sodium nitrite-potassium nitrite eutectic up to 400°C since neither oxidation-reduction reaction nor a Lux-Flood acid-base reaction were observed either from the analysis of the reaction products or from the weight loss on the thermobalance. The stability of metallic lead in the nitrite eutectic was possibly due to the formation of a protective covering of lead oxide which prevented further reaction between the metal and the melt. A similar phenomena has also been observed in lithium nitrate-potassium nitrate eutectic at 143°C where the surface of the metal was oxidized to lead oxide.(114) The formation of the lead oxide surface film probably took place according to the following equation

$$Pb + 2NO_2^- \rightarrow PbO + 2NO + O^{2-} \qquad \ldots\ V.2$$

but the weight loss was too small to be detected by the thermobalance.

Red lead Pb_3O_4 was thermally stable up to 530°C. The loss of oxygen started above this temperature forming lead monoxide

$$Pb_3O_4 \rightarrow 3PbO + \frac{1}{2}O_2 \qquad \ldots\ V.3$$

with the experimental weight losses agreeing very well with this stoichiometry.

The stoichiometry of the reaction of Pb_3O_4 in the nitrite eutectic was deduced to be close to

$$2Pb_3O_4 + 6NO_2^- \rightarrow 6PbO + 5NO_2 + NO + 3O^{2-} \qquad \ldots\ V.4$$

agreeing with the weight loss after correction for the nitrate formation according to equation II.4.

The possibility of the above reaction taking place through the thermal decomposition of Pb_3O_4 according to equation (V.3) followed by oxidation of the nitrite ion by the liberated oxygen according to the equation

$$Pb_3O_4 + NO_2^- \rightarrow 3PbO + NO_3^- \qquad \ldots \text{V.5}$$

is unlikely because this reaction implies that no nitrogen oxides are evolved whereas the thermogram showed a weight loss of 17.3% before correction for the nitrate found in the products.

Another alternative reaction mechanism is via the formation of lead nitrite in accordance with the equation

$$Pb_3O_4 + 6NO_2^- \rightarrow 3Pb(NO_2)_2 + \tfrac{1}{2}O_2 + 3O^{2-} \qquad \ldots \text{V.6}$$

followed by the decomposition of the lead nitrite

$$Pb(NO_2)_2 \rightarrow PbO + NO + NO_2 \qquad \ldots \text{V.7}$$

However, this is also unlikely since the total weight loss of equation V.6 and V.7 is 34.7% while the experimental weight loss after correction for the nitrate formation is 19.2%.

Therefore the reaction was suggested to take place via the formation of both $Pb(NO_2)_4$ and $Pb(NO_2)_2$ followed by thermal decomposition according to the following equations

$$Pb_3O_4 + 4NO_2^- \rightarrow Pb(NO_2)_4 + 2PbO + 2O^{2-} \qquad \ldots \text{V.8}$$

followed by

$$Pb(NO_2)_4 \rightarrow PbO + 3NO_2 + NO \qquad \ldots \text{V.9}$$

alternatively by

$$Pb_3O_4 + 2NO_2^- \rightarrow Pb(NO_2)_2 + 2PbO + \frac{1}{2}O_2 + O^{2-} \qquad \ldots \text{V.10}$$

followed by the thermal decomposition of $Pb(NO_2)_2$ according to V.7. These equations (V.8), (V.9), (V.10) and (V.7) do sum to equation V.4.

Lead dioxide was thermally unstable at high temperature and decomposed according to the equation

$$PbO_2 \rightarrow PbO + \frac{1}{2}O_2 \qquad \ldots \text{V.11}$$

the above stoichiometry is in agreement with the weight loss obtained from the thermogram. In a nitrite melt the reaction of lead dioxide follows the equation

$$PbO_2 + NO_2^- \rightarrow PbO + NO_3^- \qquad \ldots \text{V.12}$$

The nitrate and lead analyses with the thermogram agreed well with the above stoichiometry. The nitrite ions acted as reducing agents at all temperatures above the melting point of the eutectic.

Lead nitrite decomposed in three stages forming lead monoxide as a final solid product. The total weight loss obtained is in agreement with the overall stoichiometry (equation V.7)

$$Pb(NO_2)_2 \rightarrow PbO + NO + NO_2$$

Since the weight losses in the three stages are almost identical, and as the first intermediate product was identified as a basic lead nitrite $2Pb(NO_2)_2 \cdot PbO$, the mechanism of the decomposition suggested here, would occur in accordance with the following equations

$$3Pb(NO_2)_2 \rightarrow 2Pb(NO_2)_2 . PbO + NO + NO_2 \qquad \ldots \text{V.13}$$

followed by the decomposition of $2Pb(NO_2)_2 . PbO$

$$2Pb(NO_2)_2 . PbO \rightarrow Pb(NO_2) . 2PbO + NO + NO_2 \qquad \ldots \text{V.14}$$

and finally by the decomposition of $Pb(NO_2)$, 2PbO

$$Pb(NO_2)_2 . 2PbO \rightarrow 3PbO + NO + NO_2 \qquad \ldots \text{V.15}$$

in which the three equations V.13, V.14 and V.15 sum to equation V.7. It appears that the product of the first stage decomposition represents a new mixed lead oxide and lead nitrite which was confirmed by chemical analysis. The X-ray pattern of the lead intermediate $2Pb(NO)_2 . PbO$ (Table 3) does not correspond to any lead oxide or another lead compound listed in the A.S.T.M. powder index.

The second stage intermediate product could not be identified simply because of the difficulties in separating the second stage reaction from the third one on the thermogram even when the reaction was held on a constant temperature, i.e., that at which the second stage reaction commenced.

In sodium nitrite-potassium nitrite eutectic, the lead nitrite underwent thermal decomposition in two stages; the first stage occurred at a temperature similar to that of the first decomposition of the pure compound (Figure 3 Curve B). The intermediate product of the first stage decomposition was considered to be the basic lead nitrite $2Pb(NO_2)_2 . PbO$ since the chemical analysis and the X-ray diffraction pattern is similar to the first stage decomposition product of the pure lead nitrite. The absence of a distinct third reaction in the presence of a nitrite melt as shown by Figure 3 Curve B, might possibly be due to the availability of the oxide ion which attacks the lead compound more readily forming lead monoxide.

The reaction of lead nitrate in the nitrite melt occurred at a temperature considerably lower than that of the thermal decomposition of the pure salt (Figure 4 Curve B) and can be considered to be due to anion exchange forming lead nitrite. This anion exchange process between the nitrite ions in the melt and the nitrate ions in the lead nitrate probably takes place in the liquid phase since the weight loss on the thermogram appeared after the formation of an orange liquid layer on the eutectic particles. The small amount of weight loss around 130°C is therefore considered to be due to the decomposition of a small amount of lead nitrite formed in the thin orange liquid layer between the lead nitrate particles and the nitrite eutectic particles. The cessation in weight loss between 160 - 200°C was probably due to the formation of an insoluble lead compound which covered the lead nitrate particles and thereby prevented further contact between the solid lead nitrate and the solid nitrite eutectic.

The first main weight loss started near the melting point of the nitrite eutectic, when anion exchange in the molten state can take place rapidly to form lead nitrite which immediately decomposes. Analysis showed that the intermediate insoluble product was similar to that produced from the first stage decomposition of lead nitrite. Decomposition started once again at a temperature similar to the second stage decomposition of lead nitrite. The lead nitrate reaction then may be represented by the following stoichiometry

$$Pb(NO_3)_2 + 2NO_2^- \rightarrow Pb(NO_2)_2 + 2NO_3^- \qquad \text{... V.16}$$

followed by the decomposition of lead nitrite according to the equations V.13, V.14 and V.15.

The reaction of lead chloride in the nitrite eutectic presumably occurred via the formation of lead nitrite according to equation

$$PbCl_2 + 2NO_2^- \rightarrow Pb(NO_2)_2 + 2cl^- \qquad \ldots \text{ V.17}$$

which was followed by thermal decomposition of the lead nitrite. The low temperature at which the decomposition took place in comparison to lead nitrate and the rapid loss in weight was possibly due to the formation of a new eutectic system composed of both the nitrite eutectic and the lead chloride, in which the anion exchange led to the formation of lead nitrite which decomposed immediately.

The second stage weight loss commenced at a temperature similar to the second stage of lead nitrite in nitrite eutectic and is considered to be due to the formation of the basic lead nitrite intermediates.

The thermal reaction of lead compounds under atmospheric conditions, i.e., lead nitrate in nitrite eutectic as shown in Figure 6, was initially similar to its reaction under a flow of nitrogen. But above 400°C there was a gain in weight, probably due to reaction of lead monoxide with atmospheric oxygen, which may be represented by the equation

$$PbO + \frac{y}{2}O_2 \rightarrow PbO_{y+1} \qquad \ldots \text{ V.18}$$

At more elevated temperature PbO_{y+1} decomposed yielding lead monoxide once again.

The exchange of anions via nitrite eutectic has been observed in an earlier investigation in which both silver nitrate and silver chloride were found to undergo exchange when added to a molten nitrite to form silver nitrite. The rate of exchange of ions was suggested to be dependent on the solubility of the original compound in the melt. For example, silver chloride was found to be less soluble than silver nitrate in molten sodium nitrite-potassium nitrite eutectic and also to have a higher decomposition temperature in the same melt, in comparison with the lower reaction temperature and higher solubility of silver nitrate.(34)

In general metallic lead and the lead oxides are stable in the nitrite melt at its melting point. The reaction of PbO_2 was suggested to be an oxidation-reduction reaction, whereas the reaction of Pb_3O_4 was attributed to the formation of two lead nitrite compounds, $Pb(NO_2)_4$ and $Pb(NO_2)_2$, which then decomposed yielding lead monoxide. The reactions of the other lead compounds were attributed to the decomposition of the lead nitrite formed by exchange of anions.

CHAPTER VI

REACTIONS OF
TUNGSTEN COMPOUNDS, POTASSIUM PERMANGANATE AND METALLIC ZIRCONIUM

VI.1 INTRODUCTION

The reactions of tungsten compounds are one of the least studied elements in molten salts. In early work it had been found that the fusion of tungsten trioxide with sodium carbonate in the molar ratio 2:1 produced the ditungstate $Na_2O.2WO_3$, while fusion in the ratio 1:1 with sodium carbonate or sodium hydroxide yielded the orthotungstate $Na_2O.WO_3$.(115,116)

However, the phase diagram of potassium orthotungstate and tungsten trioxide system does not show the existence of a compound corresponding to potassium ditungstate,(117) though the phase diagram of the sodium orthotungstate and tungsten trioxide system does reveal the formation of sodium ditungstate.(118)

In recent years the acidic character of tungsten trioxide has also been studied, for example, in nitrate melts. In pure potassium nitrate at 350°C it has been shown that tungsten trioxide is quite stable, but, on the addition of sodium peroxide, neutralization occurred in a single step forming the orthotungstate WO_4^{2-}. The probable intermediate compounds to be expected, such as ditungstate were possibly overstepped.(119) But it was suggested that the above neutralization of tungsten trioxide probably takes place through the formation of several intermediate species according to the equation(119)

$$WO_3 \rightarrow M_2O.3WO_3 \rightarrow M_2O.2WO_3 \rightarrow M_2OWO_3 \qquad VI.1$$

where M represent the alkali metal.

Similarly, thermogravimetric studies of tungsten trioxide in lithium nitrate-potassium nitrate eutectic have also shown that reaction takes place stepwise according to the following scheme with the temperatures of the reactions found as follows

$$WO_3 \xrightarrow{370^oC} W_3O_{10}^{2-} \xrightarrow{495^o} W_2O_7^{2-} \xrightarrow{520^o} WO_4^{2-} \qquad VI.2$$

In sodium nitrate-potassium nitrate eutectic the reaction has been found to proceed similarly but with higher reaction temperature as shown below(60)

$$WO_3 \xrightarrow{410^oC} W_3O_{10}^{2-} \xrightarrow{535^oC} W_2O_7^{2-} \xrightarrow{550^oC} WO_4^{2-} \qquad VI.3$$

In addition to the above reactions with added base, orthotungstate has been found to undergo a condensation reaction on addition to equimolar sodium nitrate-potassium nitrate eutectic forming ditungstate between 315°C to 370°C. Since no condensed species other than ditungstate were indicated, the equilibrium was suggested to be in accordance to the equation(120)

$$2WO_4^{2-} = W_2O_7^{2-} + O^{2-}$$

Although the investigation of tungsten compounds in nitrate melt described above are not numerous, no previous study in molten nitrite has hitherto been reported. The present studies shed light on the behaviour of tungsten metal, tungsten hexacarbonyl, tungsten trioxide and sodium orthotungstate in molten nitrites. The stoichiometries of these reactions were established using thermogravimetric analysis and analyses of the products.

Beside tungsten metal and compounds, zirconium metal was also studied in this investigation. Again no previous investigation had been carried out in nitrite melt though a brief study in nitrate melts had involved the ion exchange properties of zirconium compounds. Cation exchange had been found to take place between the alkali metal ion (Na^+, K^+) in the nitrate melt and the hydrogen in zirconium hydrogen phosphate $Zr(HPO_4)_2$ thus forming zirconium sodium phosphate.(121)

A small part of the present studies had been devoted to the reaction of permanganate in sodium nitrite-potassium nitrite eutectic. Once again more studies had previously taken place of manganese compounds in nitrate melts. An example is that permangante had been found to be both soluble and stable in lithium nitrate-potassium nitrate eutectic at 160°C forming a purple coloured solution which decomposed slowly to black particles of manganese (IV) oxide.(122) Permanganate had however been stabilized with halate oxidizing agents and manganate (VI) and manganate (V) with hydroxide and peroxide.(123) In the course of the present investigation of the chemistry of permanganate in molten nitrite a paper appeared on the stabilization of manganate (V) and manganate (VI) with sodium peroxide and sodium hydroxide respectively.(40) In view of this publication the present studies were not pursued further.

In the present investigation visual observation as well as thermogravimetric analysis were employed and the stoichiometries were established by the identification of the evolved gases using mass spectral analysis and analysis of the solid products.

VI.2 EXPERIMENTAL

The materials used as reactants are listed in Table 1 together with details of grades, purities, and drying times and temperatures. The order of listing is that of appearance in the results section.

Table 1

Reagent	Grade	Purity	Drying time hrs.	Temperature
Na_2WO_4	RG*	99%	2	150°C
WO_3	RG	99%	1	120°C
W metal	RG	98%	½	120°C
$W(CO)_6$	RG	99%	-	-
$KMnO_4$	AR!	99.5%	2	120°C
Zr metal	RG	99.5%	½	120°C

* RG - Reagent grade

! AR - Analar

The sodium nitrite-potassium nitrite eutectic used in the present investigations was prepared and dehydrated according to the procedure described in Chapter I. Qualitative analysis for orthotungstate were carried out by the acidification of the aqueous solution of orthotungstate with dilute hydrochloric acid which on the addition of zinc metal formed a blue colouration which is "probably due to W_2O_5 or WCl_5".(124) Nitrate content was estimated by the method described in Chapter I.

Thermogravimetric analysis was carried out as previously described in Chapter (III) and the weight loss reported as a percentage by weight of the starting material. Identification of the gases evolved from the reactions was performed on AEI-MS12 mass spectrometer after traping the gases at liquid nitrogen temperature using a vacuum system. The details of using the vacuum line were described in Chapter I.

VI.3 RESULTS

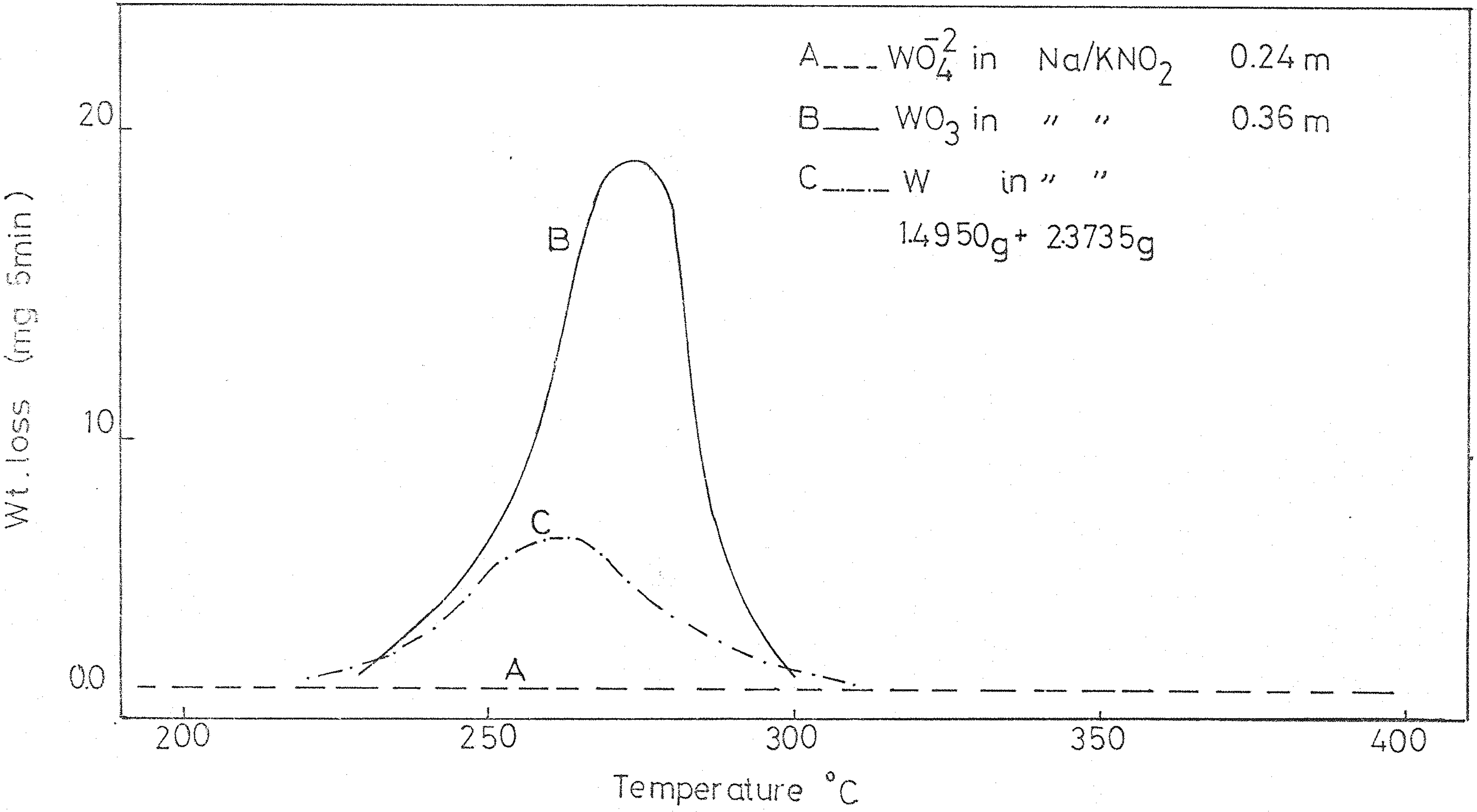
Sodium orthotungstate was found to be stable in molten sodium nitrite-potassium nitrite eutectic at 250°C, since no reaction was observed when this compound was added to the melt. Thermogravimetric analysis showed no weight loss up to the maximum temperature studied 400°C. (See Figure 1 Curve A).

Tungsten trioxide reacted immediately and violently when added to the melt at 230°C with the evolution of brown fumes of a mixture of nitrogen dioxide and nitric oxide and the formation of a white precipitate. The white precipitate remaining, after dissolving the products in distilled water, was analysed and found to contain orthotungstate.

Thermogravimetric analysis of the reaction of tungsten trioxide and nitrite eutectic showed a weight loss to begin at 230°C with a maximum rate around 270°C and to be completed at 300°C (Figure 1 Curve B). Because of the violence of the reaction, splashing of the reactants

Fig. I

T G A of Tungsten compounds in nitrite eutectic



resulted in considerable loss of solid reactants and products. In order to avoid a loss of solid materials, an inverted funnel was used to cover the reaction crucible. A weight loss was then found between 23.5% and 29.3% which, when corrected for the formation of nitrate due to the reaction of nitrogen dioxide with nitrite (equation II.4), gave an average loss of 31.2%. (Calculated for loss of 2N + 3O per WO_3 32.7%.)

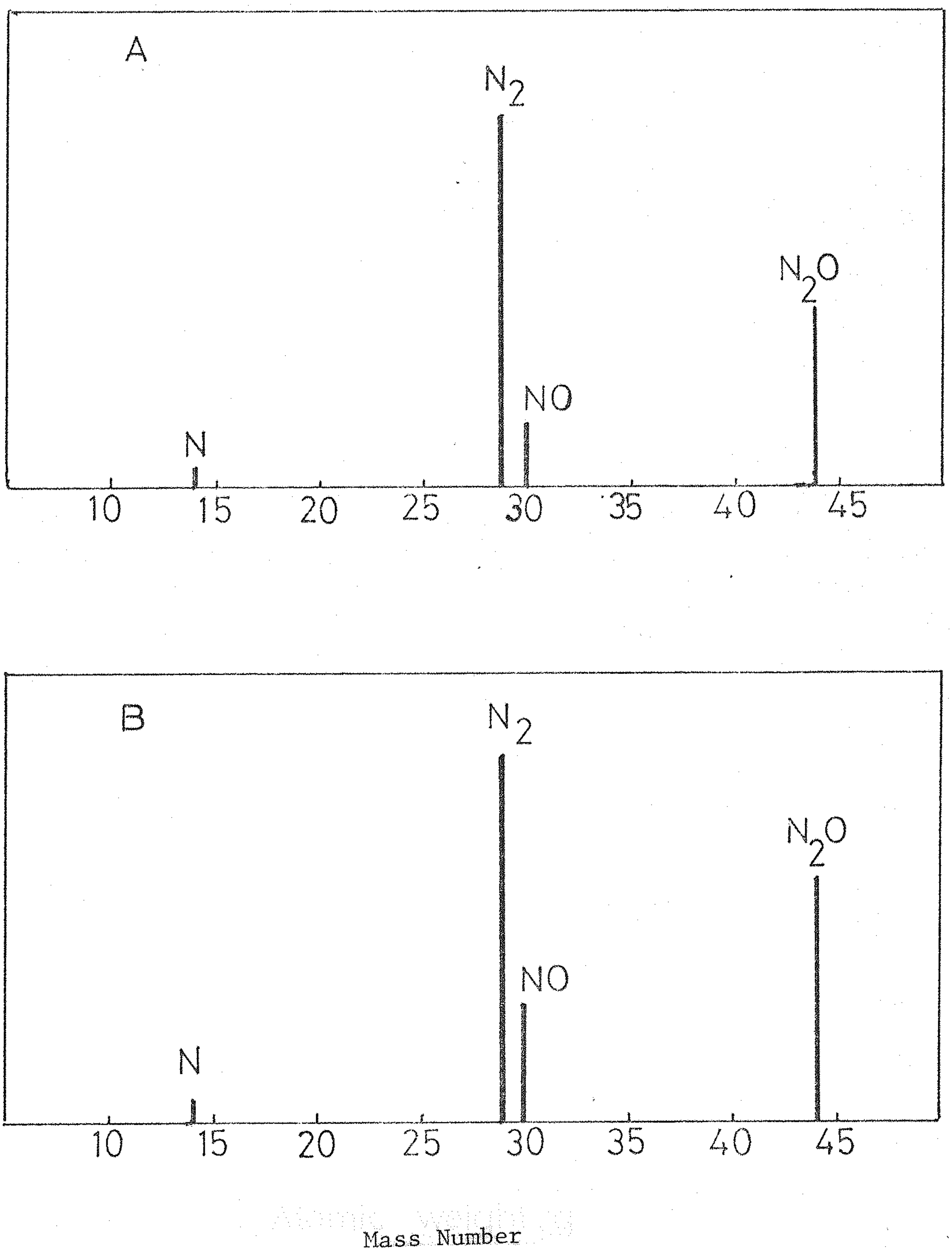
Powdered tungsten metal also reacted violently when added to the melt at 230°C with the evolution of colourless gas and the formation of a white precipitate. The quenched melt, after dissolving in water was analysed and found to contain orthotungstate. As with tungsten trioxide, an inverted funnel was used to cover the reaction crucible to avoid a loss of reactants on the thermobalance. Thermogravimetric analysis (Figure 1 Curve C) showed the reaction to be commenced at 220°C with a maximum rate of weight loss at 260°C and to be completed at 310°C. The total weight loss varied from 15.5% to 16.3%. (Calculated for loss of 2N per W 15.2%).

The mixture of gases evolved from the reaction of tungsten metal and nitrite eutectic apparently depends on the heating rate and the environment above the reactants. Under a vacuum of 10^{-2} torr and at 230°C, the addition of the powdered metal to molten nitrite caused a violent reaction associated with the evolution of gases which were found from their mass spectra to consist of nitrogen, nitrous oxide and nitric oxide (see Figure 2A). Whereas on heating a mixture of both sodium nitrite-potassium nitrite eutectic and tungsten metal powder slowly from room temperature to the melting point of the eutectic, the mass spectra revealed the production of the mixture of

Fig . 2

M.S.A. of Tungsten metal in Na/KNO_2

(Gaseous products)



nitrogen, nitrous oxide and nitric oxide but in different concentrations as shown in Figure 2.B.

Tungsten hexacarbonyl, when added to the melt at 230°C, did not show any observable reaction but just the sublimation of the compound which was then recrystallized on the upper cold surface of the tube. The analysis of the quenced melt did not indicate the presence of orthotungstate.

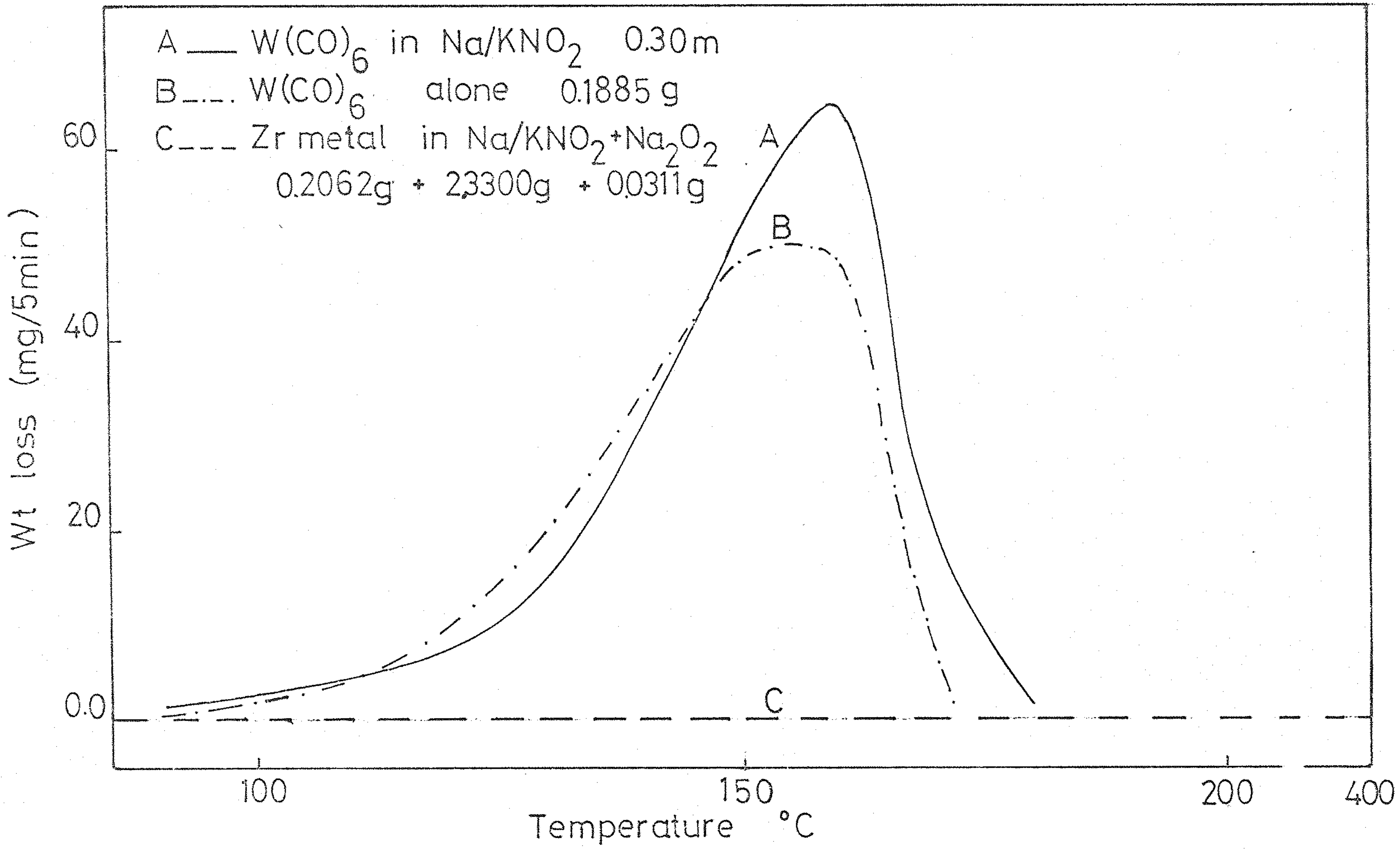
Thermogravimetric analysis of tungsten hexacarbonyl in a nitrite eutectic showed a weight loss to start at 90°C with a maximum rate at 160°C. (See figure 3 Curve A.) The weight loss was found to be 100%, i.e., the same as the weight of the tungsten hexacarbonyl used.

Potassium permanganate formed an unstable green solution when added to the nitrite eutectic at 230°C. The green compound decomposed very quickly producing a brown precipitate. Because nitrogen oxides could not be detected, the gas was assumed to be oxygen. The production of oxygen is in agreement with isothermal thermogravimetric analysis at 250°C which showed a weight loss of 3.7 ± 0.2%. (Calculated for loss of $\frac{2}{5}$O per $KMnO_4$ 4.1%.) It was originally planned to make an investigation of the behaviour of several manganese compounds in nitrite melt; but, while the work was in the initial stages, the paper by Temple and Thickett was published$^{(40)}$ covering most of the subject. Therefore further investigation was not undertaken.

Metallic zirconium did not react when added to the molten nitrite at 230°C. In addition, rendering the melt more basic by the addition of sodium peroxide did not alter the inert behaviour of the zirconium. Thermogravimetric analysis gave similar results; for

Fig. 3

T.G.A. of $W(CO)_6$ and Zr metal in Na/KNO_2



example, when 0.2062 gram of zirconium metal with 2.3333 grams of sodium nitrite-potassium nitrite eutectic was heated in the presence of 0.0311 gram of sodium peroxide, no weight loss occurred up to 400°C. The quenched melt, after dissolving in water and filtering, was analysed for the presence of zirconium species with negative results.

VI.3 DISCUSSION

Sodium orthotungstate was inert towards a nitrite melt, as neither an acid-base reaction nor an oxidation-reduction reaction were observed. Although the orthotungstate was slightly soluble in nitrite melt, no catalytic effect was observed on the decomposition of the melt as was in the case of orthovanadate (see Chapter II).

Tungsten trioxide behaved as a Lux-Flood acid, abstracting oxide ions from the nitrite melt to form orthotungstate in accordance to the equation

$$WO_3 + 2NO_2^- \rightarrow WO_4^{2-} + NO + NO_2 \qquad \text{VI.4}$$

this stoichiometry agreeing with the weight loss obtained from the thermogram after allowance was made for the formation of nitrate due to the reaction of nitrogen dioxide and nitrite eutectic (equation II.4).

In contrast to the single reaction observed in a nitrite melt, thermogravimetric analysis of tungsten trioxide in sodium nitrate-potassium nitrate eutectic had been found to reveal two overlapping stages of weight loss (as described in the introduction of this chapter) and these were attributed to the formation of tritungstate and ditungstate followed by a final stage for the formation of orthotungstate. The formations of tritungstate and ditungstate were not confirmed analytically because of difficulties in separation of the stages.(60) Similarly, three stages have been suggested in pure molten potassium nitrate at 350°C for the neutralization of tungsten trioxide with sodium peroxide in which the species were represented by equation VI.1.(119) The failure to detect intermediate stages of the reaction between tungsten trioxide in a nitrite melt, such as those obtained in a nitrate melt, can be attributed to the higher basicity of the nitrite ion which rapidly leads to the formation of orthotungstate.

With tungsten metal, the nitrite eutectic behaved as an oxidizing agent forming orthotungstate while the nitrite itself was reduced to nitrogen apparently according to the equation

$$W + 2NO_2^- \rightarrow WO_4^{2-} + N_2 \qquad \text{VI.5}$$

This stoichiometry is in agreement with the experimental weight loss obtained from the thermogram. Equation (VI.5) also has been deduced by other workers(125) from the loss in weight of a strip of tungsten metal immersed into the sodium nitrite melt at 350°C and the analyses of the reaction products.

The formation of nitric oxide and nitrous oxide as well as nitrogen (Figure 2) revealed a further reaction of tungsten metal with nitrite eutectic, to some extent depending on the environment in which the reaction had taken place (See Result section). Thus the gaseous products of the reaction of tungsten metal and nitrite under vacuum are probably due to the oxidation-reduction represented by equation VI.5 together with the following equation:

$$W + 4NO_2^- \rightarrow WO_4^{2-} + N_2O + 2NO + O^{2-} \qquad \text{VI.6}$$

The presence of a small amount of atomic nitrogen in the mass spectra is due to the dissociation of the metastabledinitrogen ion or other nitrogen oxide ions as shown by the equations below:(126,127)

$$N_2 + e \rightarrow N_2^+ + 2e \qquad \text{VI.7}$$

$$N_2^+ \rightarrow N^+ + N \qquad \text{VI.8}$$

$$\text{or} \quad NO^+ \rightarrow N^+ + O \qquad \text{VI.9}$$

$$\text{or} \quad N_2O^+ \rightarrow NO^+ + N \qquad \text{VI.10}$$

The amount of nitric oxide present (Figure 2) was greater than could be attributed to the dissociation of nitrous oxide. Therefore, nitric oxide was considered one of the reaction products.

In the case of tungsten hexacarbonyl, the weight loss was due to the volatility of this compound. The weight loss was similar to the weight of the tungsten compound initially used and the absence of any tungsten species in the quenched melt is a confirmation of the absence of any reaction.

Zirconium metal was found stable in sodium nitrite-potassium nitrite melt up to 400°C, even on increasing the oxide ion concentration by the addition of sodium peroxide. Because of this stability, zirconium crucibles were used in the determination of the solubility and reactivity of sodium peroxide in nitrite melt (see Chapter VIII) since other container materials were found to react under the same conditions. On the other hand, and at elevated temperatures (400 - 450°C) zirconium metal has been reported to react very slowly with molten sodium nitrite producing zirconium dioxide according to the equation(125)

$$Zr + 4NO_2^- \rightarrow ZrO_2 + 2O^{2-} + 2NO_2 + N_2 \qquad VI.11$$

whereas the reaction in nitrate melt at similar temperatures, as suggested by the same workers, followed the equation

$$Zr + 4NO_3^- \rightarrow ZrO_2 + 2O^{2-} + 2NO_2 + N_2 + 2O_2 \qquad VI.12$$

With potassium permanganate, the unstable green coloured solution obtained on addition to molten nitrite was possibly due to the formation of manganate (VI), MnO_4^{2-}, which in turn decomposed rapidly to form a brown precipitate which has been shown to be very close to $2MnO_2:O^{2-}$ corresponding to the manganate (IV) found by Kerridge(122) when permanganate decomposes in molten nitrates. The overall reaction of permanganate in molten nitrite can be represented by the equation

$$10MnO_4^- + 11NO_2^- \rightarrow 10MnO_2 + 5O^{2-} + 2O_2 + 11NO_3 \qquad VI.7$$

the weight loss on the thermogram was very close to the above stoichiometry. This stoichiometry is also in agreement with that found by Temple and Thickett(40) in which the reactions had been carried out in pure sodium nitrite at 300°C. The blue coloured solution obtained by them on the addition of permanganate to pure sodium nitrite melt containing peroxide ion was not observed in the present study on addition of the same compound to sodium nitrite-potassium nitrite eutectic; but, an unstable green coloured solution of manganate (VI) was produced. However, a green solution of manganate (VI) was obtained by Temple and Thickett on the addition of permanganate to molten sodium nitrite containing hydroxide ion. The difference between the initial reactions of permanganate in pure sodium nitrite melt (300°C) and sodium nitrite-potassium nitrite eutectic (230°C) could possibly be due to an increase in the working temperature.

The decomposition reaction of permanganate was suggested by Temple and Thickett(40) to take place in steps

$$KMnO_4\text{(purple)} \rightarrow K_2MnO_4\text{(green)} \rightarrow K_3MnO_4\text{(blue)} \rightarrow MnO_2\text{(brown)}$$

Temple has stated also that manganate (V) could be stablized in molten nitrite by the addition of sodium peroxide to the melt. The stabilization could be prolonged by employing a vacuum which removed the water vapour that destroyed both the peroxide ion and the manganate (V).(40)

In contrast, stabilization of manganate compounds in nitrate melts has been achieved with more varied solutes. In lithium nitrate-potassium nitrate melt, manganate (V) was formed as a blue suspension on the addition of permanganate to the melt containing hydroxide, monoxide or peroxide ions, while a purplish-blue colour was observed on the addition of manganate (VI) which was attributed to the presence of manganate (V) and manganate (VII) indicating the disproportionation of manganate (VI).

However, in sodium nitrate-potassium nitrate, manganate (VI) has been proved to be stable in the presence of sodium hydroxide, while in the presence of monoxide and peroxide in certain concentrations a mixture of manganate (V) and manganate (VI) were obtained. Therefore, the alkali metal cations of the melt have a distinct effect on the reaction products, for example, the complete reduction of permanganate to manganate (V) obtained in lithium nitrate-potassium nitrate was attributed to the formation of the insoluble lithium manganate (V).

Moreover, manganese dioxide was found to undergo oxiditation to manganate (V) and manganate (VI) in the presence of peroxide ion and the proportionation of these species was found to be dependent on the concentration of the peroxide ions.(128)

Similarly, reoxidation of manganese dioxide to manganate (V) was observed in nitrite melt on the addition of peroxide ion.(40)

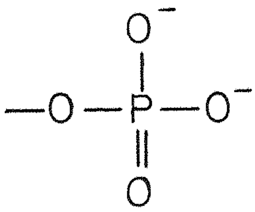
In conclusion, it may be said that manganate (V) and (VI) are more stable in nitrate melt than in nitrite melt, possibly due to the difference in working temperatures (260°C and 300°C respectively) as well as to the higher reactivity of nitrite melt.

CHAPTER VII

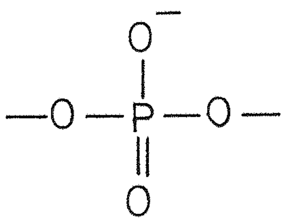
REACTIONS OF CONDENSED PHOSPHATES

VII.1 INTRODUCTION

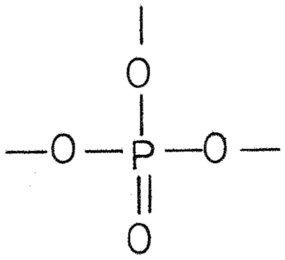
In general, phosphates are anions in which each phosphorous atom is surrounded by four oxygen atoms arranged at the corners of a tetrahedron. Apart from ortho-phosphate there are the condensed phosphates; these compounds contain more than one phosphorous atom and have P-O-P bonds. They consist of three main building groups; such groups are described as end groups, middle groups and branching groups.(129)



end group



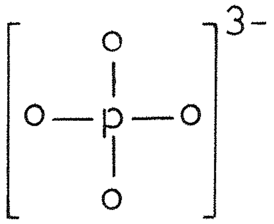
middle group



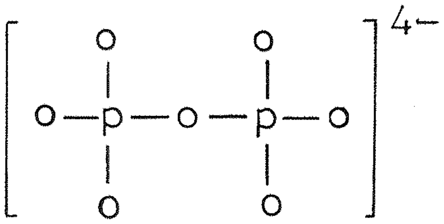
branching group

In the linear condensed phosphates there are several middle groups and two end groups, whereas in the cyclic phosphates the only group present is the middle group. These type of groups differ in their relative deficiency of oxide ions, therefore, an addition of oxide ion to a pyrophosphate group, with two end groups, becomes orthophosphate, and trimetaphosphate becomes tripolyphosphate upon the addition of oxide ion. The structural formulas for the phosphate anions used in the present work are shown in Figure 1.

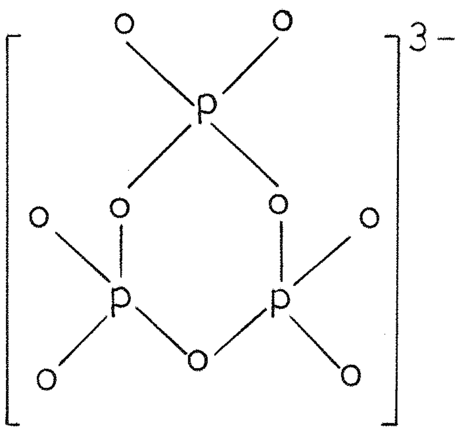
Figure 1



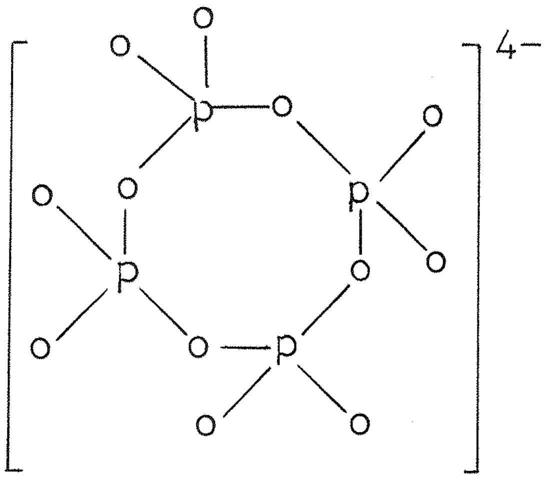
(1) orthophosphate



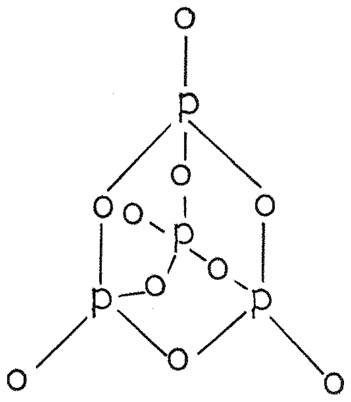
(2) pyrophosphate



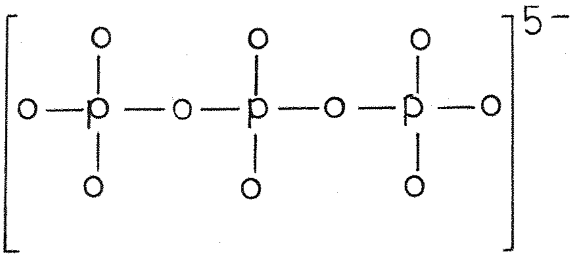
(3) trimetaphosphate



(4) tetrametaphosphate



(5) phosphorus pentoxide



(6) tripolyphosphate

According to their deficiencies of oxide ions, the Lux-Flood acid strength of these compounds in the presence of a base are in the order:

$$P_4O_{10} > (PO_3)_3^{3-} > P_3O_{10}^{5-} > P_2O_7^{4-} > PO_4^{3-}$$

The conversion of one group to another with excess oxide ion, takes place through the rupture of the P-O-P bond by the attacking oxide ion.

The acid-base reactions involving condensed phosphates and phosphorus pentoxide in molten oxyanionic saltes have been studied. These studies have included the use of molten nitrates and molten perchlorates. Shams El Din and co-workers(130) have shown that phosphorus pentoxide in potassium nitrate melt at 350°C acts as a Lux-Flood acid forming metaphosphate ions. On the addition of further oxide ions, these metaphosphate ions formed pyrophosphate ions and then orthophosphate ions. The degradation of condensed phosphates was also reported by these workers and found to depend on the base used and the molten salt solvent. Dissolving the metaphosphate in lithium chloride-potassium chloride eutectic and titrating with sodium peroxide at 400°C, pyrophosphate was obtained which did not undergo further degradation, while in molten potassium nitrate (350°C), the titration of metaphosphate with peroxide resulted in the production of orthophosphate.(25,131,132)

The reaction stoichiometries and kinetics of several condensed phosphates and phosphorus pentoxide have been studied in both lithium nitrate and potassium nitrate melts. The depolymerization of these compounds has been found to follow the degree of deficiency for the oxide ions, the greater the deficiency, the more rapid the degradation. Thus, phosphorus pentoxide has been found to depolymerize to metaphosphate which then degraded to orthophosphate through a polyphosphate intermediate.(133)

In addition to these investigations in nitrate melts, some condensed phosphates have been studied in perchlorate melts, which have also shown an acid-base behaviour. The degradation of metaphosphates in perchlorate has been found to be dependent on the cations bonded to the phosphate ion, since lithium metaphosphate degraded to orthophosphate whereas sodium metaphosphate only depolymerized to pyrophosphate. In every case, perchlorate melts showed higher basicity than nitrate melts, as the reaction of metaphosphate compounds started at lower temperatures.(134)

On the other hand, reactions of phosphate compounds in molten nitrite also seem to be useful in obtaining additional information on the acid-base properties of the melt. Since condensed phosphates have never been employed in a reaction with molten nitrite, investigation of their reactions was undertaken in the present studies. Their stoichiometries were established using the weight losses shown by thermograms and the results of the analyses of the products.

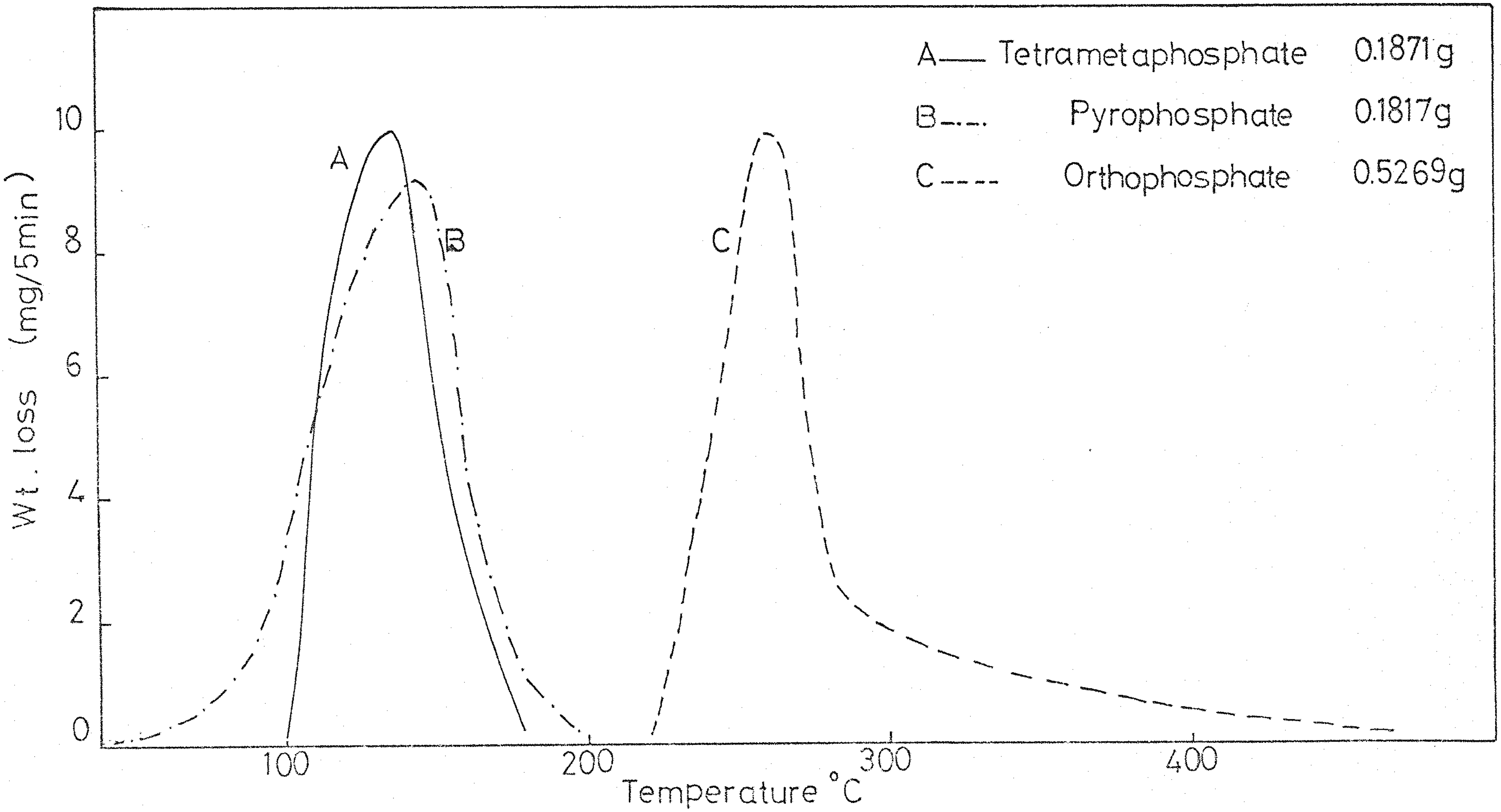
VII.2 EXPERIMENTAL SECTION

VII.2.1 Materials and Procedure

Phosphorus pentoxide P_4O_{10}, sodium metaphosphate insoluble form $(NaPO_3)_x$, B.D.H. reagents grade, and sodium trimetaphosphate $Na_3(PO_3)_3$ reagents grade obtained from Albright and Wilson were dried at 120°C for 20 hours and stored in a desiccator. Reagent grade sodium tetrametaphosphate $Na_4(PO_3)_4$ obtained from Albright and Wilson was found to be hydrated since the thermogravimetric analysis (Figure 2) showed a weight loss of 13.8% which started at 100°C and completed at

Fig. 2

T.G.A. of hydrated phosphates



150°C. This reagent was dehydrated at 150°C for 20 hours. Sodium tripolyphosphate $Na_5P_3O_{10}$ was dried at 120°C for 20 hours. Reagent grade (B.D.H.) potassium pyrophosphate was found, by analysis using the Autoanalyser, to be contaminated with orthophosphate. The approximate quantity of orthophosphate present was 2%. Reagent grade potassium orthophosphate was dried under vacuum at 220°C for 6 hours. Thermogravimetric analysis showed a water content of 11%.

Sodium nitrite-potassium nitrite eutectic used in the present investigation was prepared by mixing B.D.H. Analar sodium nitrite and Hopkins and Willims reagent grade potassium nitrite, after drying at 150°C for several hours, in the eutectic proportions. The dehydration and filtration were carried out as described in Chapter I. These chemicals, after drying, were stored in a desiccator which was evacuated and placed in a dry box.

The reactions were carried out in a B24 pyrex test tube which was fitted snugly into an electric furnace controlled by an Ether transitrol controller.

VII.2.2 Analysis

Qualitative and quantitative analyses were carried out for the reaction products in the nitrite melt. The phosphate species, after dissolving the quenched melt in water, were determined qualitatively by the addition of magnesium nitrate solution which formed a white precipitate in the presence of both pyro and orthophosphates; but, the white precipitate was soluble in excess magnesium nitrate in the former case and insoluble in the latter.(124) The nitrate content was determined, after the decomposition of the nitrite present with sulphamic acid, by the addition of ferrous sulphate and titration with a standard solution of dichromate. The details were described in Chapter I.

The gases evolved from the reactions were collected in an evacuated 10 cm potassium bromide window cell, which was connected to a vacuum line. The vacuum system and the methods of collection were described in Chapter I.

VII.2.3 Instrumentation

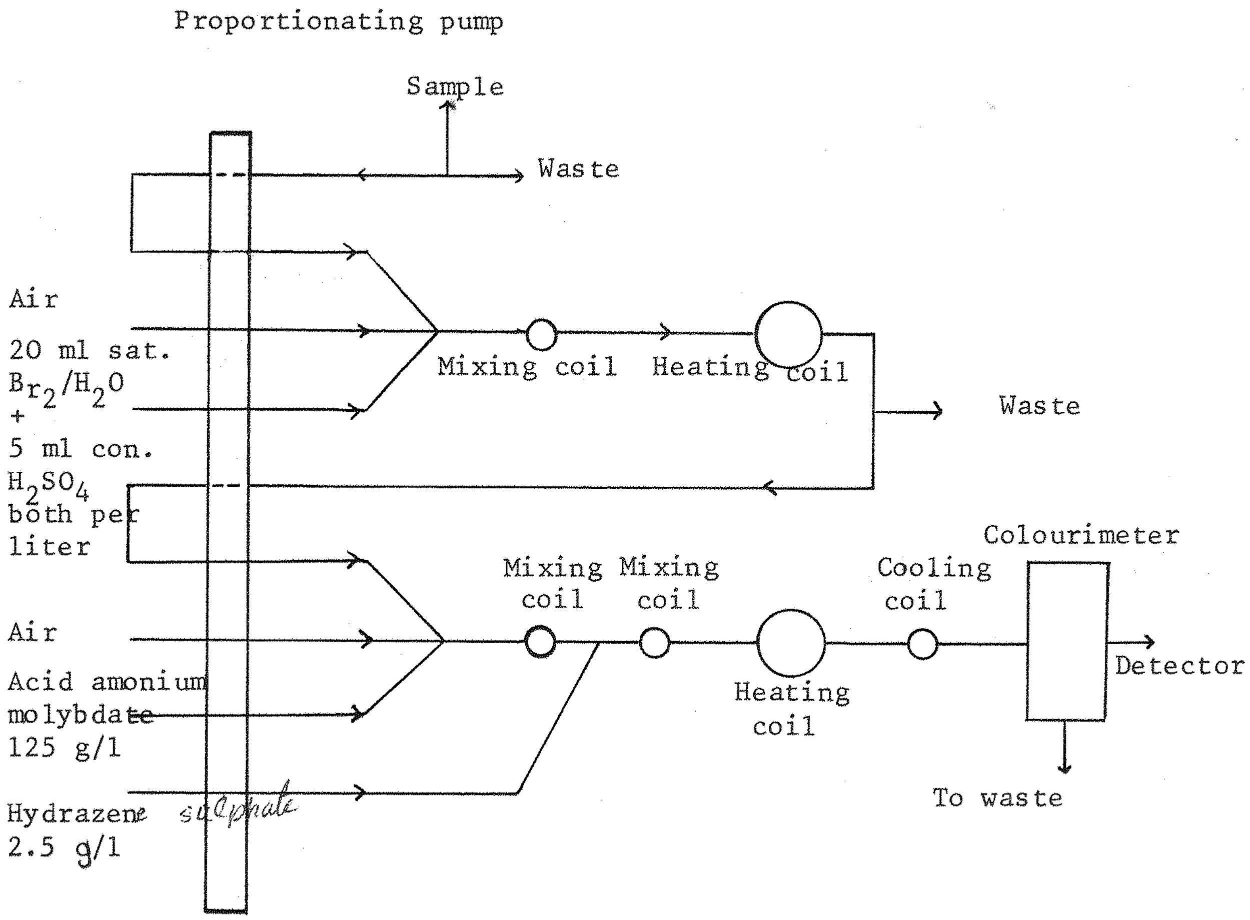
Thermogravimetric analysis was carried out on a Stanton thermobalance under a flow of oxygen-free nitrogen as described in Chapter III. The oxygen-free nitrogen was used after being passed through drying towers containing concentrated sulphuric acid and phosphorus pentoxide. Infra red spectra of the evolved gas samples were obtained using a Unicam S.P.200 I.R. spectrometer.

The n.m.r. analyses were made using a Varian H.A.100 spectrometer. The samples were prepared by dissolving the quenched melt in a minimum amount of distilled water in order to get saturated phosphate solutions. These samples were contained in special n.m.r tubes. The chemical shift reference signal, at 0.0 p.p.m., was obtained using 85% phosphoric acid in a small capillary tube placed inside the unknown sample tube. The reference sample was used for every n.m.r. determination.

VII.2.4 Autoanalyser

The phosphate compounds, whether reactants or reaction products, were analysed using anion exchange chromotography. The analytical system is based on principles used before for the separation of phosphate compounds,(135) and consists of an anion exchanger column connected to the other flowing streams as shown in Figure 3.

Figure 3



The detector for the system was based on a colorimetric procedure in which the molybdenum blue method for the determination of phosphorus was used and in this way the phosphorus concentration in the sample was detected continuously. This procedure depends on the condensation of molybdic acid with orthophosphate to give phosphomolybdic acid which, on reduction by hydrazine, gives the blue coloured complex known as molybdenum blue. The intensity of the colour is proportional to the amount of phosphate ion in the complex. All the phosphorus in the colorimetric system must be present as orthophosphate, since only orthophosphoric acid condenses with molybdic acid to form the complex acid. Therefore the phosphorus compounds must be converted to orthophosphate before mixing with acidic ammonium molybdate by pumping through a glass coil immersed in oil at 95°C after mixing with sulphuric acid. Analyses were carried out for pure orthophosphate and pyrophosphate which showed retention times of two and three hours respectively.

VII.3 RESULTS

Potassium orthophosphate was found to be stable in sodium nitrite-potassium nitrite eutectic. No reaction was observed on the addition of the orthophosphate to the melt at 220°C. Raising the temperature to 400°C did not seem to have any effect as no brown fumes were observed which could be attributed to a reaction between orthophosphate and the nitrite eutectic. Thermogravimetric analysis showed no losses in weight up to 550°C. Above this temperature the weight losses observed were due to the decomposition of the sodium nitrite-potassium nitrite eutectic, which decomposed between 550 - 600°C as described in Chapter I.

Potassium pyrophosphate did not visibly react when added to the nitrite eutectic at 220°C as no brown fumes were observed. Above 300°C, the evolution of brown gases, of nitrogen dioxide and nitric oxide indicated the beginning of a reaction. Thermogravimetric analyses showed that a loss in weight commenced at 320 ± 10°C with a maximum weight loss around 400°C (Figure 4 curve B). The experimental weight loss was found to be 19.4% which became 27.6% after correcting for the formation of nitrate due to the reaction of nitrogen dioxide and nitrite (equation II.4). The theoretical weight loss calculated for the loss of 2N + 3O per mole of potassium pyrophosphate is 28.9% which is very close to the weight loss obtained experimentally.

The quenched melt, after dissolving in a minimum amount of distilled water, was analysed by the addition of a few ml of a magnesium sulphate solution and other reagents, e.g. cadmium chloride, and showed the presence of an orthophosphate species.

In addition to the above analyses, nuclear magnetic resonance measurements were made on the phosphate saturated solution. The spectrum exhibited a peak at -3.08 ppm, with respect to 85% H_3PO_4, which corresponded to the presence of orthophosphate species as a final product of the reaction.(129,136) Nuclear magnetic resonance measurements were carried out also on saturated solutions of pure reagent grade potassium pyrophosphate B.D.H. and reagent grade potassium orthophosphate B.D.H. for the sake of comparison with the spectrum obtained for the reaction products. The pyrophosphate spectrum showed a peak with a value of 5.89 p.p.m., whereas -3.1 p.p.m. was obtained from the spectrum of orthophosphate, which are in agreement with the reaction products spectra and spectra previously reported.(136) These results were confirmed by the results obtained from the Autoanalyser which showed a peak with a two hour retention time, which corresponded to the orthophosphate as pure potassium orthophosphate

Fig . 4

T.G.A. of phosphorus pentoxide in nitrite eutectic

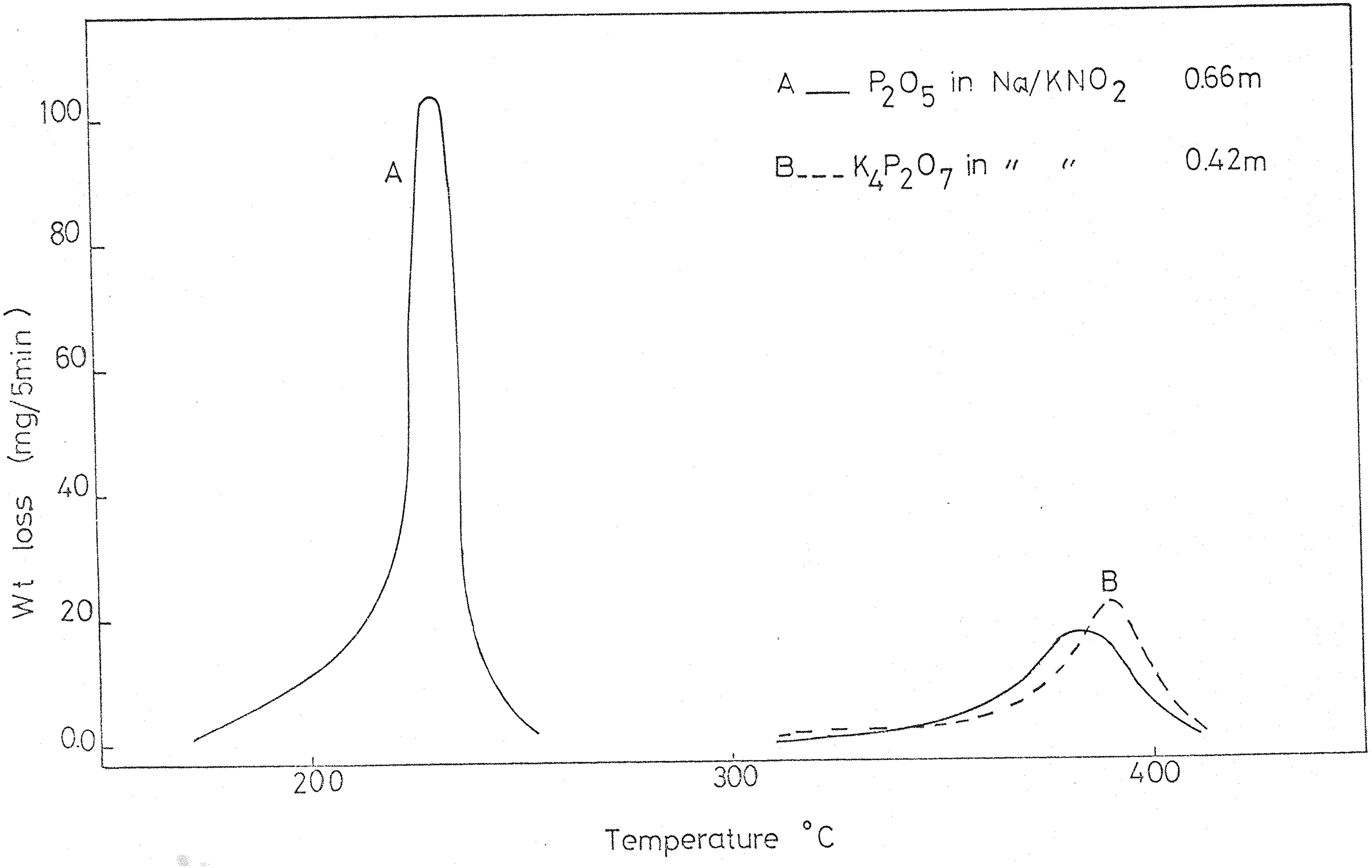
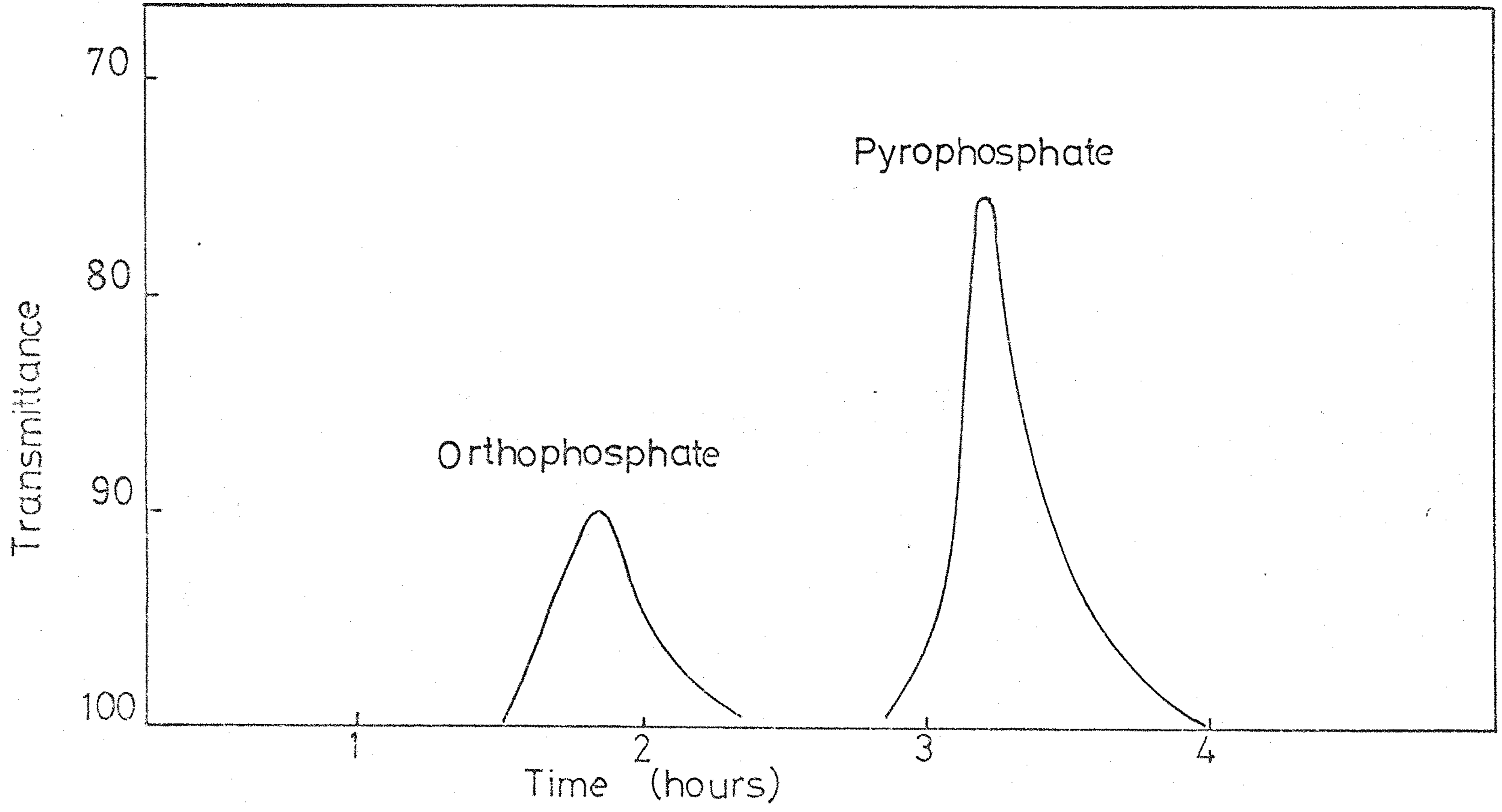


Fig. 5

Chromatographic separation of phosphate anions



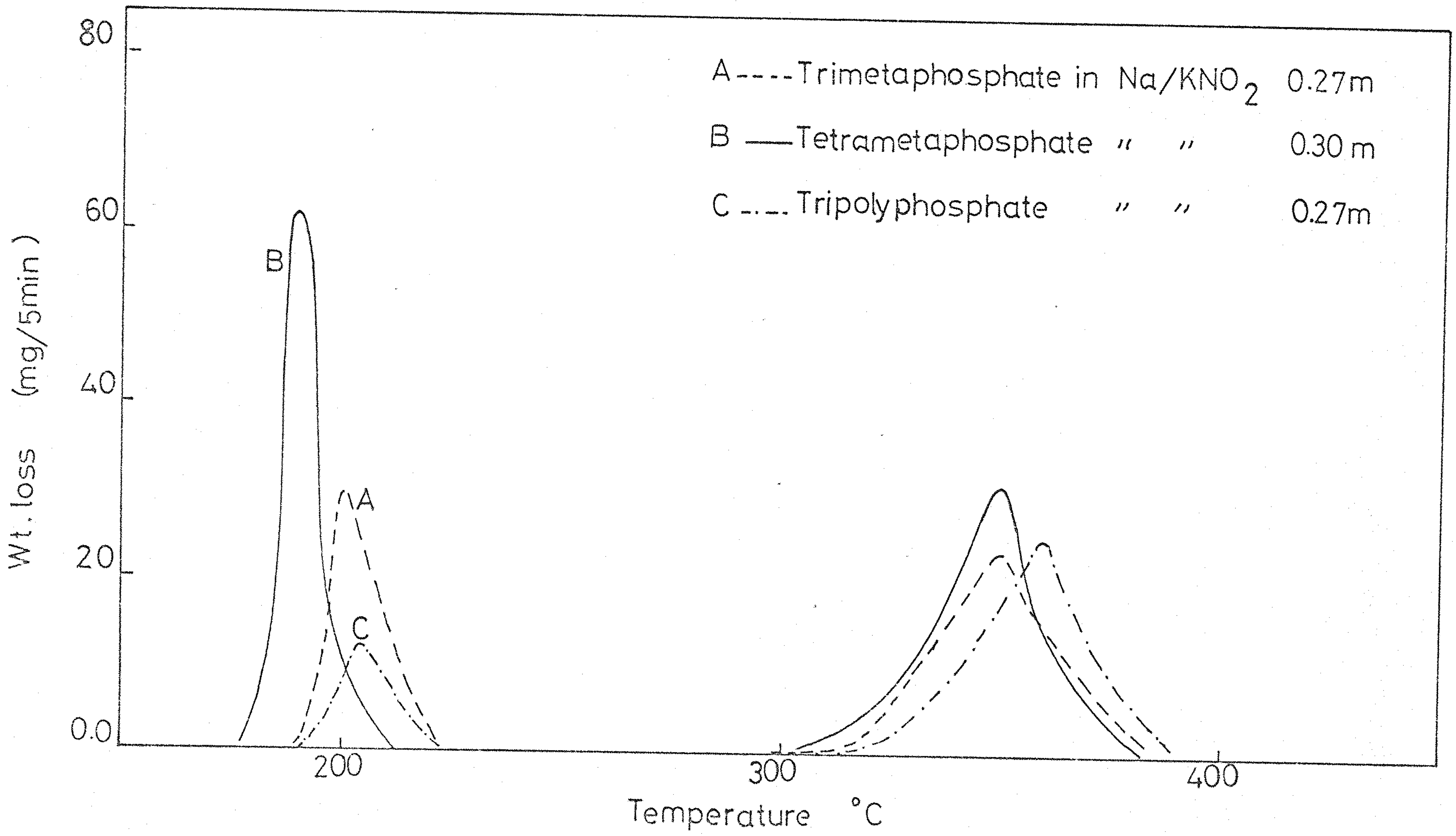
was also found to have a two hour retention time (Figure 5).

Sodium tetrametaphosphate, reacted immediately with the molten nitrite eutectic at 220°C with the evolution of brown fumes of nitrogen dioxide and the production of a white precipitate. Thermogravimetric analysis (Figure 6 curve B) showed the reaction to commence in the solid state, with two stages of weight loss. The first stage commenced at 180 ± 5°C with a maximum weight loss around 190°C and finished at 220°C. The loss of weight obtained from the thermogram for the first reaction was 30.8% which on correction for the formation of nitrate due to reaction II.4 became 36.5%. The theoretical loss in weight calculated for a loss of 4N + 60 per mol of $Na_4(PO_3)_4$ was 37.2%.

After dissolving in water, the quenched melt was analysed qualitatively and found to contain pyrophosphate. Ion exchange chromotography showed a peak with a retention time of three hours (Figure 5) and the spectrum of the nuclear magnetic resonance showed a single peak at 5.8 p.p.m. Both the ion exchange chromotography and the nuclear magnetic resonance confirmed the presence of the pyrophosphate anion.

The second stage reaction of the tetrametaphosphate and nitrite eutectic, as shown in Figure 6, commenced at 310 ± 5°C with a total weight loss varying beteen 61.7% and 62.5%, however, correcting for the nitrate formation in the melt gave a total loss of 74.1%. (Calculated for loss of 8N + 12 O per mol of $Na_4(PO_3)_4$ 74.5%). The phosphate species in the final products was found to be orthophosphate since the spectrum of nuclear magnetic resonance gave a value of −3.2 p.p.m. and the ion exchange chromotography showed a retention

Fig . 6
T.G.A. of condensed phosphates in nitrite eutectic



time of two hours, both of which correspond to the orthophosphate species.

Sodium trimetaphosphate reacted immediately when added to the nitrite melt at 220°C producing brown fumes of a mixture of nitrogen dioxide and nitric oxide. The reaction was vigorous and associated with the splashing of the melt which solidified on the cold, upper part of the reaction tube. Precautions were taken in using the thermobalance by placing an inverted funnel on the reaction crucible to minimize the errors that might occur.

Thermogravimetric analysis showed two stages of weight loss, (Figure 6 curve A) the first stage commenced in the solid state at 190°C with a rapid loss of weight reaching the maximum at 200°C and finishing at 225°C. The experimental weight loss was found to be 29.6% which, when corrected for the formation of nitrate, became 36.9%. The calculated weight loss for 3N + 4½O per one mol of $Na_3(PO_3)_3$ is 37.2%. The water soluble white product was examined and found to contain pyrophosphate. The nuclear magnetic resonance showed as well as the peak corresponding to pyrophosphate, a small peak at −3.12, which was attributed to the orthophosphate species. This was confirmed by ion exchange chromotography which showed two peaks with retention times of two and three hours, corresponding to the presence of orthophosphate and pyrophosphate, respectively. The ratio of orthophosphate to pyrophosphate calculated from the areas under the peaks was 1:600.

The second stage reaction started, as shown in Figure 6 curve A, around 310°C with a maximum rate of loss in weight at 350°C. The thermogram showed a total weight loss of 63.5% which became 74.8%

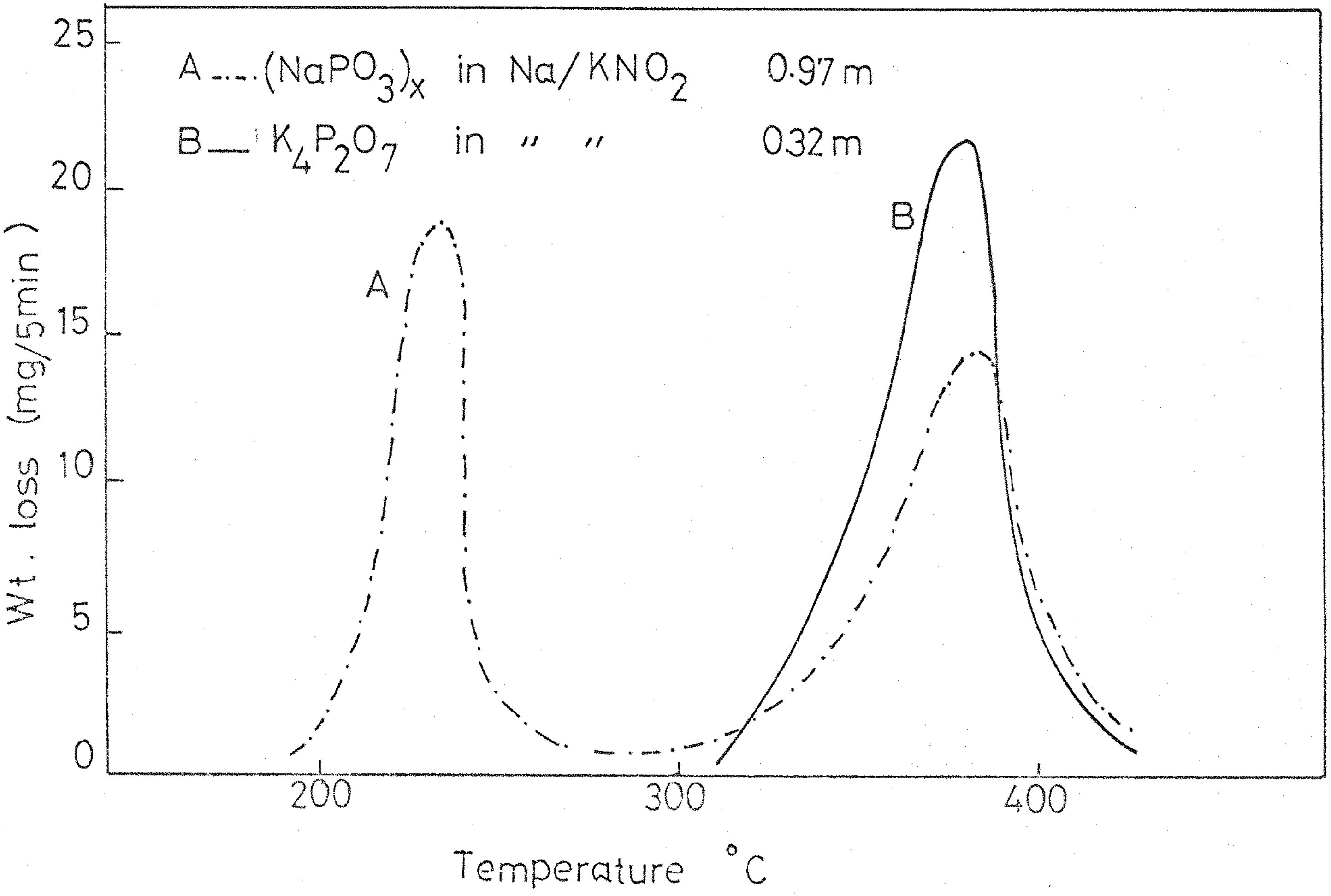
on correction for nitrate formation. (Calculated for loss of 6N + 9O per $Na_3(PO_3)_5$ 74.5%.) The analyses of the final reaction products by both nuclear magnetic resonance and ion exchange chromotography showed single peaks, which by comparison with known spectra confirmed the presence of orthophosphate.

Sodium metaphosphate insoluble form, reacted with nitrite melt, in a manner analogous to trimetaphosphate, in two stages. Thermogravimetric analysis (Figure 7 curve A) showed two distinct peaks, the first started at 200 ± 10°C with a weight loss varying between 25.6% and 27.1% which became 37.0% when corrected for the formation of nitrate due to reaction (II.4). The second stage reaction commenced at 310 ± 5°C with a total weight loss of 67.3% and became 74.3% on correction for the nitrate formation. Qualitative analyses were made using a magnesium nitrate solution, which gave a white precipitate insoluble in an excess of the reagent, indicating the presence of pyrophosphate. Ion exchange chromotography showed two peaks with retention times of two and three hours which correspond to the orthophosphate and pyrophosphate, respectively. The ratio of orthophosphate to the pyrophosphate was found to be similar to that with trimetaphosphate. The final reaction products were examined by the same methods as first stage products and was found to be orthophosphate.

Sodium tripolyphosphate commenced to react with the nitrite eutectic around the melting point, evolving brown fumes of nitrogen dioxide and nitric oxide. Thermogravimetric analysis showed a loss of weight in two stages (Figure 6 curve C). The first started at 190 ± 5°C, and the weight loss varied between 6.1% and 7.0% which, when

Fig. 7

T.G.A. of Pyro and metaphosphate in nitrite etectic



corrected for the formation of nitrate (reaction II.4), became 10.1%. The theoretical weight loss of 2N + 3O per 2 mols of $Na_5P_3O_{10}$ is 10.3%. Analyses of the solid products, by techniques similar to those for the reaction of trimetaphosphate, showed the presence of pyrophosphate with a very small amount of orthophosphate. The second stage reaction started around 310°C with a total weight loss of 29.6% and became 40.1% on correcting for nitrate formation. (Calculated for loss of 4N + 6O per mol of $Na_5P_3O_{10}$ 41%). The analysis of the second stage products showed the presence of orthophosphate.

Phosphorous pentoxide reacted immediately when added to the melt at 220°C with the evolution of brown fumes of nitrogen dioxide and the production of a white precipitate. On raising the temperature to 350°C a second visible reaction started. Thermogravimetric analysis (Figure 4 curve A) showed the first reaction to commence in the solid state at 170°C with a maximum weight loss around 230°C and to be completed at 260°C. The weight loss obtained from the thermogram was 82.4% which after correcting for the amount of nitrate formed due to reaction (II.4), became 95.5%. The calculated weight loss for 8N + 12O per P_4O_{10} is 96.5%. Examination of the quenched melt, after dissolving in water, using a magnesium nitrate solution showed the presence of pyrophosphate. This was confirmed by ion exchange chromotography, since the retention time obtained for the peak was three hours. A tiny peak with two hours retention time occurred which was due to a small amount of orthophosphate present.

The second stage reaction, as shown by the thermogram in Figure 4 curve A, started around 310 ± 10°C, with a very slow weight loss, and reached the maximum around 380°C. The total weight loss obtained from the thermogram was 133% and became 158.5% when corrected for nitrate formation (equation II.4). (Calculated weight loss for 12N + 18O per P_4O_{10} 160%). The water soluble products were analysed using ion exchange chromotography which showed a peak with a retention time of two hours corresponding to the orthophosphate species.

VII.4 DISCUSSION

The behaviour of condensed phosphates in molten nitrites represents a very interesting class of acid-base reactions in which the phosphate compounds act as Lux-Flood acids. The final product of all the reactions, as described above, was orthophosphate which was found to be stable towards the nitrite ion. The overall stoichiometry of these reactions are in accordance with the following equations:

$$(NaPO_3)_x + 2xNO_2 \rightarrow xPO_4^{3-} + xNO_2 + xNO + xNa^+ \quad \text{... VII.1}$$

$$Na_3(PO_3)_3 + 6NO_2^- \rightarrow 3PO_4^{3-} + 3NO_2 + 3NO + 3Na^+ \quad \text{... VII.2}$$

$$Na_4(PO_3)_4 + 8NO_2^- \rightarrow 4PO_4^{3-} + 4NO_2 + 4NO + 4Na^+ \quad \text{... VII.3}$$

$$Na_5P_3O_{10} + 4NO_2^- \rightarrow 3PO_4^{3-} + 2NO_2 + 2NO + 5Na^+ \quad \text{... VII.4}$$

$$P_4O_{10} . + 12NO_2^- \rightarrow 4PO_4^{3-} + 6NO_2 + 6NO \quad \text{... VII.5}$$

Potassium pyrophosphate reacted, as expected, as a Lux-Flood acid, removing oxide ions from the nitrite melt according to the equation

$$P_2O_7^{4-} + 2NO_2^- \rightarrow 2PO_4^{3-} + NO + NO_2 \quad \text{... VII.6}$$

The experimental weight loss agreed very well with the above stoichiometry after allowance was made for the reaction of nitrogen dioxide with the nitrite melt to form nitrate (see equation II.4). The reaction between pyrophosphate and a sodium nitrite-potassium nitrite eutectic was considerably more rapid and took place at a lower temperature (310°C) than the reaction of pyrophosphate with sodium nitrate-potassium nitrate eutectic. The latter reaction did not occur rapidly until 540°C, though in lithium nitrate-potassium nitrate eutectic the reaction started at a temperature of 450°C.(60)

These differences in reaction temperatures between a nitrite and a nitrate eutectics can be attributed to the higher basicity of the nitrite ion. The difference in the reaction temperature of pyrophosphate and other condensed phosphates in sodium nitrate-potassium nitrate and lithium nitrate-potassium nitrate eutectics was attributed to the strongly polarizing lithium cation which, with its high ionic potential is capable of weakening the P-O-P bridge bond by inducing polarization of the condensed phosphate added as such or formed as an intermediate product.(133) Thus one might expect reactions in nitrite melts containing lithium ions to occur at lower temperatures and more rapidly than those observed in the sodium nitrite-potassium nitrite eutectic.

In the cases of tetrametaphosphate, trimetaphosphate and the insoluble form of metaphosphate, the reactions took place approximately at the same temperature; all the metaphosphates, acting as Lux-Flood acids, abstracted oxide ions from the nitrite melt. The reactions occurred in two stages: The first stage agreed with the following stoichiometries after correcting the weight loss for the formation of nitrate due to reaction II.4.

$$Na_4(PO_3)_4 + 4NO_2^- \rightarrow 2P_2O_7^{4-} + 2NO + 2NO_2 + 4Na^+ \quad \ldots \text{VII.7}$$

$$2Na_3(PO_3)_3 + 6NO_2^- \rightarrow 3P_2O_7^{4-} + 3NO + 3NO_2 + 6Na^+ \quad \ldots \text{VII.8}$$

$$2(NaPO_3)_x + x2NO_2^- \rightarrow xP_2O_7^{4-} + xNO + xNO_2 + 2xNa^+ \quad \ldots \text{VII.9}$$

The second stage reaction between the pyrophosphate produced from the above reactions and nitrite eutectic took place with a stochiometry similar to that presented in equation VII.6. The presence of the ortophosphate species in the first stage reaction products, though in a very small amount, gives rise to the suggestion that the pyrophosphate species exhibits some instability around the temperature at which the first stage reaction occurs.

The reactions of tetrametaphosphate and trimetaphosphate were expected to occur in three stages i.e. by the conversion of these compounds to tetrapoly and tripolyphosphates similar to their reactions in the nitrate melt. In the present studies no weight losses were observed in the thermogram which could be attributed to any of these polyphosphate species and none were identified by ion exchange chromotography. However, since tripolyphosphate reacts very rapidly below the melting point, as discussed below, the failure to obtain evidence for the formation of a polyphosphate intermediate does not negate the possibility of a polyphosphate intermediate. However such intermediates were identified in nitrate melts at 400°C due to the reaction of metaphosphate.(133) This difference in behaviour between nitrate and nitrite melts is again evidence of the higher reactivity of the nitrite ion as a Lux-Flood base.

Sodium tripolyphosphate, behaving as a Lux-Flood acid, reacted with nitrite eutectic at a temperature slightly higher than that for the metaphosphate. The reaction took place in two stages. The first stage stoichiometry is in accordance with following equation

$$2P_3O_{10}^{5-} + 2NO_2^- \rightarrow 3P_2O_7^{4-} + NO + NO_2 \qquad \text{... VII.10}$$

The second stage reaction occurred at almost the same temperature as that for the reaction of pyrophosphate, and the total weight loss was in agreement with the stoichiometry (VII.4) after correction for nitrate formation.

Phosphorus pentoxide reacted at a temperature lower than the other condensed phosphates, thereby showing more acidic behaviour. The reaction produced the pyrophosphate ion in the first stage.

$$P_4O_{10} + 8NO_2^- \rightarrow 2P_2O_7^{4-} + 4NO + 4NO_2 \qquad \text{... VII.11}$$

The final product was orthophosphate (equation VII.5).

Analysis and weight losses agreed well with this stoichiometry. The first stage weight loss probably consisted of two inseparable stages i.e., the deceleration of the weight loss followed by a rapid loss in the isothermal thermogravimetric curve (200°C) can be attributed to the formation of metaphosphate as an intermediate product which afterwards reacted to form pyrophosphate.

$$3P_4O_{10} + 12NO_2^- \rightarrow 4(PO_3)_3^{2-} + 6NO + 6NO_2 \qquad \text{... VII.12}$$

The small amount of orthophosphate found in the first stage products was probably formed in a way similar to that with trimetaphosphate described above. The second stage weight loss agreed with equation (VII.5).

In contrast with the nitrite melt, the reaction of phosphorus pentoxide in the nitrate melt took place at elevated temperature and the trimetaphosphate produced was reasonably stable to further depolymirization since no additional detectable reaction was observed within a reasonable time period. In nitrite melts the only detectable product found was pyrophosphate.

It is of interest to compare, here, the behaviour of condensed phosphates in nitrite eutectic and in oxyanion melts other than nitrate. A study of the behaviour of the more common alkali metal perchlorates as sources of oxide ions in the presence of the strong polyanionic acids of condensed phosphate at high temperature has shown that the degradation of lithim metaphosphate starts at 340°C forming the pyrophosphate ion while the pyrophosphate ion itself was reported to react at 440°C. The depolymerization of sodium metaphosphate in sodium perchlorate and potassium metaphosphate in potassium perchlorate takes place at 450°C and 540°C respectively.(134) As a result of these reactions in perchlorates, the order of depolymerization of metaphosphates is Li > Na >> k and for pyrophosphate is Li >> Na >>> k.

General conclusions from the above discussion of the reactions of condensed phosphates with three different melts may be drawn. Firstly the basic character of molten nitrites is stronger than that of both molten nitrates and molten perchlorates, since the reactions of the phosphate compounds take place at temperatures lower than that with the other two melts. Secondly, the degradation of condensed phosphates probably takes place in a stepwise fashion

$$P_4O_{10} \rightarrow (PO_3)_3^{3-} \rightarrow P_3O_{10}^{5-} \rightarrow P_2O_7^{4-} \rightarrow PO_4^{3-}$$

And thirdly, the relative acidity of the alkali metal metaphosphates and pyrophosphates decreases with an increase in the atomic number of the alkali metal cations.

CHAPTER VIII

REACTION OF PEROXIDE ION O_2^{2-} IN MOLTEN NITRITE

VIII.1 INTRODUCTION

The chemistry of the monoxide ion, O^{2-}, the peroxide ion, O_2^{2-}, and the superoxide ion, O_2^-, in oxyanion melts has been the subject of intense speculations over the last ten years. However, most of these experimental studies have been made in molten nitrates.

Initially the Lux-Flood acid-base concept, which has proven very useful in the interpretation of many reactions in oxyanion melts, was employed by Kust and Duke(21) suggesting the existence of the following equilibrium in nitrate melts.

$$NO_3^- \;=\; NO_2^+ + O^{2-} \qquad \text{VIII.1}$$

the oxide ion being assumed to take a solvated form involving Na^+, K^+ or NO_3^-.

However, the stability of the oxide ion in a nitrate melt has been challenged by Jordan and Zambonin.(26,137) These workers obtained results indicating that the oxide ion can exist in molten nitrate only at a negligibly low concentration. Jordan(138) has stated that the oxidizing properties of the melt are likely to involve the superoxide ion and/or the peroxide ion, dismissing all the results that support a Lux-Flood concept.

In contrast, Kohlmuller and other workers(23,139) had earlier reported that the orthonitrate ion, NO_4^{3-}, was formed when alkali metal oxides were added to molten nitrates and that the orthonitrite ion, NO_3^{3-}, was similarly produced in molten nitrite.

Since most of the previous studies have been carried out in nitrate melt, it was of interest to investigate the reaction of the peroxide ion in molten nitrites. Thus reactions were carried out in a sodium nitrite-potassium nitrite eutectic at different temperatures using reaction vessels constructed of different materials (Pyrex, platinum and zirconium). In the course of these investigations the equilibrium constant for the oxidation of nitrite ion by peroxide ion was determined and the effect of the melt solution on metalic platinum was illustrated. The slight influence of atmospheric oxygen on the reaction was shown using the results obtained by thermogravimetric analysis.

VIII.2 EXPERIMENTAL

VIII.2.1 Materials

The sodium nitrite-potassium nitrite eutectic and the equimolar sodium nitrate-potassium nitrate were prepared as described in Chapter I.

Sodium peroxide (Hopkins and Williams Reagent grade 93% pure) was used without further treatment. Sodium monoxide was prepared by heating sodium peroxide in a recrystallized alumina boat inserted into a silica tube closed at one end. The silica tube was placed into a horizontal tube furnace, evacuated to 10^{-2} torr, and heated at 600 - 650°C until gas evolution ceased.(140) The product was analysed and found to contain 98.2% sodium monoxide and 1.4%

sodium peroxide.

Nickel gauze (Bedford Steer) which had been immersed in a nitrite melt containing sodium peroxide to form a black protective coating of nickel oxide, was used to support a drop of molten nitrite for the identification of peroxide ion by ultraviolet spectroscopy.

VIII.2.2 Procedure

Reactions were carried out in Pyrex glass tubes with B25 joints closed so that oxygen-free nitrogen could be passed over the melt. This reaction tube was fitted into an electrical furnace connected to an Ether Transitrol controller.

Since the Pyrex reaction tubes were not stable in the presence of nitrite eutectic and sodium peroxide, the use of a platinum crucible was investigated. The platinum crucible with the reactants in it was inserted into a Pyrex envelope, itself placed into a temperature controlled electrical furnace.

Similar reactions were carried out in a zirconium crucible which was itself placed inside a Pyrex tube immersed in a constant temperature molten nitrate bath. The temperature of this bath was controlled by Ether Transitrol controller and a mechanical stirrer was used to ensure a uniform temperature throughout the bath.

VIII.2.3 Analysis

(a) Sodium peroxide

Pure sodium peroxide was determined by titrating an acid solution of the peroxide with potassium permanganate solution according to the equation.(67)

$$2MnO_4^- + 5O_2^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O \qquad \text{VIII.2}$$

The peroxide solution was prepared by dissolving a known amount of sodium peroxide in water acidified with three ml of concentrated sulphuric acid and five grams of boric acid. Boric acid was added to stabilize the peroxide as perboric acid. The mixture was then titrated with a standard solution of permanganate. This method could not be employed for the estimation of peroxide ion in the presence of nitrite ion, since nitrite ion would also react with permanganate. Therefore an attempt was made to estimate the nitrate ions produced due to the reaction of peroxide with nitrite, and which is equivalent to the reacted peroxide, by destroying the nitrite ions with sulphamic acid and titrating the nitrate with standard dichromate solution.(52) However, large amounts of nitrate were produced by the reaction of peroxide with nitrite in acidic environment; therefore, this method could not be employed. Thus a method in which arsenic (III) oxide was used as a reducing agent for peroxide was developed and employed for the determination of peroxide ion in the presence of nitrite ion.

(b) Determination of sodium peroxide with arsenic (III) oxide in the presence of nitrite ion

The method employed here depends on the reaction of the peroxide ion with an alkaline solution of arsenic (III) according to the equation

$$H_3AsO_3 + O_2^{2-} + H_2O \rightarrow H_3AsO_4 + 2OH^- \qquad \text{VIII.3}$$

Since the reaction of peroxide ions and arsenic (III) solution is very slow, osimium tetraoxide solution was used as a catalyst to accelerate the reaction. The remaining arsenic (III) in the solution was then determined by back titration with a standard solution of iodine, i.e.,

$$I_2 + H_3AsO_3 + H_2O \rightarrow H_3AsO_4 + 2I^- + 2H^+ \qquad \text{VIII.4}$$

in a bicarbonate buffer at pH7.

Several analyses were carried out on different known amounts of sodium peroxide mixed with sodium nitrite, and the results obtained are listed in Table 1.

Table 1

Analyses results of sodium peroxide

Na_2O_2 used (grams)	Na_2O_2 found (grams)	% Error	$NaNO_2$ added (grams)
0.0059	0.0064	+8.4%	2.7521
0.0059	0.0060	+1.8%	3.2546
0.0092	0.0090	-2.1%	3.1556
0.0094	0.0088	-6.3%	3.5334
0.0099	0.010	+1.0%	2.332
0.0147	0.0149	+1.3%	2.7644
		average 3.4%	

The presence of a few grams of nitrite did not effect the accuracy of the method as shown in Table 1. The accuracy of the results was found to be dependent on the amount of the alkaline solution of arsenic (III) and, as a result, a minimum excess of the standard arsenic (III) solution was used. For example, a solution of 0.0128 ± 0.002 gram of peroxide in 25 ml of 0.05M arsenic (III) solution produced an error of 20 ± 2%.

Analysis procedure: The sample to be analysed was dissolved with continuous stirring in a five ml of an alkaline (20% NaOH) 0.05M arsenic (III) solution to which one drop of 1% W/V osmic acid solution (B.D.H.) had been added. After five minutes the solution was brought to pH7 by the addition of one gram of sodium bicarbonate followed by the dropwise addition of dilute hydrochloric acid until the solution was neutral as determined by using pH indicator paper The arsenic (III) was then back titrated with standard 0.05M solution of iodine using one drop of starch solution as indicator. The peroxide content was calculated from the difference between the amount of iodine solution required to react with five ml of arsenic (III) and that consumed after the reaction with sodium peroxide.

(c) Sodium monoxide

The sodium monoxide prepared from the decomposition of sodium peroxide was analysed by dissolving in ice cooled water. The solution was warmed to room temperature and then titrated with a standard solution of sulphuric acid using phenolphthalein as the indicator. The sodium peroxide impurity present was determined by titration with permanganate as described previously.

(d) Determination of platinum

The platinum oxide produced from the reaction of molten nitrite and sodium peroxide with metallic platinum was determined spectrophotometrically using a Unicam S.P.800. The platinum oxide particles were first separated by dissolving the quenched melt in water and filtering through No.4 sinter. Since the platinum oxide might be present in two oxidation states Pt(IV) and Pt(II), i.e., (PtO_2 and PtO), and, in order to avoid any alteration in the oxidation state of the platinum, a solution of 0.2M hydrochloric acid and 0.1M sodium chloride was used to dissolve the precipitate, a method originally developed by Anson and Lingane.(141)

Before dissolving the platinum oxide the air was purged from the acid solution with oxygen free-nitrogen. Because of the slow solubility of the precipitate, the solution was boiled gently until the precipitate was dissolved. The yellow solution produced was then cooled to room temperature and diluted to the required volume with water. Measurements were carried out using a spectroscopic cell with 1 cm pathlength over the wave lengths 30000 cm^{-1} - 50000 cm^{-1}.

(e) Qualitative analysis

Platinum: In addition to the spectrophotometric analysis, the platinum oxides were identified by the addition of potassium iodide solution which yielded a red colouration due to the formation of the $[PtI_6]^{2-}$ ion.(124)

Silicate: The silicate produced on adding peroxide to a nitrite melt contained in a Pyrex tube was determined qualitatively after first dissolving the precipitate in dilute sodium hydroxide. A drop of the solution and a drop of the ammonium molybdate solution were placed on a filter paper and warmed gently followed by a drop of benzidine. The paper was held over ammonia vapour and a blue colour was formed which indicated the presence of silicate.(124)

VIII.2.4 Instrumentation

The visible and ultraviolet spectra of aqueous solutions were carried out on a Unicam S.P.800. For high temperature melt solutions a Unicam S.P.700 spectrometer modified for use up to 1000°C was used. To detect the presence of peroxide ion in molten nitrite, the measurement was made on a thin film using 1 cm Spectrosil cells. A Cary 82 Raman Spectrometer was used for the identification of the peroxide ion in solid artificial mixed samples of sodium peroxide and sodium nitrite as well as the solid reaction products of the reaction of peroxide with a molten nitrite. Thermogravimetric analyses were carried out on a Stanton TR.1 thermobalance by the techniques described in Chapter III.

VIII.3 RESULTS

Sodium peroxide did not dissolve immediately when added to the melt at 250°C. The surface of the insoluble particles was found to become orange coloured. After filtering the melt, the particles were examined by Raman spectroscopy and showed two peaks at 736 cm^{-1} and 792 cm^{-1} which corresponded to the spectrum of sodium peroxide. The filtered melt did not show any indication of peroxide. Therefore, artificial mixtures of sodium peroxide and sodium nitrite in different proportions were mixed well and examined by Raman spectrometry in order to find the concentration of sodium peroxide in sodium nitrite that could be detected. The results showed that the minimum concentration which could be detected was 0.4 Mol %.

Other than Raman spectroscopy on cooled melts, ultraviolet measurements were carried out on a solution of sodium peroxide in a molten nitrite eutectic at 250°C. The measurements were made on a thin film of the melt, but the spectrum did not reveal an absorption band which could be attributed to the peroxide ion.

Since these methods were thus found not to be suitable for the determination of the concentration of peroxide ion in molten nitrite eutectic, an analytical method employing arsenic (III) was developed for the estimation of small amounts of peroxide ion, which is described in the experimental section. The results of this analytical method are presented later in this section.

Several reactions were carried out between sodium peroxide in sodium nitrite-potassium nitrite eutectic at different temperatures using containers of different materials. For example in a Pyrex test tube at 250°C the addition of 0.0486 gram of sodium peroxide to 0.893 grams of nitrite eutectic (5.7×10^{-2}m) showed that under continuous mixing the peroxide completely dissolved in the nitrite melt within 30 minutes and etching of the glass was observed after only 35 minutes.

On the other hand, in another experiment in which the glass surface area was increased by approximately 50% by inserting a glass tube into 12.6012 grams of nitrite eutectic containing 0.0399 gram of sodium peroxide (1.76×10^{-2} m), turbidity was observed in 10 minutes and on prelonged heating a white precipitate was formed. Qualitative analyses of the white precipitate formed showed silicate to be present. For a melt of a similar peroxide concentration, the attack at 300°C on the glass was found to be quicker than that at 250°C.

As glass was not inert towards a solution of sodium peroxide in molten nitrite, a zirconium metal crucible was used, since it was shown in Chapter VI that zirconium metal is stable in a nitrite melt containing sodium peroxide at temperatures less than 400°C. The reactions were carried out at temperature 275 ± 5°C

The equilibrium constants of the reaction of sodium peroxide with a nitrite melt (assuming the peroxide ion is in equilibrium with the nitrite ion) were calculated using the equation

$$K_{14} = \frac{[NO_3^-]\,[O^{2-}]}{[NO_2^-]\,[O_2^{2-}]}$$

in which $[NO_3^-] = [O^{2-}] = [O_2^{2-}]_{in.} - [O_2^{2-}]_{eq.}$ where $[O_2^{2-}]_{in}$ is the concentration of initial peroxide ion and $[O_2^{2-}]_{eq}$ is the concentration of the peroxide ion determined.

The equilibrium constant for several experiments using Pyrex were calculated from the peroxide ion analyses and the average of these results are given in Table 2.

Table 2

Results obtained from the reaction in glass tubes

Range of Initial Na_2O_2 m	Time in minutes	Temperature °C	Average value of K
$2.1 \times 10^{-2} - 4.05 \times 10^{-2}$	25	250	0.035 ± 0.02
$2.28 \times 10^{-2} - 2.74 \times 10^{-2}$	10	300	0.21 ± 0.02

The equilibrium constants determined using a zironium crucible, which was found to be inert to a solution of peroxide ion in a nitrite melt, are given in Table 3.

Table 3

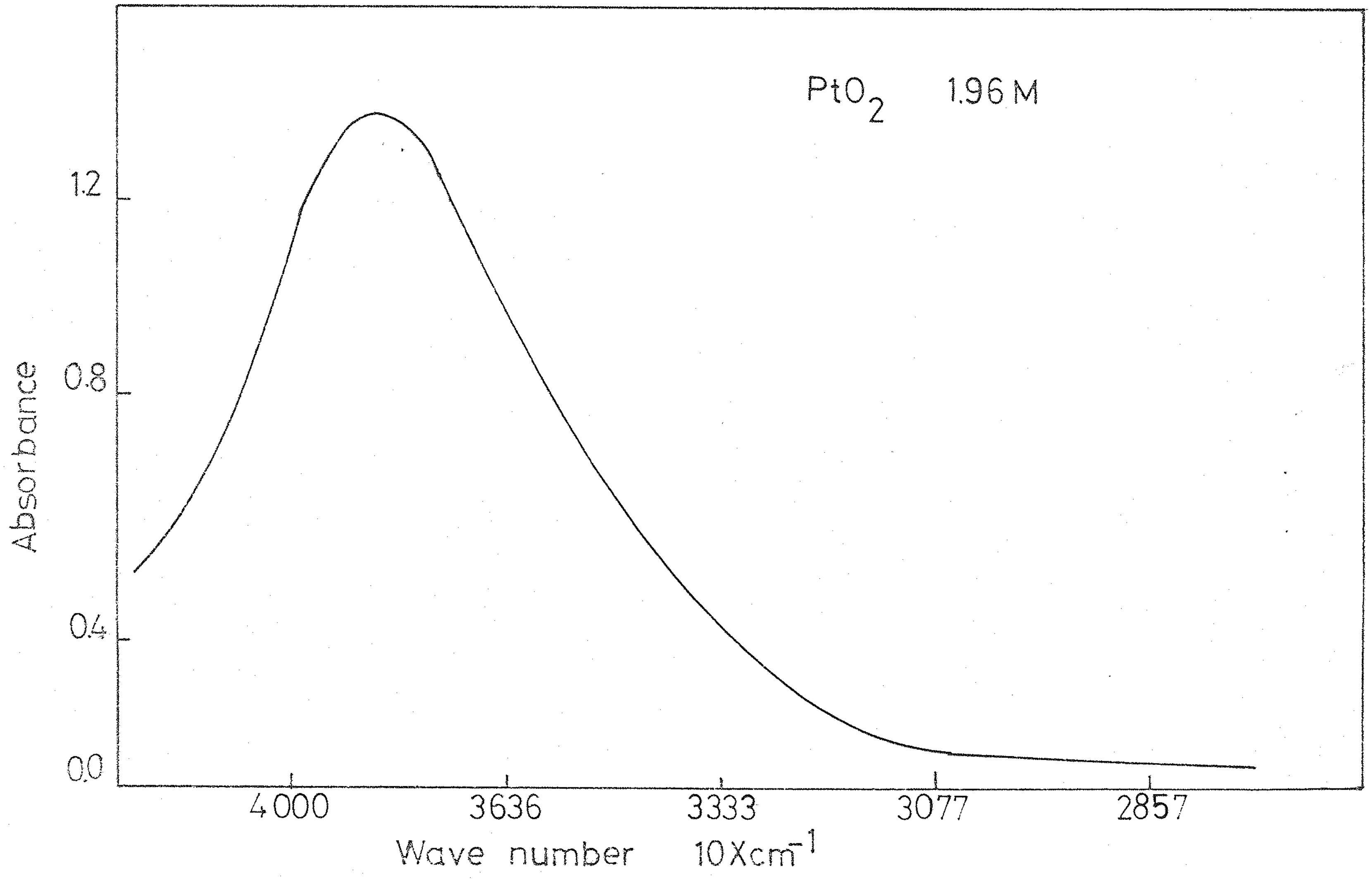
Results obtained from the reactions in a zirconium crucible

Na_2O_2 m	Time in hours	Temperature °C	K
4.3×10^{-2}	4	275	0.11
4.3×10^{-2}	8	275	0.10

In addition to the glass tubes and zirconium crucibles, a platinum crucible was used as a reaction vessel. About 0.0105 gram of sodium peroxide and 3.2057 gram of sodium nitrite-potassium nitrite eutectic (4.0×10^{-2} m) were mixed together and heated at 300°C. Immediately after the eutectic had melted the colour of the melt started to change to orange. After 10 minutes the colour became orange-red and then became red. In 30 minutes the colour of the melt changed back to yellow and black particles were observed in the melt. After dissolving the quenched melt in water the colour of the black particles changed to yellow. The yellow particles were filtered, dried, weighed, and dissolved in a solution of hydrochloric acid and sodium chloride. The ultraviolet spectra of this solution showed an absorption band at 38200 cm^{-1} indicating the presence of $PtCl_6^{2-}$ (Figure 1);(142) whereas no absorption band at 46000 cm^{-1}(143) which

Fig . I

U.V. Spectrum of Platinum(IV) in aqueous solution



would correspond to $PtCl_4^{2-}$ was observed. In other cases, the platinum crucible was extracted with the same mixture of hydrochloric acid and sodium chloride solution, but again no $PtCl_4^{2-}$ species were found.

The weight losses which the platinum crucible underwent when used for this reaction of sodium peroxide in nitrite melt are listed in Table 4.

Table 4

Weight loss of platinum crucible after reaction with
a mixture of Na_2O_2 and Na/KNO_2

Na_2O_2 m	Na/KNO_2 g	time hours	temperature °C	weight loss grams
0.28×10^{-2}m	2.7733	4	300	0.0005
4.0×10^{-2}m	3.2057	18	300	0.0007
8.3×10^{-2}m	6.3273	18	300	0.013
10.7×10^{-2}m	2.9936	2	300	0.0123
10.5×10^{-2}m*	2.5033	24	300	0.0002

* new platinum crucible.

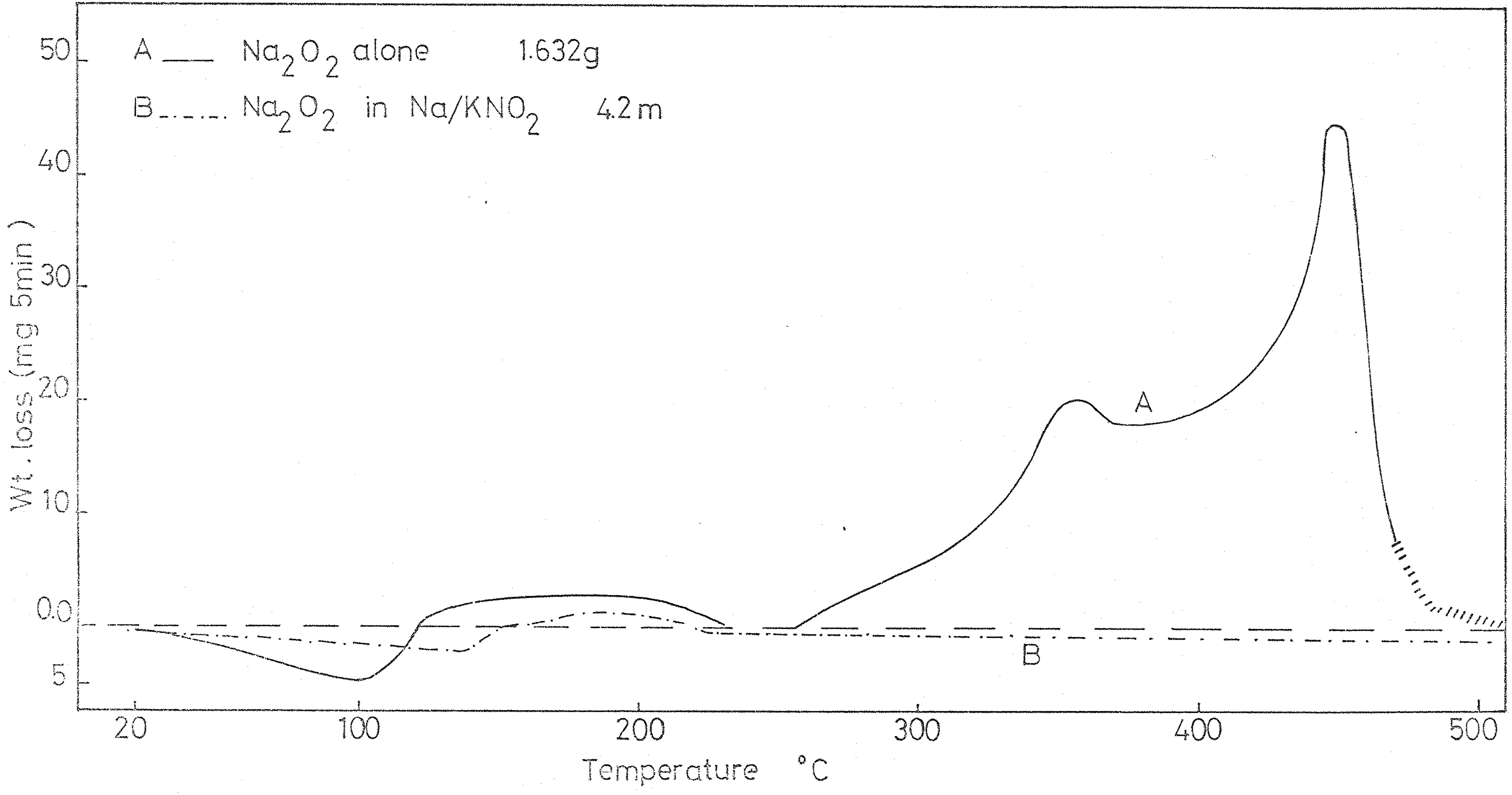
In addition to the reaction of sodium peroxide and nitrite eutectic with a platinum crucible, studies were also carried out on sodium peroxide solutions in equimolar sodium nitrate-potassium nitrate using a platinum crucible. For example, approximately 11 x 10^{-2} m of sodium peroxide in nitrate eutectic was heated at 300°C for 42 hours. No black particles were observed, neither in the molten nitrate nor in the aqueous solution after dissolving the quenched melt in distilled water.

On the addition of nitrite ion to the sodium peroxide-nitrate solutions, attack on the platinum crucible was observed, since black particles were formed, (e.g. on heating a mixture of 0.09 gram of sodium peroxide, 4.309 grams nitrate eutectic, and 2.8684 grams of nitrite eutectic at 300°C for 40 hours). The black particles, after dissolving the quenched melt in water, filtering and drying, were analysed spectrophotometrically and gave an absorption band at 38200 cm^{-1} which corresponded to the presence of PtIV (as $PtCl_6^{2-}$ in aqueous solution).

Thermogravimetric analysis of pure sodium peroxide in silica crucible (Figure 2 curve A) showed a slight gain in weight which commenced at room teperature and ceased at 120°C. This was followed by a steady loss in weight up to 240°C. A second stage of weight loss started at 260°C with a maximum rate around 460°C. The total weight loss was found to be 20.1%. (Calculated for loss of 1 O per Na_2O_2 20.5%.) However thermogravimetric analysis of sodium peroxide in sodium nitrite-potassium nitrite eutectic (Figure 2 curve B) showed a slight gain in weight from room temperature up to 150°C. At 170°C a slight loss in weight started which stopped at 220°C whereupon a slight gain in weight started once again and continued to 500°C. The second gain in weight was found to be 1.8%.

Fig . 2

T G A of Sodium peroxide in nitrite eutectic



VIII.4 DISCUSSION

The role of oxide ion, O^{2-}, in molten nitrates has been the subject of intense investigation in recent years. The existence of oxide ions as well as peroxide ion and superoxide ion were studied and two conclusions have been drawn. Zambonin and Jordan(144) have claimed that the oxide ion, O^{2-}, cannot exist in molten nitrate except at negligibly small amounts because it undergoes oxidation by nitrate ion to an equilibrium mixture of peroxide ion, O_2^{2-}, and superoxide ion, O_2^-:

$$O^{2-} + NO_3^- = NO_2^- + O_2^{2-} \qquad \text{VIII.5}$$

$$O_2^{2-} + 2NO_3^- = 2NO_2^- + 2O_2^- \qquad \text{VIII.6}$$

They also suggested that the oxide ion concentration in solutions with excess atmospheric oxygen is lower still because of the following equilibria

$$2O^{2-} + O_2 = 2O_2^{2-} \qquad \text{VIII.7}$$

$$O_2^{2-} + O_2 = 2O_2^- \qquad \text{VIII.8}$$

But, adopting the contrary view, Temple and Thickett(145) have recently concluded from potentiometric studies that oxide ions exist in nitrate melts, thus agreeing with the hypothesis postulated originally by Duke and co-worker(21) who reported that the oxide ion could exist in some solvated forms.

Temple and co-workers(145) criticised Zambonin's results on three counts. Firstly, because it is difficult to remove water completely from the nitrate melt, the following equilibrium takes place

$$H_2O + O^{2-} = 2OH^- \qquad \text{VIII.9}$$

thus decreasing the oxide ion concentration in the melt. Therefore, Temple and Thickett pointed out that if Jordan and Zambonin had not taken sufficient care to maintain a dry melt, the oxide may have been removed in accord to equation VIII.9 rather than an oxidation. Secondly, the presence of nitrite ion in measurable quantities, even in a carefully purified nitrate melt (1.9 x 10^{-4}m at 300°C)(146) might be sufficient to ensure that oxide ion O^{2-} is the predominant oxo-species present in the melt. And thirdly, the value of K_5which have been calculated partly from data obtained in molten hydroxide leads to an incorrect determination of the following equilibrium constant.

$$K_5 = \frac{[NO_2^-]\,[O_2^{2-}]}{[NO_3^-]\,[O^{2-}]} \qquad \text{VIII.10}$$

A value of approximately three for this constant was calculated by Jordan and Zambonin by utilizing data obtained in molten hydroxide as well as in molten nitrate. Whereas the K_5 value calculated by Temple, assuming that 99% of the oxide ion added is to remain unchanges at a level of 10^{-4}m in the presence of 10^{-4}m NO_2^-, has been found to be 10^{-6}.(145) In very recent work, Burke and Kerridge have reported a K_5 value of 1.2 based on a chemically determined equilibrium constant for the thermal decomposition of nitrate melt and a thermodynamically calculated equilibrium constant for the solid state oxidation of sodium monoxide to sodium peroxide by oxygen.(147)

Recently, Zambonin(148) restated his results in answer to the criticisms of Temple and Thickett and stated that in a dry, oxygen-free nitrate melt the concentration of oxide ion, O^{2-}, is much lower than that of the products of its oxidation, peroxide and superoxide, and the presence of traces of nitrite ion do not exclude reactions VIII.5 and VIII.6. He confirms his statement by the calculation of the equilibrium concentrations of the various oxide ions.

By a similar calculation, Zambonin reinforced his result when he found that in the presence of oxygen the conversions of oxide ion and peroxide ion to superoxide ion are more complete. Therefore, under such experimental conditions, the superoxide ion became the predominant oxo-species. This result was confirmed by Schlegel(149) who monometrically determined an equilibrium constant for

$$K_8 = \frac{[O_2^-]^2}{[O_2^{2-}]\,[O_2]} \qquad \text{VIII.11}$$

which was in agreement with that calculated by Zambonin.

In the presence of water and other acidic species, i.e., CO_2 and SiO_2, Zambonin reported that the formation of peroxide and superoxide ions can be limited by a reduction in the oxide ion concentration as follows

$$CO_2 + O^{2-} = CO_3^{2-} \qquad \text{VIII.12}$$

$$SiO_2 + O^{2-} = SiO_3^{2-} \qquad \text{VIII.13}$$

Finally Zambonin dismissed any influence from the use of a platinum crucible since he obtained similar results when the experiments were carried out in teflon.

All the previous work described above has been done in nitrate melts and the equilibrium constants have always been estimated and not directly determined, whereas in the present study the investigation has been carried out in nitrite melt and the equilibrium constant has been directly determined.

In sodium nitrite-potassium nitrite the reaction of peroxide ion and nitrite ion was found to be

$$NO_2^- + O_2^{2-} = NO_3^- + O^{2-} \qquad \text{VIII.14}$$

with the equilibrium constant calculated to be

$$K_{14} = \frac{\left[[O_2^{2-}]_{in} - [O_2^{2-}]_{eq}\right]^2}{[NO_2^-]\,[O_2^{2-}]} \simeq 0.1 \qquad \text{VIII.15}$$

Since reaction (VIII.5) is the reverse of the reaction which occurs when sodium peroxide is added to a nitrite melt (reaction VIII.14), the reciprocals of the equilibrium constant K_5 estimated by Zambonin can be compared to K_{14} determined in nitrite melt. The previously estimated value $\frac{1}{K_5} = 0.33$, compares favourably with that $K_{14} \simeq 0.1$ directly determined in the present work. The differences are small considering that K_5 has been derived from results in both nitrate and hydroxide melts and the nitrate melt work involved the use of a platinum crucible which means that some error may have occurred due to the attack on platinum.

The equilibrium concentration of peroxide ion determined in several experiments was small when compared with the initial concentration of the same ion (Table 5) which led to the conclusion that the equilibrium concentration of monoxide ions in the melt is approximately equal to the initial peroxide ion concentration.

Table 5

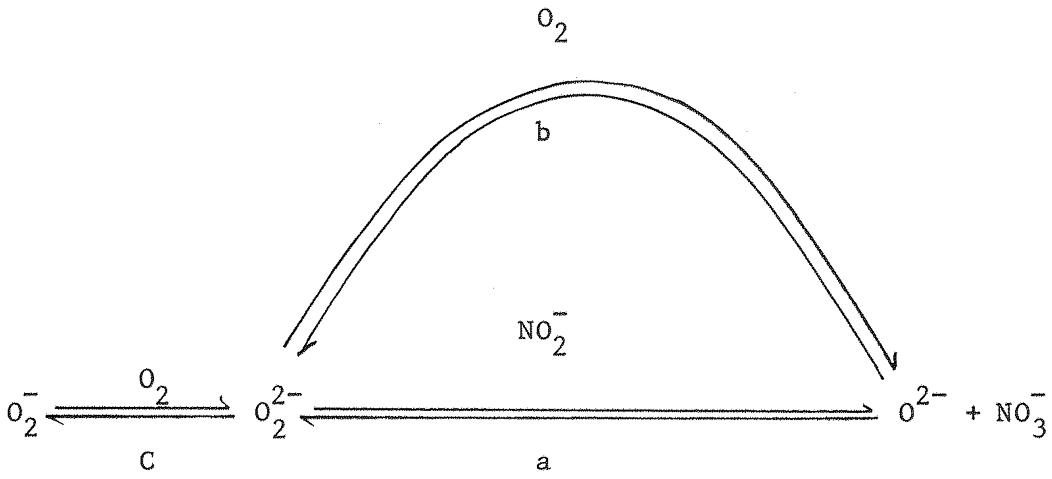
Vessel	Temperature °C	Time	Initial conc.	Equilib. conc.
Pyrex	250	15 minutes	2.1×10^{-2}	0.09×10^{-2}
"	250	15 minutes	4.0×10^{-2}	0.16×10^{-2}
"	250	25 minutes	1.76×10^{-2}	0.07×10^{-2}
"	300	25 minutes	2.74×10^{-2}	0.039×10^{-2}
Zirconium	275	4 hours	4.3×10^{-2}	0.12×10^{-2}
"	275	8 hours	4.3×10^{-2}	0.14×10^{-2}

Since the equilibrium concentration of peroxide ion using zirconium crucible is very similar to that obtained using a Pyrex tube, the attack on the glass can be considered negligible and to have a negligible effect on the oxide ion concentration over a short period of time.

The effect of water on the oxide ion concentration is not considered significant since the melt was dehydrated under vacuum at 230°C for 24 hours.

The presence of oxygen in the melt can effect the equilibrium concentration of the peroxide ion as well as that of the oxide ion according to reactions VIII.7 and VIII.8. Thermogravimetric analysis of sodium peroxide in a nitrite eutectic showed a steadily slight gain in weight which was considered to be due to the reaction of oxygen with oxo-species. If this suggestion were true, then the gain in weight would be a cyclic reaction as shown in Figure 3.

Figure 3



The reaction of peroxide with oxygen to form superoxide (reaction "c") could be excluded since the reaction of peroxide with nitrite (reaction "a") is more probable.

The fact that no weight loss was obtained which could be attributed to the decomposition of peroxide(85) ion indicates the consumption of peroxide ion with the formation of a high concentration of oxide ion by reaction "a". Therefore, the slight gain in weight is probably due to the reaction of oxide ion and oxygen to form peroxide ion which in turn reacts with the nitrite ion to form the nitrate and oxide ion. The cyclic series of reactions ("a" and "b") would take place until the nitrite ion were totally consumed.

It is considered that the slight uptake of oxygen would have only a negligible effect on the equilibrium constants determined experimentally for reaction VIII.14 since this gain in weight was obtained only after 6 hours while the equilibrium constants were normally calculated from the analyses of samples taken within 30 minutes. Furthermore, the equilibrium constants determined using a zirconium crucible at four and eight hours (see Table 3) show that the absorbed oxygen did not have a major effect.

The extent of attack on glass was found to depend on several factors temperature, peroxide concentration, and the surface area of the glass in contact with the melt. The amount of etching was proportional to these factors. The white precipitate which occurred on prolonged heating of the peroxide ion in a nitrite melt in a Pyrex container was shown to be silicate rather than an alkali metal oxide. Furthermore, since the initial peroxide concentration was 1.76×10^{-2}, and sodium monoxide was found to be soluble to at least 4.8×10^{-2}m at the same temperature the precipitate could not have been sodium monoxide produced by reaction VIII.14.

A platinum crucible containing a mixture of peroxide and nitrite was also found to be attacked.

The black particles which formed were identified as PtO_2 from the ultraviolet spectrum of the aqueous solution of these particles. The absorption band, corresponding to that of $PtCl_6^{2-}$ at 38200 cm^{-1}, was present.(141) No peak at 46000 cm^{-1} was observed which could be attributed to the presence of $PtCl_4^{2-}$.(142)

The attack on platinum cannot be considered to be due to a direct reaction by peroxide ion, since peroxide ion in nitrate melt did not show any attack within 42 hours. Therefore, the presence of nitrite ion must be an essential factor in attacking platinum. Since neither peroxide alone nore nitrite alone is reactive towards platinum, an additional new intermediate species is suggested to be present. The oxidizing species may well be the peroxonitrite ion which would be formed by the reaction

$$O_2^{2-} + NO_2^- = [ONOO^-] + O^{2-} = NO_3^- + O^{2-} \qquad \text{VIII.16}$$

followed by

$$2ONOO^- + Pt \rightarrow PtO_2 + 2NO_2^- \qquad \text{VIII.17}$$

The change in colour of the melt observed on the addition of peroxide (yellow → red → yellow) is possibly due to the formation of peroxonitrite which then degraded via the reaction with platinum or by isomerization to nitrate.(150)

The formation of peroxonitrite in aqueous solution from acidified hydrogen peroxide and sodium nitrite solution, followed by immediate addition of alkali to stabilise the peroxonitrite, has been studied.(151,152) The formation of peroxonitrite ion probably takes place between molten nitrite and peroxide ion as follows:

$$NO_2^- = NO^+ + O^{2-} \qquad \text{VIII.18}$$

$$NO^+ + O_2^{2-} = ONOO^- \qquad \text{VIII.19}$$

The above reactions are analogous to those given for the formation of peroxonitrite in water, which recently has been reviewed.(153)

From the above discussion a general conclusion can be drawn which can be summarised as follows:

Firstly, oxide ion can exist at an appreciable concentration in a nitrite melt whereas in nitrate melts it exists in a negligible low concentration.

Secondly, platinum metal is not inert in the presence of a mixture of peroxide and nitrite. Therefore, the estimation of the equilibrium constant from the result obtained in a platinum crucible can definitely be effected by the side reaction as shown by the present study. However, it is still not known at what concentration of nitrite ion and peroxide ion and over what time intervals the attack on platinum would affect the results obtained by electrochemical methods which emply platinum electrodes in a nitrate melt contained in platinum vessel.

Thirdly, oxygen has an effect on the concentration of the peroxide ion, but that can be minimized or excluded if the reaction is carried out within a short period of time.

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