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REACTION OF SOME BISMUTH COMPOUNDS AND SOME COMPOUNDS OF PLATINUM METALS IN A MOLTEN NITRATE EUTECTIC

A Thesis presented to the University of
Southampton for the degree of
Master of Philosophy

by
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ABSTRACT

FACULTY OF SCIENCE

CHEMISTRY

Master of Philosophy

REACTION OF SOME BISMUTH COMPOUNDS AND SOME COMPOUNDS OF PLATINUM METALS IN A MOLTEN NITRATE EUTECTIC

by

ABOLFAZL ZELLIPOUR

The reaction of three compounds of bismuth in the two common oxidation states of (III) and (V), and chlorides of palladium, ruthenium and rhodium have been studied in pure molten lithium nitrate-potassium nitrate eutectic and also in the presence of acidic and basic species and of chloride ligands. Results have elucidated both oxidation reduction and acid-base reactions of bismuth (III) chloride, bismuth (III) nitrate pentahydrate , sodium metabismuthate (V), palladium (II) chloride, hydrated ruthenium (III) chloride and hydrated rhodium (III) chloride.

The reaction of bismuth (III) chloride in pure melt or in the presence of acidic species gave bismuth (III) oxyanion products (e.g. BiO_xCl_y, $(BiO)_zCrO_4$ or Bi_2O_3) but more interestingly when bismuth (III) chloride and bismuth (III) nitrate pentahydrate reacted in a melt containing basic species (NaOH, Na_2O_2), lithium bismuthate (V) was formed.

In the case of platinum metal compounds, palladium (II) chloride and hydrated rhodium (III) chloride were soluble in the pure molten nitrate and in the presence of ligands probably with the probable formation of the nitrato-chloro and nitrito-chloro complexes respectively. In every case the initial insoluble reaction products of palladium (II) chloride were palladium (II) oxide and for hydrated rhodium (III) chloride were the rhodium (III) oxide mixed with rhodite (III). Hydrated ruthenium (III) chloride reacted in pure melt and in the presence of basic species to form ruthenium (IV) oxide, but this was mixed with ruthenate (VI) when a high concentration of sodium hydroxide was used. Absorption spectra of the above in melt and in aqueous solutions were determined.

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CHAPTER ONE: INTRODUCTION

1.1 General introduction

The investigations of molten salt systems have increased so rapidly that molten salt chemistry has become a well defined field owing to its application in modern technology, and due to the special properties of molten salts which can give them advantages over aqueous solvents or other room temperature non-aqueous solvents.

The most important scientific studies in this field were carried out in the nineteenth century by Sir Humphrey Davy.(1) In these, he found that perfectly dried potassium hydroxide was virtually a non-conductor but it would 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 8×10^6 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 as fluxes, in other high temperature metallurgical processes such as brazing, coating and soldering, and have long been used by analysts to render soluble metals, ores and precipitates which were otherwise insoluble in ordinary solvents.

Despite such early uses and studies due to their advantages, their studies in molten salts have mainly been confined to the determination of physical, electrochemical(5-9) or spectroscopic properties of these systems. The study of chemical reactions in molten salts, their uses in industries(10) and other useful applications in modern life are only now receiving relatively intense attention.

The application of molten salts to nuclear technology was, in fact, begun in the early 1940's in the United States to develop nuclear power for both military and commercial uses. Molten fluoride appeared particularly appropriate in this respect due to their high solubility for uranium, plutonium, cerium and many other radioactive rare earth metals(12-14), 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(11). More recently the Molten Salt Reactor Experiment (M.S.R.E.) has successfully shown that a molten salt nuclear reactor can be operated for a number of years for the generation of electrical power using a fluid fuel of uranium fluoride, lithium fluoride, beryllium fluoride and zirconium fluoride at a temperature greater than 625°C. 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.

Molten salts, due to their electrochemical properties, have been used as the electrolytes in fuel cells for the production of electric power, one type of high temperature fuel cells utilizes as the electrolyte a mixture of lithium, sodium and potassium carbonates(16). Cells of this type can operate continuously for several months, between 550°C and 700°C, using town gas, hydrogen, carbon monoxide and natural gas. Requirements for a high energy conversion device have led to the study of a lithium-chloride battery(17). The open circuit voltage was found to be about 3.5 volts in a system which operates at 650°C using molten lithium chloride as the electrolyte.

The chemistry of solutes and their behaviour in molten salts has offered an interesting line of studies. New species have been shown to exist in fused salts, such as the formation of a low oxidation state of zinc (Zn_2^{2+}) in zinc-zinc chloride melts at 500°C-700°C(5). The formation of monovalent bismuth (Bi^+) has also been claimed when bismuth metal added to molten bismuth trichloride or bismuth trichloride to either molten aluminium bromide-sodium bromide eutectic at 250°C or in molten $AlCl_3$-NaCl at 310°C. This ion was found to exist in equilibrium with another species $(Bi_5)^{3+}$ in dilute solution and $(Bi_8)^{2+}$ at higher concentrations, the equilibrium and spectra of these species have been studied (6-9). However, more recently it has been reported that this supposed solid monochloride is in fact $Bi_{24}Cl_{28}$, which x-ray diffraction has shown to consist of $4(BiCl_5)^{2-}$, $(Bi_2Cl_8)^{2-}$ and $2(Bi_9)^{5+}$ ions(60). The low oxidation states Pb^{2+}, Cd_2^{2+} and Sn_2^{2+} have been reported to be produced by one electron reduction in molten $NaAlCl_4$(11). Electrochemical studies in molten salts have led to the suggestion that some condensed species of molybdate, tungstate and chromate ($Mo_2O_7^{2-}$, $W_2O_7^{2-}$ and $Cr_2O_7^{2-}$) were present in equilibrium with oxide ions in nitrate melts.(12-14)

The development of high temperature ultraviolet and visible spectrophotometers has stimulated studies of the chemistry of the coordination of transition metals in molten salts. The wide range of melts, from single alkali halide melts through cyanides and cyanates to oxyanion melts such as nitrates, sulphates, etc., provides a good environment for the coordination of transition metal ions. The liquid range of molten salts makes them particularly useful for a study of the effect of temperature on coordination number. For example, trivalent titanium ion in lithium chloride-potassium chloride eutectic showed a change in coordination number from six to four over the temperature range 400-1000°C.(15)

1.1.1 Acid-base reactions

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 reactions in aqueous chemistry, and an operational acid-base definition has been formulated for oxyanion systems. One of the earliest theories used to describe acid-base reactions in molten salts was that due to Lewis. A Lewis acid is defined by an electron deficiency and its ability to behave as an acceptor of a pair of electrons, while a Lewis base is visualised as an electron pair donor and in molten salts is invariably an anion.

According to Lux(16), acids and bases can be defined on the basis of the equation:

$$\text{Base} \rightleftarrows \text{Acid} + O^{2-} \tag{I.1}$$

The above equation is analogous to the acid-base definition of Bronsted for the protolytic systems 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,(17-20) and his name is often used in conjunction with Lux when these systems are discussed.

The first studies of nitrate acid-base reactions were made by Duke and coworkers on a series of reactions involving the acid-base equilibrium in molten sodium nitrate-potassium nitrate eutectic. They suggested from measurements of e.m.f.(21) kinetic studies(22), acid-base titrations(23) and stoichiometry of a number of oxidation reactions(24-27), that the nitryl ion (NO_2^+) was the acidic species in fused nitrates. Duke and co-workers(21,28), suggested that this species was formed by the self dissociation of nitrate ions as equation:

$$NO_3^- \overset{K}{\rightleftarrows} NO_2^+ + O^{2-} \tag{I.2}$$

The extent of this ionisation, as calculated from potentiometric measurements, is very small, with a value of 2.7 ± 0.3 x 10^{-26} at 250°C and 5.7 ± 0.1 x 10^{-24} at 300°C in sodium nitrate-potassium nitrate eutectic. Thus an oxide acceptor would act as an acid by displacing the equilibrium (I.2) to the right and increasing nitryl ion concentration would be found with increasing strength of the acid. The general reaction will be:-

$$A + NO_3^- \rightleftarrows AO^{2-} + NO_2^+ \qquad I.3$$

The nitryl ion was thought to react with excess of nitrate thus:

$$NO_2^+ + NO_3^- \rightleftarrows \{N_2O_5\} \rightarrow 2NO_2 + \tfrac{1}{2}O_2 \qquad I.4$$

Support for this mechanism has been obtained from study of the reaction of bromide when added to the fused nitrate-dichromate solution(22). The gaseous products from this reaction were found to be nitrogen dioxide and bromine:-

$$NO_2^+ + Br^- \rightarrow \{NO_2Br\} \rightarrow NO_2 + \tfrac{1}{2}Br_2 \qquad I.5$$

The equilibria postulated above have been criticised by Topol and co-workers(29), who did not find any evidence for the existence of the nitronium ion in their voltammetric and chronopotentiometric studies on solutions of acids and bases in sodium nitrate-potassium nitrate eutectic between 280°C and 350°C. They suggested that the acidic species was nitrogen dioxide itself, arising from the acid-base equation:-

$$2NO_3^- \rightarrow 2NO_2 + \tfrac{1}{2}O_2 + O^{2-} \qquad I.6$$

This hypothesis has been criticised and it has now become less popular. The electrochemical results indicating that nitrogen dioxide to be the acidic species are not completely substantiated and they do not provide any explanation of the pathway by which the pyrosulphate could react to produce the end products, nitrogen dioxide and oxygen. Topol and co-workers concluded that the behaviour of nitrogen dioxide is equivalent to that attributed to nitryl ion. However in every case acid-base reaction pathways can be more easily explained by postulating a nitryl ion than using nitrogen dioxide alone.

The nature of the basic anion in nitrate melts is complex and remains an area of major controversy. Most of the early workers assumed that the oxide ion, O^{2-}, was the basic species and was stable in the melt. Among these, Duke and co-workers(31), for example, suggested a Lux-Flood acid-base type equilibrium (I.2) in which oxide ions were the active species. According to this, nitrate melts would serve as a medium for oxide ion transfer reactions with nitrate ion acting as the oxide ion source itself.

Using this hypothesis the behaviour of oxygen electrodes in molten salts has been widely studied(32,33). The interest in these electrodes is due to the possibility of detection oxide ions, which may involve acid-base equilibria such as (I.2) and (I.3). The electrode reaction generally assumed by many workers(21,33,35), is:-

$$\tfrac{1}{2}O_2 + 2e^- \rightleftarrows O^{2-} \qquad \text{I.7}$$

The pioneering work of Zambonin and Jordan(36) was in conflict with the earlier assumption. These workers maintained that the classic supposition about the high stability of oxide ion cannot be correct, and instead suggested that oxide is actually oxidized to peroxide (O_2^{2-}) and superoxide (O_2^-) in molten nitrates, according to the equilibria:-

$$O^{2-} + NO_3^- \rightleftarrows NO_2^- + O_2^{2-} \quad K \simeq 3 \qquad I.8$$

$$O_2^{2-} + NO_3^- \rightleftarrows 2NO_2^- + 2O_2^- \quad K = 7 \times 10^{-11} \qquad I.9$$

Additionally, under a dry oxygen atmosphere, the species are interrelated by the disproportionation equilibria:-

$$2O_2^{2-} \rightleftarrows O_2 + 2O^{2-} \quad K = 10^{16} \qquad I.10$$

$$2O_2^- \rightleftarrows O_2 + O_2^{2-} \quad K = 2 \times 10^6 \qquad I.11$$

While in the presence of water, the oxide ion is converted into hydroxide, due to the reaction between superoxide and the water$^{(37)}$.

$$O^{2-} + H_2O \rightleftarrows 2OH^- \qquad I.12$$

Another hypothesis on the stability of the oxide ion considered the possibility of solvation with nitrate ion in the melt to give the orthonitrate ion, NO_4^{3-}, as is suggested by the classical works of Zintl and Morawietz$^{(38)}$ and of Kuhlmuller$^{(39)}$. Lately Shams El-Din and El-Hosary$^{(40)}$, have suggested the existence of the pyronitrate ion, $N_2O_7^{4-}$, in which the oxide ion is solvated with two nitrate ions. A stabilisation of this type can be represented by the general Lux-Flood acid-base equation (A is an oxide acceptor):

$$A + O^{2-} \rightleftarrows AO^{2-} \qquad I.13$$

In their recent work Burke and Kerridge developed an evaluation of the way that the stabilisation of oxide ion by nitrate can effect the concentrations of the various anionic oxygen species (O^2, O_2^{2-}, O^{2-}) in a nitrate melt. They found that the main species were the superoxide and the stabilised oxide, AO^{2-}, while the free oxide ion could only be in a concentration of less than 0.001 per cent of the initial value. Therefore, they suggested that the electrode reaction might be better written as:

$$AO^{2-} \rightleftarrows A + \tfrac{1}{2}O_2 + 2e^- \qquad \text{I.14}$$

One of the most important factors which can explain those differences found by the several groups of workers is the type of container they used. One electron slope behaviour is observed if Teflon(43) or platinum(52) containers are used, whereas the two electron behaviour is observed only if glass or silica containers are used. These results suggest the participation of some silicate from the container. Therefore reactions (I.13) and (I.14) are more exactly represented by equations (I.15) and (I.16) respectively:

$$X\,SiO_2 + O^{2-} \rightleftarrows (SiO_2)_X.O^{2-} \qquad \text{I.15}$$

$$(SiO_2)_X.O^{2-} \rightleftarrows X\,SiO_2 + \tfrac{1}{2}O_2 + 2e^- \qquad \text{I.16}$$

The Lux-Flood acid-base equilibrium constants which have been determined using an oxygen electrode in nitrate melts contained in glass vessels can then be represented by the reaction:

$$A + (SiO_2)_X.O^{2-} \rightleftarrows AO^{2-} + X\,SiO_2 \qquad \text{I.17}$$

If, however, the equilibrium was measured in a silica-free nitrate melt, the reaction would be equation (I.13).

I.I.2 Oxidation-reduction reactions

A number of metals have been found(24) to be oxidized in molten lithium nitrate potassium nitrate eutectic, producing in some cases insoluble oxides (e.g. MgO, CaO) or oxyanion ($Cr_2O_7^{2-}$), while in other cases the oxidation is only superficial (Ti,V, etc.). In the presence of an acidic species, the reaction may be different. For example, vanadium metal does not react with the nitrate melt, but in presence of $S_2O_7^{2-}$, an insoluble oxide is formed.

Spink(25), Gruen(44) and co-workers have reported that a number of salts initially dissolve in nitrate melts, subsequently oxidizing either to anion species or to oxides. For example, Cr(III), Nb(IV) and Pu(III), after dissolving in nitrate melt are oxidized to anionic species, while Mn(II), Th(IV) and Ce(IV) have been found to oxidize to insoluble oxides. The oxidation of U(IV) to U(VI) has been reported(45) to occur at the temperature of 175°C in lithium-nitrate-sodium nitrate eutectic as in equation:-

$$U^{4+} + 2NO_3^- \rightarrow UO_2^{2+} + 2NO_2 \qquad I.18$$

Other reactions have been reported to involve both acid-base reactions and oxidation-reduction reactions. Van Norman and Osteryoung[27] have found that the melt oxidized the iodide ion to give iodine in the presence of a Lux-Flood acid as in equation:-

$$NO_3^- + PO_3^- + I^- \rightarrow PO_4^{3-} + \tfrac{1}{2}I_2 + NO_2 \qquad I.19$$

and it may be visualised that the nitryl ion if formed is a stronger oxidizing agent than nitrate ion, hence:-

$$NO_3^- + PO_3^- \rightarrow NO_2^+ + PO_4^{3-} \qquad I.20$$

$$NO_2^+ + I^- \rightarrow NO_2 + \tfrac{1}{2}I_2 \qquad I.21$$

1.1.3 Object of the present work

The main justification for the study of molten nitrate chemistry, as for any other non-aqueous solvent, is to understand the acid-base reactions, oxidation-reduction and complexing reactions involved.

Most of the research reported on molten nitrate systems has centred on the study of transition metal compounds, perhaps the largest contribution in this area has come from the University of Southampton by several workers like Brough,(46) Tariq(47), Habboush(48), Cancela Ray(49) and Shakir(50).

In the present work, the reactions chosen for study were those of compounds of elements for which little or no data in nitrate melt has been reported. Chapter III deals with reactions of bismuth compounds in the lithium nitrate-potassium nitrate eutectic and in the melt containing acidic, basic species. In Chapter IV the reactions of some platinium metals and their spectra in lithium nitrate-potassium nitrate eutectic and in the nitrate melt containing potassium chloride, are discussed.

A wide variety of techniques was used in order to obtain the necessary information, such as themogravimetry analysis, when a volatile product was obtained in the reaction,x-ray diffraction for the study of the precipitates, intermediate products and sublimates. Quantitative and qualitative analysis were also used, in order to determine the stoichiometry of the reactions.

CHAPTER TWO: EXPERIMENTAL

2.1 Introduction

The nitrates of the alkali metals both pure and in eutectic mixture have been the subject of many investigations. The melting points of the alkali metal nitrates increase with the molecular weight, for example, $LiNO_3$, 225°C, $NaNO_3$, 306.8°C and KNO_3 334.5°C. But in their binary eutectic, the melting point does not always increase with the mean molecular weight, it also depends on the difference in size of cations in the eutectic mixture, a larger difference giving a lower melting point. For example, $LiNO_3$-KNO_3 (43:57 mole %) with the average molecular weight of 77.2 g melts at 132°C, $LiNO_3$-$NaNO_3$(54:46 mole %) with average molecular weight of 76.2 g melts at 193°C and $NaNO_3$-KNO_3(50:50 mole %) with the average molecular weight of 93g melts at 220°C.

2.2 Preparation of the eutectic

The eutectic was prepared as required by heating separately hydrated lithium nitrate (B.D.H. Reagent Grade) and potassium nitrate (Hopkin and Williams, General Purpose Reagent) in an oven at 150°C for one day to obtain either nitrate in the anhydrous state. Great care had to be taken with the lithium nitrate which tended to froth and run down the side of the dish. The two compounds were allowed to cool in desiccator, and then weighed and mixed to give a eutectic mixture of 43 mole % lithium nitrate. This was melted at 180°C-200°C and stirred at intervals. After about 15 hours, the melt was filtered to remove solid matter, in a forced convention oven at about 180°C, then poured into a porcelain dish and allowed to cool in a dessicator. The melt could then be conveniently broken up for storage in a bottle kept in a dry box.

Final dehydration was carried out by heating the melt to about 250°C and evacuating to about 10^{-2}mm Hg for about 12 hours. If the melt was evacuated too quickly, bubbling and bumping could be quite violent, causing the melt to splash and solidify on the upper, cooler parts of the apparatus before it could be dehydrated. To avoid this, the pressure was gradually reduced using an Edwards needle valve.

An alternative method of preventing bumping, was to evacuate the solid melt with the needle valve closed, and slowly raise the temperature. The latter method proved to be best and was adopted.

2.3 Furnaces and their control

The furnace used in all experiments consisted of a 8cm deep steel pot with an inner diameter of 3 cm, wound with nichrome resistance wire, threaded with insulating refractory beads and embedded in alumina cement. The pot was held in a square asbestos box and the free space filled with "Micafil" as thermal insulation. A typical furnace had a rating of about 150 watts and a temperature range up to 800°C, depending on the resistance wire and the number of windings.

The furnace was controlled by an Ether Transistor Controller. The voltage was reduced to the optimum value for the furnace by a Variac. Temperature measurements were made using glass filter insulated Chromel-Alumel thermocouple placed between the tube and the furnace wall. This system gave a furnace temperature control of ± 2°C through the range 20-800°C.

2.4 Thermogravimetric analysis

The weight loss due to gaseous reactions products, the temperature at which the reaction began, the temperature of maximum rate of loss and the presence of multistage reactions were determined on a Stanton TR-1 recording thermobalance. This provided a continuous record of the weight loss up to a maximum of one gram with one milligram sensitivity. The crucible and sample were placed inside the vertical furnace suitable for use to 1000°C.

2.4.1 Factors relating to the use of the thermobalance

The temperature at which the decomposition of a pure substance or the reaction between two substances commences is not a fixed quantity, but depends on a considerable number of variables which are summarised below(51). It was found that the weight losses recorded were usually reproducible, within the limits of experimental error (3-5% of weight loss), if a number of precautions were taken.

(I) Differenttypes of thermocouple and crucible material have an effect on decomposition temperature, for example, it is stated(57) that there is a difference in the thresholds of decomposition in a metal crucible (i.e. platinium, gold, nickel) which have high thermal conductivities and those in crucibles made of oxides or silicates. These differences may run as high as 5-10°C. However, these were eliminated by using the same type of thermocouple and the same type of vitrosil crucible in all cases.

(II) The rate of heating has a marked influence on reaction temperatures, particularly when the reaction is taking place in several stages. A low heating rate lowers the temperature of the reaction stages and brings out the individual stages clearly, whereas at a high rate the stages tend to merge with loss of detail. In the present investigation, the slowest heating rate available, 2°C per minute, was always used to obtain as much detail as possible.

(III) The mass of reactants affected the reaction temperature by causing a temperature lag between furnace and reactants, the lag naturally becoming greater with a larger total weight of reactants. To avoid this approximately the same total weight of reactants was used for each thermogram.

(IV) The particle size of the reactants and the extent of mixing were also important variables, since the decomposition of a single substance has been found to begin at a lower temperature the smaller the particle size(52). In addition, the temperature of reaction can be much lower with well mixed reactants than with unmixed, while for certain reactants and melts different proportional weight losses have been obtained. As would be expected, the reactions in which different degrees of mixing caused most change in the reaction temperatures were those starting at temperatures below or at the melting point of the eutectic. In suchcases, reaction probably began as a result of solid state diffusion or in the low melting ternary eutectic formed at the interface between solute and solvent particles. Thus in order to obtain a better mixture, the reactants were finely ground before use.

2.4.2 Isothermal operation of thermobalance

The Stanton TR-1 thermobalance has a control which allows it to maintain the temperature at a constant value. In a multi-stage reaction, this has great value when, under steady heating, a reaction causing weight loss is followed, while it is still incomplete by a second higher-temperature reaction also causing loss. In such cases, the weight loss from the first reaction will tend to merge, with a more or less obvious point of inflection, into the loss from the second. In these cases, the first reaction may sometimes be completed by holding the furnace at a constant temperature corresponding to the maximum rate of the first reaction, where the second reaction had not started or was proceeding at a negligible rate. This practice was, of course, unnecessary when the two reactions were separated by an appreciable temperature range of negligible weight loss. Then the thermogram could also be stopped between the two reactions and the melt could be quenched and analysed for the species produced in the first reaction.

2.5 X-ray diffraction

A Philips x-ray powder diffractometer was used to identify the reaction products. The diffractometer consists of a goniometer for measuring the diffraction angles and a system of electronic circuits for determination of the intensity of diffraction at any angle. The goniometer employed a large flat sample combined with a parafocussing arrangement to increase the intensity of diffraction and x-ray counter to detect the diffracted radiation. Glass slides were used for the preparation of the specimen. A large amount of the finely ground powder was spread on the glass and smoothed so that it was flat. The apparatus recorded automatically the relative intensities of the peaks for the various values of 2θ. From the chart it is then possible to get the values of the "d"-spacings,

$$\lambda = 2d \sin \theta \qquad \text{II-1}$$

providing the value of λ is exactly known. The "d"-spacing and intensity values were compared with those found in the American Society for Testing and Materials (53) (A.S.T.M.) index whose has lately been changed to the Joint Committee on Powder Diffraction Standards (54) (J.C.P.D.S.).

2.6 Spectrometer and heating methods

The spectrometer used in this work was a Unicam SP-700 model with a range from 53,000 cm^{-1} to 3000 cm^{-1}. This spectrometer was modified for high temperature work by inclusion of a suitable insulated heating compartment. In the wave number range of 50,000 cm^{-1} to 13,000 cm^{-1} the transmitted radiation was detected and measured by use of a photomultiplier. For wave numbers between 13,000 cm^{-1} and 4000cm^{-1}, a lead sulphide photocell detector was used, and in this region the optics were reversed by the placing of the monochromator after the sample and before the detector, this meant that interference reaching the detector from the black body radiation emitted by the cell department was greatly reduced.

The use of a conventional wire wound resistance furnace to heat the sample and reference cells was found to be unsuitable. Thus a radio frequency induction heating method was used as follows. The sample and reference cells were made of standard silica spectrosil U.V-cells, the path lengths being 10mm. A cylindrical silica tube having a B.19 joint at the top was joined to each cell, the overall length being about 180 mm. Two steel susceptors were constructed to act as holders for the cells, with holes to allow light to pass through. The susceptors were located in the cell compartment at the centres of two copper coils, again suitably constructed to allow the passage of light through the cells. A radio frequency current was passed through the coils, the current being generated by a Redifon Electronic Heater type IH42B, and the power supplied to the coils controlled by a 20 amp Variac variable transformer. The radio frequency current caused an alternating magnetic field to be produced in the copper coils which in turn induced a high current in the steel susceptors and thus rapid heating.

The coils were made of $\frac{1}{4}$" diameter copper pipe and cooling water was passed through them when in use. The cell compartment was insulated from the rest of the spectrometer by water cooled plates.

2.7 Methods for qualitative analysis

After dissolving the quenched melt in water, either insoluble and soluble products were identified by using analysis methods given in "Vogel"(55).

2.8 Methods for quantitative analysis

Bismuth:

Xylenol orange as indicator was added to a bismuth solution which was prepared from dissolving the bismuth compounds in dilute nitric acid. Then titrated with standard solution of EDTA until the end point was reached when the red colour of the solution changed to yellow(56).

Chloride:

25ml of the test solution were placed in a conical flask containing 5ml of 6M-nitric acid. A small excess of standard 0.1M silver nitrate was added, then 2-3ml of nitrobenzene and one ml. of ferric alum indicator were added. The solution was shaken vigorously to coagulate the precipitate. The titration of the residual silver nitrate with standard 0.1M thiocyanate was carried out until a permanent faint reddish-brown coloration appeared. Every 1 ml. of $M\text{-}AgNO_3$ = 0.03546 g Cl.(56)

Lithium:

Lithium was determined by the atomic emission spectrophotometry (wavelength 670.8 nm), using the Varian Techtron model 1100. A stock solution of lithium was prepared as described in "Vogel"(56), then diluted to give four solutions containing 20, 10, 5 and 2 ppm. of lithium. A calibration curve was prepared from these. Then the reading for the solution which contained an unknown amount of lithium was taken, and from this reading the concentration of lithium in the test solution was determined from the calibration curve.

Palladium:

15 ml. of one per cent solution of dimethylglyoxime in 96 per cent ethanol was added to 200 ml of test solution and allowed to stand for one hour. The orange-yellow precipitate was filtered

through a weighted gooch crucible, then washed with cold and hot water, dried at 110°C and weighted as $Pd(C_4H_7O_2N_2)_2$ (56).

Rhodium:

Rhodium can be determined by reducing its compounds to metal by using hydrogen at the temperature of 1000°C.

Ruthenium:

The ruthenium can be determined by bringing it into the solution as ruthenate (VI), for example, fusing with potassium nitrate and potassium hydroxide, and determining the RuO_4^{2-} spectrophotometrically.

2.9 Materials

Potassium pyrosulphate

The Analar potassium pyrosulphate contained an impurity, believed to be potassium bisulphate, so potassium pyrosulphate was prepared by the thermal decomposition of Analar potassium persulphate (57) according to the equation:-

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

This method involved heating Analar potassium persulphate at 250°C for ten hours. A sample dissolved in water gave no blue colour with starch-iodide paper, indicating the absence of persulphate ion. Analysis by titration against sodium hydroxide solution corresponded to 98.0% potassium pyrosulphate.

Sodium Peroxide

A British Drug Houses (BDH) Analar grade was used. The titration against permanganate gave 84.6% of peroxide. It was always handled in a dry box to prevent hydration and carbonation.

Sodium hydroxide

The product used was BDH, Analar grade. To facilitate reaction and solution in the melt, this compound was ground and dried in the oven at 100°C for four hours. Quantitative analysis gave 98.0% purity.

Potassium nitrite

This was BDH, Analar grade, which dried at 200°C for 6 hours and quantitative analysis gave 95.0% purity.

Potassium chloride

It was BDH, Analar grade, which after drying at 150°C for 2 hours gave 99.7% purity.

Bismuth trichloride

This was Hopkin and Williams laboratory reagent grade. For purification, about 5 g of bismuth trichloride was loaded into a silica boat, which was placed in a 500 mm, B24 tube in a horizontal furnace at the temperature of 140 °C, with a continuous flow of chlorine gas for 2 hours. Quantitative analysis of this bismuth trichloride gave 65.6% Bi and 33.2% Cl, while the calculated percentages for $BiCl_3$ are 66.3% Bi and 33.7% Cl.

Bismuth nitrate pentahydrate

This Hopkin and Williams general purpose reagent, was used directly from the bottle. Quantitative analysis of nitrate and bismuth gave 38.0% NO_3 and 42.8% Bi. While the calculated percentages for $Bi(NO_3)_3.5H_2O$ are 38.34 NO_3^- and 43.08 Bi.

Sodium bismuthate

This BDH Analar grade compound was used directly from the bottle. Quantitative analysis for bismuth indicated 80.2% purity.

Palladium dichloride

This was kindly supplied by the Johnson Matthey Research Centre and had an analysis of 59.6% Pd and 39.5 % Cl, while that the calculated for $PdCl_2$ are 60.0% Pd and 39.9% Cl.

Rhodium trichloride monohydrate

This compound was also kindly supplied by the Johnson Matthey Research Centre and had an analysis of 40.5% Rh and 41.4% Cl, while those calculated for $RhCl_3.H_2O$ are 45.2% Rh and 46.8% Cl.

Ruthenium trichoride monohydrate

This compound was also kindly supplied by the Johnson Matthey Research Centre and had an analysis of 41.8% Ru and 43.8% Cl, while that calculated for $RuCl_3.H_2O$ are 48.7% Ru and 47.2% Cl.

CHAPTER THREE

Reaction of some bismuth compounds in pure nitrate melt and in the melt containing acidic and basic species

3.1 Introduction

The chemistry of bismuth has been little studied in molten nitrates, so it is useful to review certain properties of different bismuth compounds in order to more fully understand the behaviour of these compounds in nitrate melt.

The main sources of this element are native bismuth and its sulphides (Bi_2S_3), but oxidized minerals are also known, such as bismuth ochre, which is mainly Bi_2O_3. Bismuth metal is mainly used in the preparation of fusible alloy, as a constituent of medicinal preparations, in pigments, enamels and special glasses and also in electrical equipment.

Elementary bismuth is obtained by heating bismuth trioxide with carbon using sodium carbonate as a flux, or by the reduction of bismuth trichloride with hypophosphorous acid. Morris, Douglas and Vaughan(58) reported successful deposition of bismuth from fused electrolytes containing 10 or 25% bismuth trioxide in a calcium chloride - sodium chloride eutectic mixture or in the individual salts at temperatures of 600-900°C.

Chemically metallic bismuth is attacked only by oxidizing acids, such as nitric acid or hydrochloric acid in the presence of oxygen, while hypochlorites act slowly on bismuth, forming higher bismuth oxides (i.e. Bi_2O_4). It is attacked by steam at high temperature and by moist halogens. It burns in air with a blue flame. It can also show reducing properties towards metal cations, for example according to M. Kohn(59), bismuth reduces copper II salts to the copper I state in ammonia and tartaric acid solutions:

$$Bi + 3CuCl_2 \rightarrow BiCl_3 + 3CuCl \qquad III.1$$

whilst potassium hydroxide or Fehling solutions of copper II salts are reduced to copper metal

$$2Bi + 3CuCl_2 \rightarrow 2BiCl_3 + 3Cu \qquad III.2$$

The typical salts of bismuth are all derived from the trivalent oxidation state. They are mostly colourless and those derived from strong acids are soluble in water. However, dissolution to form a clear solution takes place only if there is an appreciable excess of acid. Basic salts are otherwise formed by hydrolysis and these are obtained as insoluble precipitates. A number of the basic salts are derived from the bismuthyl cation $(BiO)^+$. The bismuthyl salts are almost insoluble in water. One salt which is soluble in water and which forms a clear solution even without excess acid, is bismuthyl perchlorate, which can be obtained by dissolving bismuth trioxide in dilute perchloric acid.

Double salts crystallize from mixed solutions of bismuth salts and alkali salts. These show that bismuth salts have some tendency to bond to additional acid anions, to form complex acido anions, e.g.

$$BiCl_3 + Cl^- \rightarrow (BiCl_4)^- \qquad III.3$$

The concentration of free bismuth ions Bi^{3+}, in bismuth salt solutions is therefore calculated by a set of simultaneous equilibria such as

$$Bi^{3+} + H_2O \rightleftarrows (BiO)^+ + 2H^+ \qquad III.4$$

and

$$Bi^{3+} + 4X^- \rightleftarrows (BiX_4)^- \qquad III.5$$

and thus this concentration is often difficult to specify with accuracy.

The commonest halides are all of the type BiX_3 (X=F,Cl,Br or I). Bismuth trichloride has been reported to be made by many methods. For example, by passing excess of chlorine over bismuth or by dissolving bismuth in aqua regia, and evaporating the solution, when crystals of $BiCl_3.2H_2O$ are obtained, from which, the anhydrous salt may be obtained by dehydration. Bismuth trichloride, a white crystalline solid is hydrolyzed by water to bismuth oxychloride (BiOCl). Lower bismuth halides, for example, black bismuth "monochloride" have been made by dissolving metallic bismuth in molten bismuth trichloride or molten aluminium chloride-sodium chloride eutectic mixture. This solid supposed monochloride is in fact $Bi_{24}Cl_{28}$ which x-ray diffraction has shown to consist of four $BiCl_5^{2-}$, one $Bi_2Cl_8^{2-}$ and two Bi_9^{5+} ions(60). Other low-valent bismuth species have been suggested to be present in various molten salt solutions(61-63), among these are Bi^+ and Bi_5^{3+} and perhaps other such as Bi_3^+, Bi_4^{4+} and Bi_8^{2+}. X-ray crystallographic study of $Bi_{10}Hf_3Cl_{18}$ has demonstrated the presence of Bi^+ in the cyrstalline compound, which consisted of Bi^+, Bi_9^{5+} and $3HfCl_6^{2-}$ ions. The Bi_9^{5+} cation has the same structure as that found in $Bi_{24}Cl_{28}$(60).

Bismuth tribromide and bismuth tri-iodide closely resemble bismuth trichloride in their structure and chemistry. The tribromide forms yellow crystals and the tri-iodide forms black to brown crystals. Bismuth tri-iodide is much less soluble in water than the chloride and bismuth III may be precipitated from solution by iodide ions. Bismuth tribromide is readily converted by water into the white oxybromide, whereas the iodide, because of its low solubility is hydrolyzed only on boiling. Both bismuth tribromide and tri-iodide form halo complexes with stoichiometries of $MBiX_4$, where X = Br or I and M is a large quarternary cation. Raman studies have shown that Bi (III) in aqueous hydrochloric acid forms the ions $BiCl_4^-$, $BiCl_5^{2-}$, and $BiCl_6^{3-}$.

Bismuth nitrate is obtained by dissolving powdered bismuth in nitric acid, when the solution is evaporated, $Bi(NO_3)_3.5H_2O$ will crystallize. When these crystals are heated, they lose both water and nitric acid, so that bismuthyl nitrate, $BiO(NO_3)$ remains. This is also formed with other basic nitrates, according to the conditions when the nitrate dissolved in water. $BiO(NO_3)$ and $Bi_2(OH)(NO_3)$ can also be made by treatment of bismuth trioxide with nitric acid. Bismuth nitrate also forms double nitrates of formula $3M''(NO_3)_2$, $Bi(NO_3)_3$, $24H_2O$, where M" may be Zn, Cd, Co, or Ni.

Bismuth sulphate is obtained by dissolving the bismuth trioxide in concentrated sulphuric acid. Above 400°C this salt will decompose to basic salt and bismuth trioxide.

The most stable bismuth oxide, Bi_2O_3, which is obtained by heating the metal, the hydroxide, the basic carbonate, nitrate or sulphate to redness in air, is pale yellow when cold and red when hot. Bismuth trioxide dissolves in acids, forming the corresponding bismuth salts, but it is insoluble in dilute alkali hydroxide. Bismuth oxide exists in three crystalline modifications. At room temperature, the monoclinic α-phase is the stable form. On heating, the α-phase transforms at 740°C to the cubic δ-phase, which is stable up to the melting point (830°C)(64). On cooling the one intermediate metastable tetragonal β-phase appears at 650°C(65,66)(the transition temperature) but at 545°C forms the α-phase.

It appears that higher oxides of bismuth also exist, but they are extremely unstable and have never been obtained in a pure form. For example, bismuth (v) oxide obtained by the action of powerful oxidizing agents on bismuth trioxide is red brown and rapidly loses oxygen at about 80°C. Bismuth tetraoxide (Bi_2O_4) has been reported to be made by melting the trioxide with an excess of alkali metal hydroxide, while exposed to air.(67-69)

Though higher oxides are unstable, compounds containing bismuth(v) may show greater stability. Thus when bismuth hydroxide or oxide, in concentrated alkali hydroxide solution, is treated with strong oxidants such as chlorine, alkali metal bismuthates are obtained. Yellow sodium metabismuthate $NaBiO_3$, brown sodium orthobismuthate Na_3BiO_4 and violet potassium bismuthate $KBiO_3$ have been reported. It was found by Zintl(70) that sodium orthobismuthate was more readily prepared pure by a dry method, that of heating bismuth trioxide with sodium perioxide. Various lithium bismuthates such as Li_3BiO_4, Li_5BiO_5 and Li_7BiO_6 have been reported to be made by heating mixtures of lithium oxide and bismuth trioxide in an oxygen atmosphere.(71)

The above discussion has introduced the chemical behaviour of bismuth compounds in various aqueous solutions. However, the chemistry of bismuth compounds in molten nitrates is largely unknown and little information has been published. Among the few facts to be found in the literature is that the electromigration of bismuth III ion in lithium nitrate-potassium nitrate eutectic has been studied(72) at 255°C, which showed that bismuth III cation at this temperature can exist in solution, i.e. they are both soluble and stable. The behaviour of bismuth III cations during the acidimetric titration in molten equimolecular mixture of sodium nitrate-potassium nitrate at 240°C with electrolytically generated oxide ions has also been studied, using platinized platinium foil as the indicator electrode. In this titration the bismuth III ion appeared to be a very strong Lux-Flood acid and partially decomposed the nitrate to nitrogen dioxide and oxygen[73]. Similarly a polarographic study of bismuth nitrate pentahydrate in a ternary eutectic melt of 30 mole% lithium nitrate, 17 mole% sodium nitrate and 53 mole% potassium nitrate at 160°C has been claimed to cause the melt to froth and produce suspensions which yielded erratic current voltage curves.(74) Finally, the coulometric titration of bismuth III cation with iodide ions in molton lithium nitrate-potassium nitrate eutectic at a temperature of 160°C under a continuous flow of nitrogen has been reported(75), when bismuth oxyiodide was produced.

3.2 Reaction of bismuth trichloride

3.2.1 Reaction alone in air and in pure melt

Bismuth trichloride was found to be stable up to 200°C, when it was heated alone in air, though a white sublimate was noticed above this temperature. At about 260°C, the solid formed a yellow liquid, but above this temperature the liquid solidified and at 350°C the colour changed to white. At about 600°C a second sublimate was noticed while at 700°C the product was still white and sublimation was no longer visible.

Thermogravimetric analysis (Fig. 1) showed the first weight loss started at 150°C with the maximum rate of reaction at 300°C, and a second weight loss began at around 650°C. Above 940°C the product was red but after cooling the colour had changed to yellow and the solid had adhered to the crucible walls. The first step gave a 26.9% weight loss, while the second step gave 25.6%(overall 52.5%). Qualitative analysis gave a negative test for chloride but was positive for bismuth. Quantitative analysis gave 89.5% Bi (calculated for Bi_2O_3 is 89.7% Bi).

When the experiment was repeated but only heated to 500°C, the single weight loss was 22.5% while quantitative analysis of the white product gave 79.8% Bi and 13.2% Cl (calculated for BiOCl 80.2% Bi and 13.6% Cl).

Bismuth trichloride was observed to react with lithium nitrate-potassium nitrate melt very slowly at about 200°C with evolution of nitrogen dioxide, forming a white suspension and a white precipitate with some froth. At 350°C nitrogen dioxide evolution was no longer visible and at 400°C there was a white precipitate with a colour less liquid but at 480°C the white precipitate started to change to pale yellow and a very small amount of nitrogen dioxide was evolved. When the reaction mixture was kept at 500°C for twenty hours the product was an orange precipitate. After cooling the quenched melt was dissolved in water and a pale yellow insoluble product was filtered off, dried and analysed for bismuth and chloride. (Found 87.7% Bi and 3.0% Cl, in contrast, calculated for BiOCl, 80.2% Bi and 13.6% Cl). Qualitative analysis of the aqueous filtrate gave a positive test for nitrite and chloride ions but was negative for bismuth ion. X-ray diffraction of this pale yellow product gave the "d" values shown in Table (1).

Table (1) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the nitrate melt at 500°C.

Pale Yellow Product		From J.C.P.D.S. Index (A.S.T.M.)			
		$Bi_{24}O_{31}Cl_{10}$		BiOCl	
d-spacing	I/Io	d-spacing	I/Io	d-spacing	I/Io
4.39	31.6	4.11	40	7.38	40
3.81	5	-	-	-	-
3.64	6	3.69	60	3.69	16
-	-	3.55	60	-	-
3.34	28	3.40	20	3.44	100
-	-	3.10	60	-	-
-	-	3.08	80	-	-
3.05	-	3.02	80	-	-
-	-	2.96	80	-	-
2.98	100	2.82	80	-	-
-	-	2.80	80	2.75	12
2.71	46	-	-	2.67	95
2.51	51	2.52	20	2.57	10
-	-	2.47	40	2.45	12
-	-	2.39	40	-	-
2.35	5	2.36	40	-	-
2.30	6	-	-	-	-
2.19	11	2.21	100	2.20	30
-	-	2.08	80	-	-
-	-	2.02	80	-	-
1.99	24	1.99	80	-	-
1.91	14	-	-	1.94	35

When this experiment was repeated but only heated to 400°C, the white quenched melt was dissolved in water and a white insoluble solid was filtered off, which after drying was analysed, giving 79.8% Bi and 13.0% chloride (Calculated for BiOCl, 80.2% Bi, and 13.6% Cl). This product was examined by X-ray diffraction, giving the d-spacings shown in Table (2), while some other results of experiments in tubes are given in Table (3).

Thermogravimetric analysis (Fig. 1) of bismuth trichloride in pure lithium nitrate-potassium nitrate eutectic, showed that the weight loss started at 200°C with a maximum rate of reaction at 325°C, and a total weight loss of 30.7% at 400°C (Calculated for loss of 2N + 5O per bismuth trichloride is 34.25%). After dissolving the quenched melt in water and filtering, the white insoluble product was dried at 100°C for two hours. Qualitative analysis showed only the presence of bismuth and chloride, while quantitative analysis gave 79.9% Bi and 13.8% Cl . (Calculated value for BiOCl is 80.2% Bi and 13.6% Cl.)

When the experiment was repeated, but taken to a higher temperature, the first weight loss also started at about 200°C with maximum rate at 325°C but a second weight loss started at 425°C and when the reaction was kept at 500°C for twelve hours, this weight loss was 57.5%. Qualitative analysis of the filtrate gave a positive test for nitrite and chloride ion but was negative for bismuth. Quantitative analysis of the pale yellow insoluble product in water gave 82.9% Bi and 8.5% Cl. This product was examined by x-ray diffraction, giving the d-spacings shown in Table (4) and some typical results are collected in Table (5).

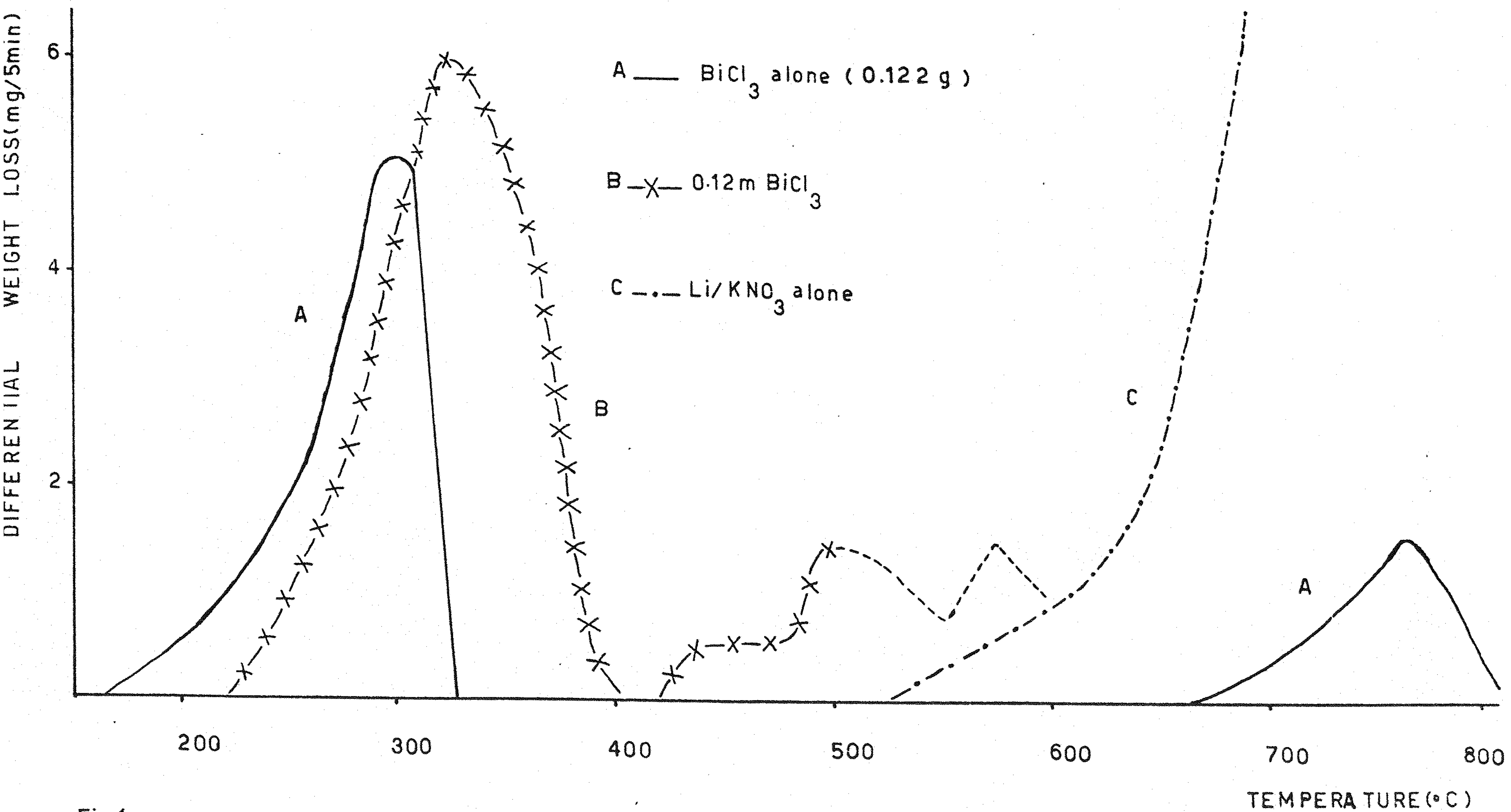


Fig 1 Thermogravimetric analysis of BiCl$_3$ alone in air and in pure melt.

Table (2) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the melt at 400°C

White product at 400°C		BiOCl from J.C.P.D.S. Index (A.S.T.M.)	
d-spacings	I/Io	d-spacings	I/Io
7.30	100	7.38	40
3.66	41.5	3.69	16
3.44	80	3.44	100
2.74	11	2.75	75
2.66	26	2.67	95
2.45	31	2.45	12
2.19	6	2.20	30
1.93	5	1.83	85
1.83	5	1.83	25
1.69	3	1.69	25
1.66	14	1.66	30
1.56	5	1.57	30

Table (3) Some results of experiments in tubes

$BiCl_3$		Max. Temp. °C	Time h	%Bi	%Cl
g	molal				
0.4285	0.29	370	4	79.7	12.9
0.5072	0.23	400	2	80.4	12.8
0.6837	0.37	490	4	81.7	7.7
0.4406	0.15	500	18	87.7	3.0
1.1244	0.33	500	16	85.1	3.1
0.3481	0.09	500	24	87.4	2.4

Calculated for BiOCl 80.2% Bi 13.6% Cl

$Bi_{24}O_{31}Cl_{10}$ 85.5%Bi 6.0% Cl

$Bi_{12}O_{15}Cl_6$ 84.7%Bi 7.2% Cl

Table (4) X-ray diffraction of product obtained from reaction of $BiCl_3$ in pure melt, at 500°C.

Pale yellow product		From J.C.P.D.S. Index (A.S.T.M.)			
		$Bi_{24}O_{31}Cl_{10}$		BiOCl	
"d"-value	Intensity	"D"-value	I/Io	"D"-value	I/Io
5.71	12				
4.97	32				
4.62	28				
4.38	8				
4.15	12	4.11	40		
3.99	10				
3.77	8				
3.69	36	3.69	60	3.69	16
3.40	22	3.40	20	3.44	100
3.09	100	3.10	60		
3.05	80	3.08	80		
3.00	92	3.02	80		
2.95	22	2.96	80		
2.93	40				
2.88	24				
2.87	46				
2.81	40	2.82	80		
2.78	18			2.75	75
2.69	14			2.68	95
2.62	12			2.58	10
2.50	16	2.52	20		
2.49	18	2.47	40	2.46	12
2.31	40				
2.20	12	2.21	100	2.20	30
2.11	12				
2.08	24	2.08	80		
2.07	40				
1.99	16	1.99	80		
1.93	12			1.94	35
1.78	14				
1.76	14				
1.69	46			1.69	25
1.66	32			1.66	18

Table(5) Some thermogravimetric results from the reaction of bismuth trichloride in the pure melt

$BiCl_3$		first weight loss		Max. Temp °C	second weight loss		Max Temp °C	Total reaction time h	%Bi	%Cl
g	molal, conc	mg	%		mg	%				
0.1303	0.1287	40	30.7	400	-	-	-	4	79.9	13.8
0.1992	0.1739	64	32.2	440	-	-	-	3.5		
0.1854	0.1201	59	31.8	420	34	18.3	500	8		
0.1712	0.1351	52	30.4	435	38	22.2	500	16	83.6	5.4
0.1508	0.1194	45	29.8	420	44	29.2	500	19	82.9	12.5

3.2.1.1 Discussion

When bismuth trichloride was heated alone in air, it decomposed in the first stage to bismuth oxychloride and chlorine gas according to the equation III.6.

$$2BiCl_3 + O_2 \rightarrow 2BiOCl + 2Cl_2 \qquad III.6$$

with the theoretical weight loss of 17.4%. This is similar to the report of V.A. Jacquelain(76) that when bismuth trichloride was heated to its vaporization temperature in air, bismuth oxychloride was formed. The larger experimental weight loss than that calculated from equation III.6 could thus be due to volatilization of bismuth trichloride.

At the second stage bismuth oxychloride was oxidized to bismuth trioxide and chlorine as in the equation:-

$$2BiOCl + \tfrac{1}{2}O_2 \rightarrow Bi_2O_3 + Cl_2 \qquad III.7$$

which has a theoretical weight loss of 8.7% (i.e. overall 26.1%) based on bismuth trichloride. According to C. Duval bismuth oxychloride is stable up to 805°C, while above this temperature it will lose the chlorine and at 950°C the product will be Bi_2O_3. Now bismuth oxychloride has been reported previously to have been heated up to over 800°C without volatilizing or decomposing(77), but it has also been reported to sublime when heated, forming tiny glistening crystals.[78] Recently, it has been claimed that bismuth oxychloride does volatilize in nitrogen gas, when analysis showed the final solid product at 900°C was a mixture of bismuth trioxide and unreacted bismuth oxychloride while the condensate was bismuth trichloride as in the equation:-

$$3BiOCl \rightarrow Bi_2O_3 + BiCl_3 \qquad III.8$$

which has a theoretical weight loss of 40.3%. The very much larger experimental weight loss than calculated from equation III.7 suggested that some of the observed formation of bismuth trioxide also involved the volatilization of bismuth trichloride as equation III.8, or perhaps even direct volatilization of bismuth oxychloride[78].

The reaction of bismuth trichloride in a pure lithium nitrate potassium nitrate eutectic occurred at 220°C, with the cation behaving as a Lux-Flood acid, i.e. abstracting an oxide ion from the nitrate to form bismuth oxychloride, evolving nitrogen dioxide(66) and following the stoichiometry:

$$NO_3^- \rightarrow NO_2^+ + O^{2-} \qquad \text{III.9}$$

$$NO_3^- + NO_2^+ \rightarrow 2NO_2 + \tfrac{1}{2}O_2 \qquad \text{III.10}$$

$$BiCl_3 + O^{2-} \rightarrow BiOCl + 2Cl_2 \qquad \text{III.11}$$

$$Bi\,Cl_3 + 2NO_3^- \rightarrow BiOCl + 2NO_2 + \tfrac{1}{2}O_2 + 2Cl^- \qquad \text{III.12}$$

which has a theoretical weight loss of 34.25%.

The hypothesis of a possible formation of bismuth trioxide according to reaction III.13,

$$2BiCl_3 + 6NO_3^- \rightarrow Bi_2O_3 + 6NO_2 + \frac{3}{2}O_2 + 6Cl^- \qquad \text{III.13}$$

cannot be accepted as it would give a weight loss of 51.35%. Moreover if there was some bismuth trioxide present in the final precipitate, we would expect a higher value for bismuth, that is nearer the 89.7% calculated for Bi_2O_3 than the 80.2% of bismuth in

BiOCl. Though the most important evidence is the presence of substantial chloride ion concentration in the final product, The analysis value of 13.0%Cl indicated that the white solid was largely bismuth oxychloride (calculated for BiOCl, 80.2% Bi and 13.6% Cl).

However, in the case of second reaction at a higher temperature (460°C) there was some replacement of chloride by oxide in the oxychloride leading to a higher percentage of bismuth and a lower percentage of chloride, Table (3). The oxide could be made available either by the self ionisation equilibrium III.9, giving a higher concentration of oxide and consequently evolution of nitrogen dioxide as equation III.10 or even perhaps by the known catalysis of the decomposition of melt by chloride ion.(80) The solid product may in fact be a mixture of several bismuth oxychlorides, for example, Arppe's bismuth oxychloride ($Bi_{24}O_{31}Cl_{10}$) which has an analysis of 85.5% Bi and 6.1% Cl, $Bi_{12}O_{15}Cl_6$ with a 84.7% Bi and 7.2% Cl analysis or after further replacement chloride by oxide in $Bi_{24}O_{31}Cl_{10}$ giving $Bi_{24}O_{33}Cl_6$ which would analyse as 87.1% Bi and 3.7% Cl, i.e. close to the values found experimentally. If these compounds were formed, the overall stoichiometry would be of the following type:

$$24BiOCl + 14NO_3^- \rightarrow Bi_{24}O_{31}Cl_{10} + 14NO_2 + \frac{7}{2}O_2 + 14Cl^- \qquad III.14$$

with a theoretical weight loss of 12.1%, or

$$12BiOCl + 6NO_3^- \rightarrow Bi_{12}O_{15}Cl_6 + 6NO_2 + \frac{3}{2}O_2 + 6Cl^- \qquad III.15$$

which has a theoretical weight loss of 10.3%, or

$$24BiOCl + 18NO_3^- \rightarrow Bi_{24}O_{33}Cl_6 + 18NO_2 + \frac{9}{2}O_2 + 18Cl^- \qquad III.16$$

with a theoretical weight loss of 15.5%. Arppe's bismuth oxychloride ($Bi_{24}O_{31}Cl_{10}$) has been reported to be made by heating BiOCl above 700°C$^{(81)}$, or by keeping a mixture of equal mol Bi_2O_3 and BiOCl at 800-900°C for a few hours in a sealed quartz.$^{(82)}$ $Bi_{12}O_{15}Cl_6$ has been reported to be made by heating a mixture of Bi_2O_3 and BiOCl in the ratio 1:2 for 24 hours at 860°C$^{(83)}$. In the case of the present investigation, it was shown that both BiOCl and $Bi_{24}O_{31}Cl_{10}$ were present in the end product together with some unknown d-spacings (Table (2)) indicating a further compound. Therefore we might have expected a lower percent weight loss than the 12.1%, equation III.14, but the analysis figure is explained if the unknown d-spacings are attributed to a bismuth oxychloride in which even more chloride has been replaced by oxide. However, the higher second weight loss shown in Table (5) was perhaps largely due to the self decomposition of melt as equation III.17, or catalysis of this decomposition by chloride ion$^{(23)}$.

$$2NO_3^- \rightarrow 2NO_2^- + O_2 \qquad \text{III.17}$$

The crystal structure of Arppe's bismuth oxychloride ($Bi_{24}O_{31}Cl_{10}$) has been reported by Sillen and Edstrand(82) to be monoclinic. They found that the x-ray data obtained for this compound was difficult to analyse, therefore they had not been able to compute the exact atomic positions, however they reported that "ideal structure is probably not far from the real structure". X-ray data, chemical analysis and density were reported to agree with the formula $Bi_{24}O_{31}Cl_{10}$ per unit cell. The compound contained planar metal-oxygen sheets and single halogen sheets in a step-like arrangement. The reported unit cell is shown in Fig (2).

The crystal structures of $Bi_6O_7FCl_3$ and $Bi_{12}O_{15}Cl_6$ have been reported to be both orthorhombic, by Hoffgarten(85-86). In a recent paper(85), he reported that the above structure can both be derived from a hypothetical non-stoichiometric parent structure with the composition $Bi_6O_{7+n}Cl_3$ with $0 \leq n \leq 1$. The reported structure is shown in Fig (3). The parent structure consists of one planar $(BiX^+)_\infty$ sheet, one zigzag $(Bi_3X_5\ )_\infty$ sheet, and trigonal-prismatic $(Cl_3^{\ 3-})_\infty$ columns. If one five-coordinated bismuth atom in the BiX_5) sheet has a vacancy (marked by dotted lines in Fig. 3) in one of its corners, the twin operation on a double block would give $Bi_{12}O_{15}Cl_6$ as (reported structure) shown in Fig.4.

The structure of bismuth oxychloride (BiOCl) has been reported by Swanson et al(86) to be tetragonal. Wells 89) has described, bismuth oxychloride structure as consisting a central sheet of coplanar oxygen atoms with a sheet of chloride atoms on each side, and the metal atoms between the Cl-O-Cl sheets. In this structure a bismuth atom is surrounded by four oxygen and four chloride atoms. The reported structure is shown in Fig. 5.

3.2.1 Reaction in acidic melt

3.2.2.1 Introduction

Nitrate melts, in the majority of cases studied, have been found to participate chemically in reactions, frequently acting as an oxidizing agent, but in the presence of an acidic species this reaction may be different from that with a pure nitrate melt. For example, cobalt and zinc metals, which do not react in pure nitrate melt, are oxidized to cobalt (II) and zinc(II) ions respectively in a nitrate melt containing potassium pyrosulphate(24).

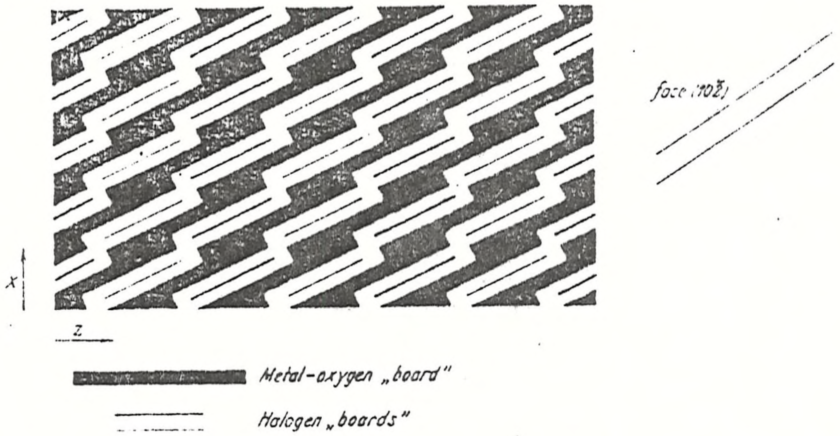


Fig. **2**. Section of 5 × 3 unit cells of an Arppe compound, showing the step-like arrangement of the metal-oxygen "boards". The orientation of the largest crystal face, (10$\bar{2}$), is also shown. The "boards" are infinite in *y*-direction (perpendicular to the plane of the paper).

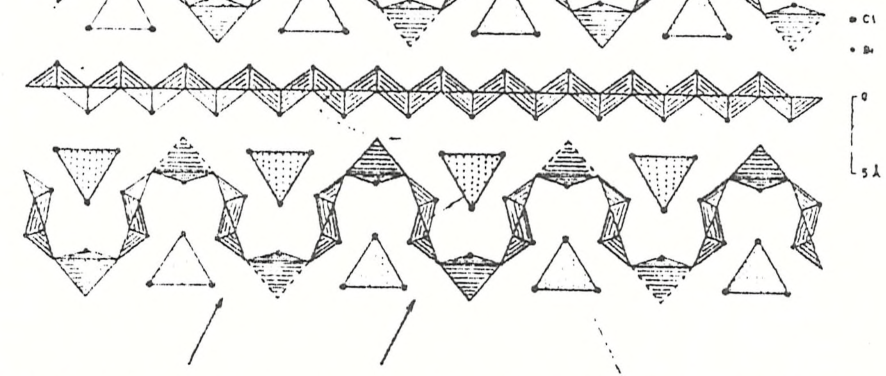


Fig. **3**. The hypothetical non-stoichiometric parent structure $Bi_6X_{7+x}Cl_3$ projected along *y*. The coordination polyhedra of Bi, described as square pyramids and octahedra, are connected to one planar sheet and one zigzag sheet parallel to [010]. The Cl ions form trigonal-prismatic columns running along [010]. The polyhedra drawn in heavy and thin lines are *b*/2 apart.

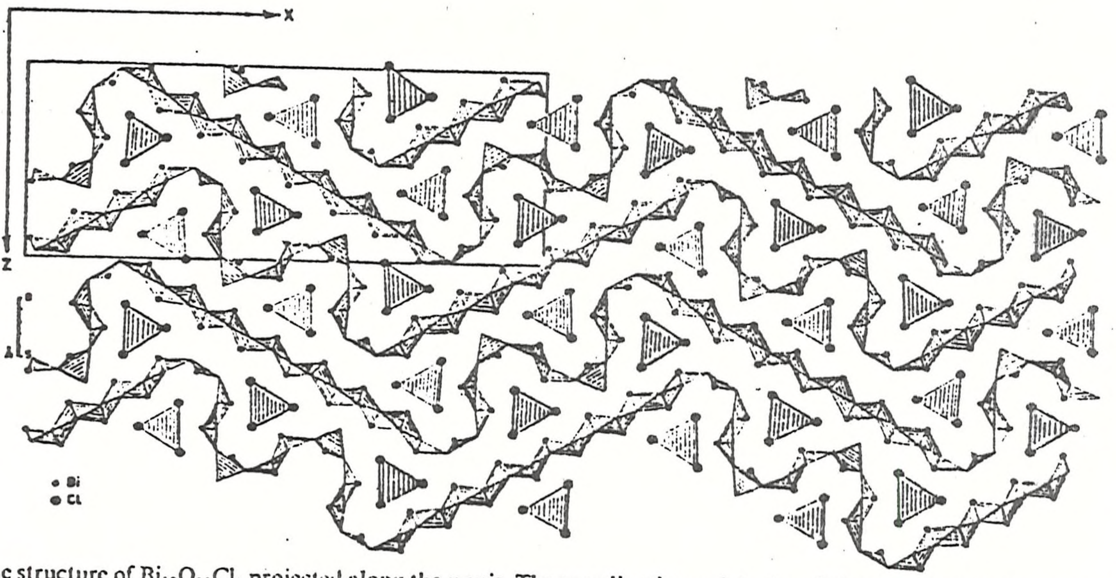


Fig.4. The structure of $Bi_{12}O_{15}Cl_6$ projected along the y axis. The coordination polyhedra of bismuth, described as square pyramids and octahedra, are connected to form infinite zigzag layers parallel to [010]. The polyhedra drawn by heavy and thin lines are $b/2$ apart. The chloride ions form trigonal prisms, running along [010]. All atoms are at the heights $y = \pm\frac{1}{4}$.

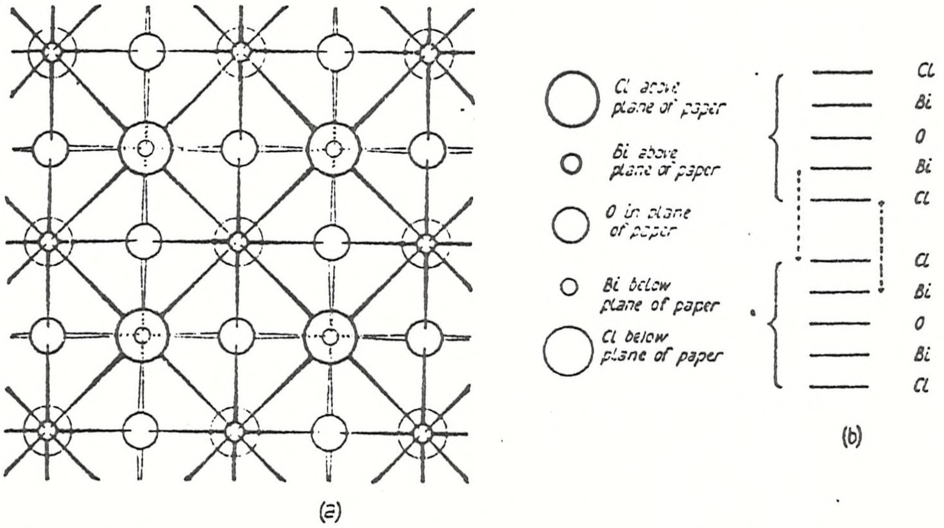


FIG. 5. (a) Atomic arrangement in a layer of the structure of BiOCl (or PbFCl). (b) Sequence of atoms in a direction normal to the layer (a).

The chemistry of acidic melts containing a Lux-Flood acid as a solute has claimed the attention of many workers, including Duke and co-workers who studied the kinetics of the reaction of potassium dichromate and potassium pyrosulphate(91,21) in sodium nitrate-potassium nitrate eutectic. They found that the rate of decomposition of dichromate and pyrosulphate could be explained if the reaction consisted of two steps as in the equilibria:-

$$Cr_2O_7^{2-} + NO_3^- \rightleftarrows NO_2^+ + 2CrO_4^{2-} \qquad III.18$$

$$S_2O_7^{2-} + NO_3^- \rightleftarrows NO_2^+ + 2SO_4^{2-} \qquad III.19$$

followed by a slow step:-

$$NO_3^- + NO_2^+ \rightarrow NO_2 + O_2 \qquad III.20$$

Shams El-Din and co-workers have carried out a series of acid-base reactions in molten potassium nitrate at 350°C, using a potentiometric titration method. The neutralisation of potassium dichromate by both potassium hydroxide and sodium peroxide were followed and shown to exhibit rapid e.m.f. changes at the stoichiometric equivalence point for the reaction:-

$$Cr_2O_7^{2-} + O^{2-} \rightleftarrows 2CrO_4^{2-} \qquad III.21$$

Both bases were assumed to decompose at the temperatures employed to yield their oxides.

A quantitative investigation into the stoichiometry of the reaction of relatively weak Lux-Flood acid potassium dichromate in lithium nitrate-potassium nitrate eutectic has been reported.(99-100) From this, dichromate was found to be soluble in the melt at 350°C but at 400°C it reacted with melt to give chromate, nitrogen dioxide and oxygen, conforming to the equation:-

$$Cr_2O_7^{2-} + 2NO_3^{-} \rightarrow 2CrO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \text{III.21}$$

while the strong Lux-Flood acid, potassium pyrosulphate was reported to react at 160°C to form sulphate, nitrogen dioxide and oxygen.

$$S_2O_7^{2-} + 2NO_3^{-} \rightarrow 2SO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \text{III.22}$$

Thermogravimetric analysis showed three maxima for this reaction, and also for the analogous reaction in sodium nitrate-potassium nitrate eutectic, but in the latter these maxima were completely separated and extended over a wide temperature range from 200°C to about 700°C.

In a previous section, the behaviour of bismuth trichloride in pure melt has been reported having been found to react giving a mixture of several bismuth oxychlorides. In this section, the behaviour of bismuth trichloride in a melt in presence of weak or strong acid species will be discussed.

3.2.2.2 Reaction in a presence of potassium dichromate

A mixture of bismuth trichloride and potassium dichromate (ratio of $Bi^{3+}:Cr_2O_7^{2-} = 1:1$) in lithium nitrate-potassium nitrate was observed to become dark brown at about 110°C, but at 180°C a yellowish-brown suspension and dark brown precipitate were formed. Nitrogen dioxide was evolved at 260°C and the colour of the suspension changed to red. At 320°C nitrogen dioxide was evolved more rapidly with frothing. At 400°C nitrogen dioxide evolution ceased but at 430°C it was again evolved and the colour of precipitate changed to orange. After keeping the reaction mixture at 500°C overnight, a red precipitate and a yellow liquid were formed.

The solid obtained by quenching this melt was dissolved in water and when the yellow water insoluble product was dried, qualitative analysis showed the presence of bismuth, chromium and the absence of chloride ion, whereas on the filtrate tests for nitrite and chloride were positive. Quantitative analysis gave 83.1% Bi and 6.2% Cr. Slightly different values were obtained with different initial ratios of bismuth trichoride and potassium dichromate and are shown in Table (6).

The experiment was repeated, but kept at 400°C until the evolution of nitrogen dioxide was no longer observed. The resultant mixture was dissolved in water, filtered and the pale yellow precipitate collected and dried, when qualitative analysis showed positive tests for bismuth and chloride, but negative for chromium, while quantitative analysis gave 80.0% Bi and 13.2% Cl (calculated for $BiOCl$, 80.2% Bi and 13.6% Cl). This product was examined by x-ray diffraction and gave the d-spacings shown in Table (7). Tables (8) and (9) show the d-spacings of products formed at 500°C for one day and overnight respectively.

Thermogravimetric analysis showed the first weight loss started at about 260°C and the second at 450°C which after keeping at 500°C overnight, Fig. 6, gave a 27.3% weight loss for the first step on the basis of bismuth trichloride and 56.6% for the second step on the basis of potassium dichromate. Some typical results are collected in Table (10).

Qualitative analysis of the above product, which was yellow in colour gave positive tests for bismuth and chromium and a negative test for chloride ions. Quantitative analysis gave 82.8% Bi and 6.8% Cr.

When the above experiment was repeated but kept at 370°C isothermally for four hours, Fig. 6, it gave a 33.5% weight loss and qualitative analysis of the water insoluble product gave positive tests for bismuth and chloride ions while quantitative analysis gave 79.8% Bi and 13.1% Cl.

Table (6) Some typical results of quantitative analysis of water insoluble product at 500°C

Ratio of $Bi^{3+}:Cr_2O_7^{2-}$	Experimental value		Theoretical for $(BiO)_2CrO_4$	
	Bi%	Cr%	Bi%	Cr%
1:2.2	82.1	6.9	73.81	9.2
1:0.45	83.1	6.2		
1:0.25	83.5	6.6		

Table (7) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the melt containing $K_2Cr_2O_7$ at 380°C

Pale yellow product at 380°C Bi^{3+} : $Cr_2O_7^{2-}$ 2 : 1		From J.C.P.D.S. Index (A.S.T.M.)			
		BiOCl		$(BiO)_2CrO_4$	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
7.30	100	7.38	40	10.5	50
3.65	26.5	3.69	16	4.90	10
3.42	28.5	3.44	106	3.55	10
3.20	8	-	-	3.20	100
				2.93	10
2.73	20	2.75	75	2.80	10
2.66	32	2.67	95	2.58	10
2.44	15	2.44	12		
2.19	8	2.20	30		
1.93	8	1.94	35		
1.83	8	1.83	25		
1.69	5	1.69	25		
1.66	8	1.66	18		
1.56	8	1.57	30	1.58	10

Table (8) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the melt containing $K_2Cr_2O_7$ at 500°C for one hour

Yellow product Bi^{3+} : $Cr_2O_7^{2-}$ 3.6 : 1		From J.C.P.D.S. Index (A.S.T.M.)			
		Bi_2O_3		$(BiO)_2CrO_4$	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
-	-	-	-	10.5	50
-	-	-	-	4.90	10
-	-	-	-	3.55	10
-	-	3.45	20	-	-
-	-	3.31	35	-	-
3.25	40	3.25	100	-	-
3.21	100	3.18	25	3.20	100
2.88	20.5	-	-	2.93	10
2.87	17.5	-	-	2.30	10
2.75	38	2.76	6	-	-
2.74	25	2.71	40	-	-
-	-	2.69	40	-	-
-	-	2.64	6	-	-
-	-	2.56	16	2.58	10
-	-	2.53	10	-	-
-	-	2.50	8	-	-
-	-	2.39	14	-	-
2.00	16	2.00	6	-	-
1.98	35	1.96	25	-	-
1.94	16	-	-	-	-
1.72	12	1.75	10	-	-
1.67	16	-	-	-	-
1.66	26	-	-	-	-

Table (9) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the melt containing $K_2Cr_2O_7$ at 500°C overnight

Yellow product Bi^{3+} : $Cr_2O_7^{2-}$ 4 : 1		From J.C.P.D.S. Index (A.S.T.M.)			
		Bi_2O_3		$(Bi_3O)_2CrO_4$	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
10.4	30	-	-	10.5	50
-	-	-	-	4.90	10
3.99	9	-	-	-	-
3.66	12.5	3.62	8	-	-
-	-	-	-	3.55	10
-	-	3.45	20	-	-
3.39	21	3.31	35	-	-
3.22	75	3.25	100	3.20	100
-	-	3.18	25	-	-
3.06	61	-	-	-	-
2.99	30	-	-	-	-
2.93	100	-	-	2.93	10
-	-	-	-	2.80	10
2.76	21	2.76	6	-	-
2.72	32	2.71	40	-	-
-	-	2.69	40	-	-
2.61	10	2.64	6	-	-
2.56	10	2.56	16	2.58	10
2.51	18	2.53	10	-	-
2.47	18	2.50	8		
2.44	21	2.42	6		
2.20	15	2.17	6		
1.99	20	2.00	6		
1.96	10	1.96	25	-	-
1.93	18	-	-	-	-
1.89	10	1.88	10	-	-
1.85	18	1.87	18	-	-
-	-	1.75	10	-	-
1.67	21	-	-	-	-
1.62	22	-	-	-	-
1.53	12.5	-	-	1.58	10

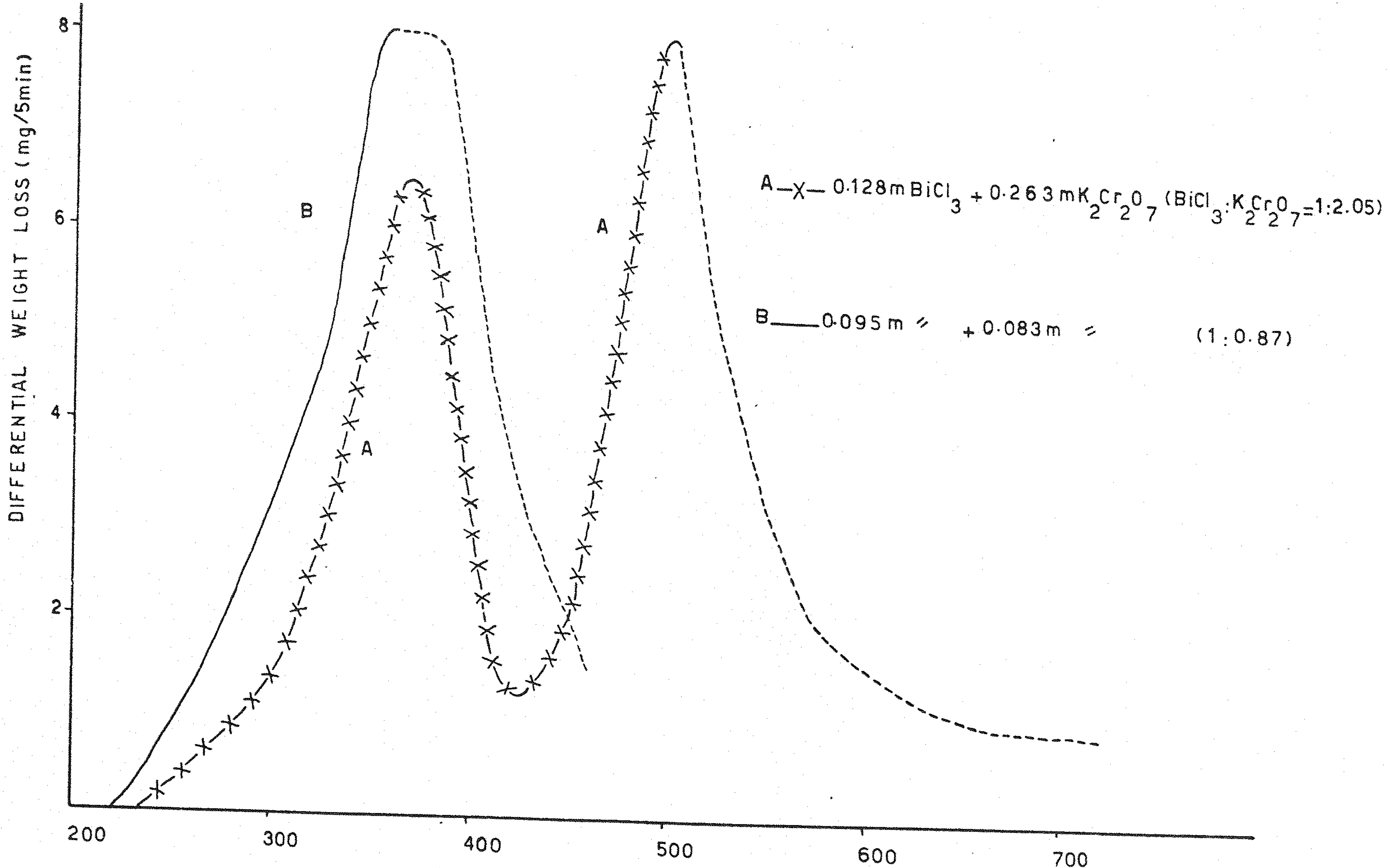


Fig 6 Thermogravimetric analysis of $BiCl_3$ in the melt containing $K_2Cr_2O_7$.

Table (10) Some thermogravimetric analysis results of reaction of $BiCl_3$ in a various concentration of $K_2Cr_2O_7$.

Ratio $Bi^{3+} : Cr_2O_7^{2-}$	Per cent weight loss		Time at 500°C h
	1st step	2nd step	
1 : 1.07	24.4	41.4	1
1 : 0.92	29.2	63.8	2
1 : 2.05	25.2	41.7	2
1 : 0.48	26.3	63.8	4
1 : 0.83	28.5	78.8	22

3.2.2.3 Reaction in the presence of potassium pyrosulphate

The evolution of nitrogen dioxide was noticed in a mixture of bismuth trichloride and potassium pyrosulphate (ratio of $Bi^{3+}:S_2O_7^{2-}=$ 3.6:1) in pure lithium nitrate-potassium nitrate eutectic at 160°C but at 200°C the result was a white suspension and nitrogen dioxide was no longer visible, while at 250°C it again started to evolve and at 320°C more became visible and the result was a white suspension and a white precipitate. At 450°C nitrogen dioxide was no longer visible and the products were a white precipitate and a colourless liquid, but after keeping the reaction at 500°C for three hours the colour changed to pale yellow.

This quenched melt was dissolved in water and the pale yellow insoluble product was analysed qualitatively, when it gave positive tests for bismuth and chloride ions, while quantitative analysis gave 84.0% Bi and 7.0% Cl (calculated for $Bi_{24}O_{31}Cl_{10}$, 85.5% Bi and 6.0% Cl and for $Bi_{12}O_{15}Cl_6$ 84.7% Bi and 7.2% Cl). Qualitative analysis of the aqueous filtrate gave a positive test for nitrite and chloride ions. This product was examined by x-ray diffraction, giving the d-spacings shown in Table (11).

When the experiment was repeated (ratio of $Bi^{3+}:S_2O_7^{2-} = 3:1$) but only heated to 400°C, the colour of the water insoluble product was white. Quantitative analysis gave 79.8% Bi and 14.0% Cl (Calculated for BiOCl is 80.2% Bi and 13.6% Cl). This product was also examined by x-ray diffraction and the d-spacings are shown in Table (12).

Thermogravimetric analysis (ratio 1.5:1), showed the first weight loss (Fig. 7) started rapidly at about 160°C, a second weight loss at 240°C and a third weight loss occurred when the experiment was kept at 480°C isothermally for twenty hours, continuously losing 2 milligrams in an hour. The first step gave a 33.5% weight loss on the basis of potassium pyrosulphate, the second step gave 33.4% weight loss on the basis of bismuth trichloride and the third step gave 33.2% weight loss after 20 hours on the basis of bismuth trichloride (overall weight losses of second and third steps, 66.4%).

Qualitative analysis of the product insoluble in water showed the presence of bismuth and chloride and quantitative analysis gave 83.4% Bi and 7.6% Cl (calculated for $Bi_{24}O_{31}Cl_{10}$, 85.5% Bi and 6.0% Cl and for $Bi_{12}O_{15}Cl_6$, 84.7% Bi and 7.2% Cl).

Table (11) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the melt containing $K_2S_2O_7$ at 500°C overnight

Pale yellow product $Bi^{3+} : S_2O_7^{2-}$ 3 : 1		From J.C.P.D.S. Index			
		$Bi_{24}O_{31}Cl_{10}$		BiOCl	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
4.35	35.5	4.11	40	7.38	40
3.79	5	-	-	-	-
3.64	4	3.69	60	3.64	16
-	-	3.55	60	-	-
3.34	30	3.40	20	3.44	100
-	-	3.10	60	-	-
-	1	3.08	80	-	-
3.03	100	3.02	80	-	-
		2.96	80	-	-
2.89	100[a]	2.82	80	-	-
-	-	2.80	80	2.75	12
2.69	37	-	-	2.67	95
2.50	82	2.52	20	2.57	10
-	-	2.47	40	2.45	12
-	-	2.39	40	-	-
2.35	9	2.36	40	-	-
2.28	80	-	-	-	-
2.18	16	2.21	100	2.20	30
-	-	2.08	80	-	-
-	-	2.02	80	-	-
1.98	22	1.99	80	-	-
1.91	15	-	-	1.94	35
				1.83	25
				1.69	25

a = peak was off chart

Table (12) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the melt containing $K_2S_2O_7$ at 400°C

White product $Bi^{3+} : S_2O_7^{2-} = 3 : 1$		BiOCl from J.C.P.D.S. Index	
d-spacings	I/Io	d-spacings	I/Io
7.24	100	7.38	40
3.66	41	3.69	16
3.42	18	3.44	100
2.74	12	2.75	12
2.66	30	2.67	95
2.56	2	2.57	10
2.44	27	2.45	12
2.19	6	2.20	30
1.94	4	1.94	35
1.82	6	1.83	25
1.68	4	1.69	25
1.66	12	1.66	18
1.57	6	1.57	30

When the experiment was repeated, the first weight loss also started rapidly at 160°C, the second at 240°C, but the reaction was kept isothermally at 450°C in order to avoid the decomposition of the nitrate melt. Fig. 7. As before the first step gave 33.2% weight loss on the basis of potassium pyrosulphate and the second step gave 33.1% weight loss on the basis of bismuth trichloride. However, this time quantitative analysis of the water-insoluble product gave 79.8% Bi and 12.9% Cl (calculated for BiOCl, 80.2% Bi and 13.6% Cl).

3.2.2.4 Discussion

In the melt containing potassium dichromate as a weakly acidic species, the first weight loss started at nearly the same temperature as that of bismuth trichloride alone with melt (Fig. 2), according to the equation III.12, to give bismuth oxychloride as a final product (Table 7). This reaction had not gone to completion, when the second reaction began. The second weight loss was expected to conform to the acid-base reaction of potassium dichromate with nitrate melt to give chromate and nitrogen dioxide as equation III.23.

$$Cr_2O_7^{2-} + 2NO_3^- \rightarrow 2CrO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \text{III.23}$$

which has a calculated weight loss of 36.7%. However, at a higher temperature (460°C), there was firstly replacement of chloride by chromate in the oxychloride, forming oxychromate according to equation III.24, which is an ion exchange reaction.

$$2BiOCl + CrO_4^{2-} \rightarrow (BiO)_2CrO_4 + 2Cl^- \qquad \text{III.24}$$

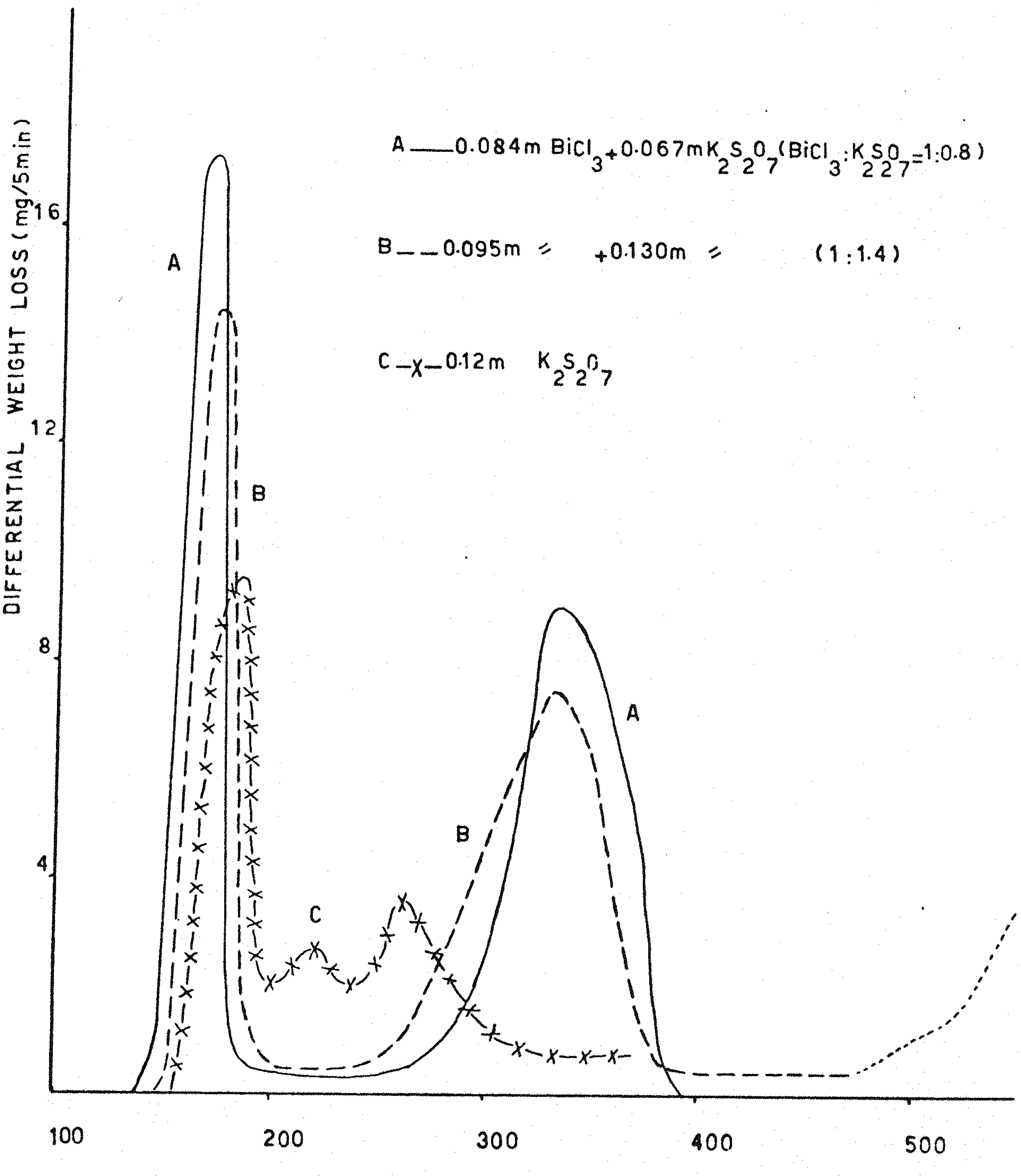


Fig 7 Thermogravimetric analysis of $BiCl_3$ in the melt containing $K_2S_2O_7$.

According to the x-ray results in Tables (8) and (9), it seems that a second replacement of chromate by oxide occurred to some extent, perhaps due to the self ionisation of melt as in equation III.9 and consequently shown by the evolution of nitrogen dioxide. The higher second weight loss in this reaction was probably due to self decomposition of melt as equation III.17 or decomposition due to catalysis by chloride ion.(80)

A comparison between reactions of bismuth trichloride in the pure lithium nitrate-potassium nitrate eutectic and in the melt containing potassium dichromate showed that both gave bismuth oxychloride (BiOCl) at temperature of 400°C, but the products were of different colours, white and pale yellow respectively. In comparing the final products at a higher temperature (500°C) the x-ray patterns show these to be a mixture of several bismuth oxychlorides (Table 1) and of bismuth oxychromate and bismuth oxide respectively, Tables (8) and (9) indicate that the replacement of chromate by oxide, giving bismuth oxide, was achieved more easily than the replacement of chloride by oxide.

In a strongly acidic melt containing potassium pyrosulphate, the weight loss started at 160°C which is the same temperature as that of pyrosulphate reaction alone with lithium nitrate-potassium nitrate eutectic (Fig. 3) and the curve also showed approximately the same maximum rate of weight loss, the products being nitrogen dioxide, oxygen and sulphate as equation III.25.

$$S_2O_7^{2-} + 2NO_3^- \rightarrow 2NO_2 + \tfrac{1}{2}O_2 + 2SO_4^{2-} \qquad \text{III.25}$$

which has a theoretical weight loss of 42.0%. This step was probably completed before the start of the second reaction (Fig.3) which is that of bismuth trichloride with melt to give nitrogen dioxide, oxygen and bismuth oxychloride as equation III.11. In a similar fashion to the previous discussion (section 3.3), it was found that in the reaction at a higher temperature there was again some replacement of chloride by oxide in the oxychloride (equations III.14, III.15, and III.16) originally formed again because of the self ionisation of melt as in equation III.9. This gave a higher concentration of oxide and consequently caused evolution of nitrogen dioxide (equation III.10). The higher third weight loss as expected was similar to the second weight loss found in the reaction of bismuth trichloride in the melt alone, (section 3.3) probably due to self decomposition of melt as equation III.16, possibly assisted due to catalysis by chloride ion.(80)

A comparison between the x-ray diffraction patterns of the two final products Tables (1) and (11) indicated that reaction of bismuth trichloride in the melt originally containing pyrosulphate as a strong acid was similar to that of bismuth trichloride alone in melt, (section 3.3), mainly because of the first reaction which is due to the pyrosulphate reaction with the melt, giving sulphate as in equation III.25. Therefore the second reaction occurred in presence of sulphate instead of pyrosulphate. However, qualitative analysis and x-ray diffraction gave no sign of sulphate in the product insoluble in water. Thus, these results indicated that sulphate ion had no apparent effect on the reaction of bismuth trichloride in the melt though chromate reacted by giving bismuth oxychromate as in equation III.24.

3.2.3 Reaction in basic melt

3.2.3.1 Introduction

The basic species in the nitrate melt have been studied by many workers (Chapter one) but perhaps the most unexpected results have been found by Zambonin and Jordan (36). They claimed that the oxide ion exists in the nitrate melt, but only in very small concentration. They postulated that the basic species was in fact the peroxide and superoxide ions (equations I.8 and I.9). But other workers have assumed the existence of the orthonitrate(39) or pyronitrate(34) ions where the oxide ions are combined with one or two nitrate ions. However a more extended discussion of basic species in the nitrate melt has been given in Chapter I, while in this section the behaviour of basic solutes like sodium peroxide, sodium hydroxide and potassium nitrite in the lithium nitrate-potassium nitrate melt will be discussed.

The first basic solute, sodium peroxide, has been reported by Habboush and Kerridge (101) to be slightly soluble in this melt and at 260°C there was a change in the colour of the solid from yellow to white. They reported that the decomposition (equation III.26) became more rapid above 300°C, but had ceased at 350°C.

$$Na_2O_2 \rightarrow Na_2O + \tfrac{1}{2}O_2 \qquad \text{III.26}$$

This equation has a theoretical weight loss of 20.5%, but they found a 10.7% weight loss. They concluded that this lower percentage weight loss was due to the formation of sodium monoxide on the surface of the peroxide where it was in contact with the melt and that this surface layer eventually became thick enough to protect the peroxide at the centre of the particles from further attack. The reaction between sodium peroxide and molten equimolar lithium nitrate-potassium nitrate at 250°C has also been studied using a potentiometric titration technique(102). El-Hosary and S hams El-Din reported that, melts containing lithium ions are more acidic than those with sodium or potassium ions. In particular they suggested that sodium peroxide reacts with lithium nitrate as in equation III.27:

$$4LiNO_3 + 2Na_2O_2 \rightarrow Li_4N_2O_7 + Na_4N_2O_7 + O_2 \qquad \text{III.27}$$

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

The behaviour of sodium hydroxide in the lithium nitrate-potassium nitrate has also been reported by Habboush and Kerridge.(101) They found that sodium hydroxide is stable in this melt up to 400°C, while above this temperature, it decomposed to sodium monoxide and water as in the equation III.28.

$$2NaOH \rightarrow Na_2O + H_2O \qquad \text{III.28}$$

Finally potassium nitrite was used in this investigation as an oxide donor because it dissociates and reacts as in the following equations;

$$NO_2^- \rightleftarrows NO^+ + O^{2-} \qquad \text{III.29}$$

$$NO_2^- + NO^+ \rightleftarrows (N_2O_3) \rightarrow NO_2 + NO \qquad \text{III.30}$$

The equilibrium constant for equation III.29 has been reported by

Kust and Burke(103) to be 1.3×10^{-9} in molten sodium nitrate-potassium nitrate eutectic at 300°C while Fredericks and Temple[104] reported the value of 1.8×10^{-9} in the same melt at 300°C. A comparison between these values and 5.7×10^{-24}, the value of the equilibrium constant for dissociation of the nitrate ion as in the equation I.2 ($NO_3^- \rightleftarrows NO_2^+ + O^{2-}$) in the sodium nitrate-potassium nitrate eutectic at 300°C given by Duke and co-workers (21,28) indicates that nitrite should be a stronger Lux-Flood base than the nitrate, but still much less basic than peroxide or hydroxide.

As previously described (in Section 3.1) bismuth III compounds in strongly alkaline aqueous solutions can be oxidized to a higher oxidation state, the penta valent. This oxidation has claimed the attention of several workers. For example, it has been reported that when bismuth III oxide was heated with an excess of an aqueous alkali hydroxide solution in air, the bismuth III oxide takes up oxygen, forming what was earlier called bismuth peroxide(67). Later, J.Lorch (105) reported that he did not succeed in washing out all alkali. Therefore he supposed that product to be an alkali bismuthate, while H. Martin(106) has reported that sodium metabismuthate ($NaBiO_3$) could be produced by oxidation of bismuth III oxide in a concentrated sodium hydroxide solution with hot concentrated sodium persulphate ($Na_2S_2O_8$).

Zintl and Scheiner(70) reported the synthesis of sodium bismuthate using a dry method, by heating a mixture of bismuth III oxide and sodium monoxide in dry air or in an oxygen atmosphere. They reported that the oxidation began at 170°C, but was not complete below 650°C. They also claimed that at first oxygen was absorbed, but toward the end of the reaction oxygen was evolved. Therefore they supposed that sodium peroxide was first formed and then this oxidized the bismuth III oxide to the bismuth V oxide with evolution of oxygen, this bismuth V oxide then reacting with sodium monoxide to form sodium orthobismuthate (Na_3BiO_4).

Scholder and Stobbe(144) reported that violet to red hydrated potassium bismuthate ($KBiO_3 \cdot \frac{1}{3} H_2O$) could be prepared by oxidizing a mixture of bismuth III oxide and 60% potassium hydroxide solution with bromine. They also reported that by double decomposition of sodium bismuthate with calcium chloride and potassium bismuthate with silver nitrate giving respectively calcium bismuthate and silver bismuthate.

Finally, various lithium bismuthates such as Li_3BiO_4, Li_5BiO_5 and Li_7BiO_6 have been reported to be made by heating mixtures of lithium oxide and bismuth III oxide in an oxygen atmosphere(71).

3.2.3.2 Reaction in the presence of sodium hydroxide

I. Bismuth trichloride was observed to react with lithium nitrate-potassium nitrate eutectic containing sodium hydroxide (ratio of bismuth trichloride to sodium hydroxide being 1:1) at 200°C forming a white precipitate and a white suspension. At 270°C nitrogen oxide started to be evolved at 350°C in large quantities, forming a white precipitate with some froth. Finally, at 380°C nitrogen dioxide was no longer visible and after half an hour at this temperature, a white precipitate and colourless liquid were formed. After cooling and dissolving the white quenched melt in water, the white insoluble product was filtered off and was dried in the oven at 120°C for two hours.

Qualitative analysis of this product showed the presence of both bismuth and chloride and quantitative analysis gave 79.8 per cent bismuth and 13.1 per cent chloride. (Calculated for BiOCl, 80.2% Bi and 13.6% Cl). This product examined by x-ray diffraction, gave the d-spacings as shown in Table (13).

II. When this experiment was repeated with a 1:7 ratio of bismuth trichloride to sodium hydroxide, observation showed a white precipitate and a pale yellow suspension had been formed at 190°C, which at 210°C had changed to a dense pale yellow precipitate and at 230°C to white. There was no evolution of nitrogen dioxide even after keeping the reaction for about two hours at this temperature. However, after cooling the quenched melt and dissolving in water, a pale yellow insoluble product was filtered off and dried. Qualitative analysis gave positive tests for both bismuth and chloride ions, while quantitative analysis gave 86.6 per cent bismuth and 3.7 per cent chloride. X-ray diffraction of this product gave d-spacings as shown in Table (14).

III. In another experiment heated to 400°C with the ratio of bismuth to hydroxide being 1:18, after the quenched melt was dissolved in water, a pale yellow insoluble product filtered off and dried in the oven at 120°C. Qualitative analysis gave a positive test for bismuth but negative for chloride and quantitative analysis gave 89.3 per cent bismuth. X-ray diffraction of this product gave d-spacings as shown in Table (15).

IV. This experiment was repeated with a ratio of bismuth to

Table (13) X-ray diffraction of white product obtained from the reaction of $BiCl_3$ in a melt containing NaOH (Ratio of $Bi^{3+} : OH^- = 1:1$)

White product at 380°C		BiOCl from J.C.P.D.S. Index (A.S.T.M.)	
d-spacings	I/Io	d-spacings	I/Io
7.36	100	7.38	40
3.67	42	3.69	16
3.43	85	3.44	100
2.74	46	2.75	75
2.67	92	2.69	95
2.57	8	2.57	10
2.45	40	2.45	12
2.20	25	2.20	30
1.94	20	1.94	35
1.82	20	1.83	25
1.69	15	1.69	25
1.66	27	1.66	18
1.57	20	1.57	30

Table (14) X-ray diffraction of pale yellow product obtained from the reaction of $BiCl_3$ in a melt containing NaOH (Ratio of Bi^{3+} : OH^- = 1:7)

Pale yellow product at 230°C		From J.C.P.D.S. Index (A.S.T.M.)			
		BiOCl		Bi_2O_3	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
7.36	99	7.38	40		
3.67	53	3.64	16		
3.42	23	3.44	100	3.45	20
3.29	29			3.31	35
3.24	100			3.25	100
3.17	16.5			3.18	25
2.76	10			2.76	6
2.74	18	2.75	75		
2.69	34			2.71	40
2.67	54.5	2.68	95	2.69	40
2.59	32	2.58	10		
2.54	12.6			2.56	16
2.49	6.5			2.50	8
2.44	34			2.42	6
2.38	10			2.39	14
2.20	6.5	2.20	30		
2.12	6.5			2.13	8
1.95	12.6	1.94	35	1.96	25
1.87	7.5	1.88	10	1.87	18
1.85	10	1.83	25		
1.75	7.5			1.75	10
1.69	5	1.69	25		
1.66	10	1.66	18		
1.59	7.5	1.57	30		

Table (15) X-ray diffraction of product obtained from the reaction of $BiCl_3$ in a melt containing NaOH (Ratio of $Bi^{3+}:OH^- = 1:18$)

Pale yellow		Bi_2O_3 from J.C.P.D.S. Index (A.S.T.M.)	
d-spacings	I/Io	d-spacings	I/Io
4.48	9	4.49	4
3.62	9	3.62	8
3.45	23	3.45	20
3.30	34	3.31	35
3.25	100	3.25	100
3.18	23	3.18	25
2.76	8	2.76	6
2.71	36	2.71	40
2.69	42	2.69	40
2.64	8	2.64	6
2.56	10	2.56	16
2.53	8	2.53	10
2.50	8	2.50	8
2.42	5	2.42	6
2.39	9	2.39	14
2.24	5	2.24	6
2.17	4	2.17	6
2.13	6.5	2.13	8

hydroxide being 1:13, the reaction being kept at 450°C for 6 hours, when a yellowish-orange precipitate formed which on cooling changed to yellow. After dissolving this solid in water, the water insoluble product was filtered off and dried in the oven. But during the washing the colour changed from yellow to brown. However, qualitative analysis still showed the presence of both bismuth and lithium, but the absence of chloride while nitrite ion was positive in the aqueous filtrate and quantitative analysis gave 79.8% Bi and 1.9% Li and an oxidizing power of 1.8 (calculated for $LiBiO_3$, 79.17% Bi and 2.65 % Li). X-ray diffraction of this product gave d-spacings as shown in Table (16).

Table (16) X-ray diffraction of product obtained from reaction of $BiCl_3$ in a melt containing NaOH (Ratio of $Bi^{3+}:OH^- = 1:13$)

d-spacings	I/Io
8.98	94
4.48	89
3.32	2
2.99	100
2.58	5
2.24	5
1.95	3
1.90	1.5
1.79	12.5

V. The experiment was repeated with the ratio of bismuth trichloride to sodium hydroxide being 1:14.5, heated to 500°C and kept at this temperature for 48 hours. The colour of the precipitate was orange, which was filtered off from the melt in the oven at 200°C and, while at this temperature, the colour changed to yellow. X-ray diffraction of this product shown in Table (17). This product had an oxidizing power of 2.05.

VI. Thermogravimetric analysis of bismuth trichloride in pure lithium nitrate-potassium nitrate eutectic containing sodium hydroxide, (the ratio of bismuth trichloride to sodium hydroxide being 1:0.4) showed that the weight loss started at 230°C with maximum rate of reaction at 330°C and a total weight loss of 24.8 per cent on the basis of bismuth trichloride at 370°C (Fig. 8). The white solid obtained by quenching the melt was dissolved in water, a white insoluble product being filtered off and dried in the oven at 120°C for two hours. Qualitative analysis showed the presence of both bismuth and chloride, but the absence of sodium, lithium and potassium ions, while quantitative analysis gave 79.2 per cent bismuth and 13.4 per cent chloride (calculated for $BiOCl$, 80.2% Bi and 13.6% Cl). X-ray diffraction of this product gave d-spacings as shown in Table (18).

VII. In another thermogravimetric analysis of bismuth trichloride in pure lithium nitrate-potassium nitrate eutectic containing sodium hydroxide, with a ratio of bismuth trichloride to sodium hydroxide of 1:13, the weight loss started at 220°C with a maximum rate of reaction at 350°C. This reaction was kept isothermally at 470°C for

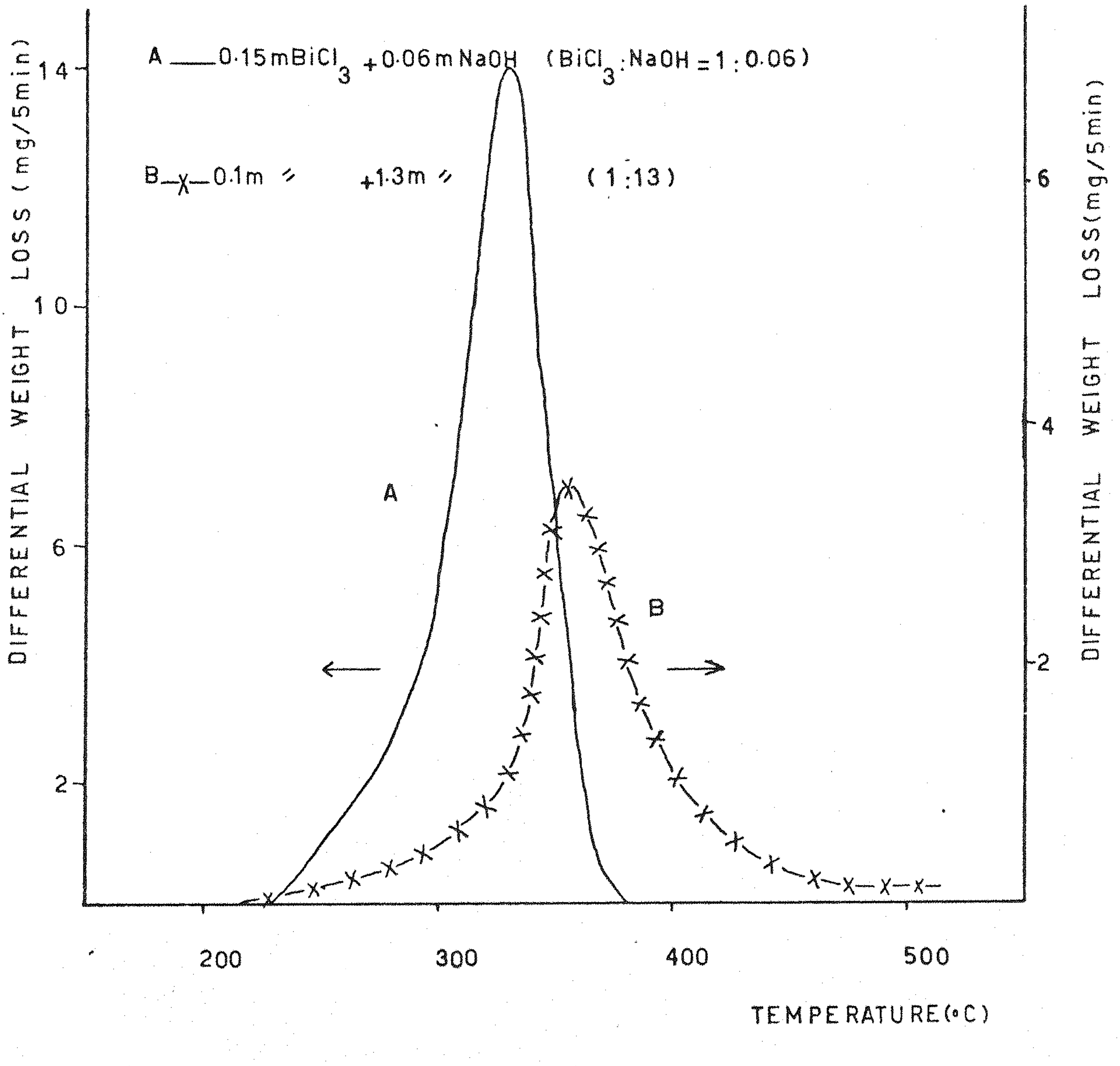


Fig 8 Thermogravimetric analysis of $BiCl_3$ in the melt containing NaOH.

Table (17) X-ray diffraction of product obtained from the reaction of $BiCl_3$, in a melt containing NaOH (Ratio of $Bi^{3+}:OH^- = 1:14.5$)

Product at 500°C		From J.C.P.D.S. Index (A.S.T.M.)			
		Li_3BiO_4		KNO_3	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
6.16	51.5	6.17	100		
4.64	4	-	-	4.66	23
3.90	100	3.91	100	-	-
3.79	84	3.80	100	3.78	100
3.72	8.5	-	-	3.73	56
3.48	44	3.48	60	-	-
3.03	13	-	-	3.03	55
2.75	23	2.76	40	2.76	28
2.65	6	-	-	2.66	41
2.49	28.5	2.49	50	-	-
2.41	14	2.42	30	-	-
2.40	31.5	2.39	50	2.40	7
2.31	17	2.31	25	2.33	9
2.18	37	2.18	100	2.19	41
2.11	15.7	2.10	100	2.15	20
2.96	6	-	-	2.07	13
1.99	6	1.99	10	2.05	18
1.89	21.5	1.89	40	-	-
1.85	23	1.85	50		
1.67	7	1.67	20		
1.62	13	1.62	20		
1.61	18.5	1.61	40		
1.58	14	1.59	30		
1.54	10	1.54	60		
1.51	20	1.51	60		

Table (18) X-ray diffraction of product obtained from the reaction of $BiCl_3$ in a melt containing NaOH (Ratio of Bi^{3+} : OH^- = 1:0.4)

White product at 370°C		BiOCl from J.C.P.D.S. Index (A.S.T.M.)	
d-spacings	I/Io	d-spacings	I/Io
7.36	100	7.38	40
3.67	40	3.69	16
3.43	45	3.44	100
2.74	25	2.75	75
2.67	45	2.69	95
2.45	25	2.45	12
2.20	10	2.20	30
1.94	10	1.94	35
1.82	10	1.83	25
1.69	10	1.69	25
1.66	17	1.66	18
1.57	10	1.57	30

20 hours, giving 23.4 per cent weight loss. The quenched melt was dissolved in water, and the yellow insoluble product was filtered off. During this washing the colour changed to light brown and after drying in the oven at 120°C for 2 hours the colour became darker. Qualitative analysis of this product gave positive tests for both bismuth and lithium but negative for chloride, sodium and potassium ions, while testing the aqueous filtrate showed the presence of nitrite. Quantitative analysis gave 77.5 per cent bismuth and 1.5 per cent lithium.

3.2.3.3 Discussion

The reaction of bismuth trichloride in the melt containing a low concentration of sodium hydroxide (Fig. 8) occurred at nearly the same temperature as that of bismuth trichloride alone with melt (Fig. 2, eq. III.12), and according to chemical analysis and x-ray results (Tables 13 and 18), gave the same product, bismuth oxychloride (BiOCl).

The experimental percentage weight loss (24.8% calculated on the bismuth trichloride was lower than the 34.25% weight loss calculated on bismuth trichloride from equation III.12 ($BiCl_3 + 2NO^-_3 \rightarrow BiOCl + 2NO_2 + \frac{1}{2}O_2 + 2Cl^-$). This difference is probably due to the reaction of some of the bismuth trichloride with sodium hydroxide according to the equation:-

$$BiCl_3 + 2NaOH \rightarrow BiOCl + NaCl + H_2O \qquad \text{III.29}$$

which has a calculated weight loss of 22.5% on the basis of sodium hydroxide or 5.7% weight loss based on bismuth trichloride.

In the presence of a high concentration of sodium hydroxide in the melt, the reaction of bismuth trichloride was quite different from that in the presence of a low concentration of sodium hydroxide. According to the x-ray results as shown in Table (17), the final product of this reaction was lithium bismuthate (Li_3BiO_4), which during the washing, was hydrolysed probably, to the brown lithium metabismuthate(71) ($LiBiO_3$), according to the chemical analysis, (79.8% Bi, 1.9% Li, calculated for $LiBiO_3$, 79.2% Bi and 2.65% Li).

The intermediate products were, according to x-ray results (Tables 14 and 15) firstly a mixture of bismuth oxychloride and bismuth III oxide but later entirely bismuth III oxide, formed by reaction of sodium hydroxide with bismuth trichloride as in equation III.29, the bismuth oxychloride reacting as in equation (III.30).

$$2BiOCl + 2NaOH \rightarrow Bi_2O_3 + 2NaCl + H_2O \qquad \text{III.30}$$

The latter equation giving a calculated weight loss of 3.45% on the basis of the bismuth oxychloride. The overall equation could thus be expressed as equation (III.31).

$$2BiCl_3 + 6NaOH \rightarrow Bi_2O_3 + 6NaCl + 3H_2O \qquad \text{III.31}$$

with a theoretical weight loss of 8.55% calculated on bismuth trichloride.

The second reaction, the oxidation of bismuth III (Bi_2O_3) to bismuth V (Li_3BiO_4) occurred at higher temperature (450°C), possibly according to equation (III.32):-

$$Bi_2O_3 + 8NaOH + 6Li^+ + 2NO_3^- \rightarrow 2Li_3BiO_4 + Na_2O + 4H_2O + 6Na^+ + 2NO_2^- \qquad \text{III.32}$$

with a theoretical weight loss of 15.45% based on the bismuth III oxide. Finally, then the overall reaction for this process would be as equation:-

$$2BiCl_3 + 14NaOH + 6Li^+ + 2NO_3^- \rightarrow 2Li_3BiO_4 + Na_2O + 6NaCl + 7H_2O + 6Na^+ + 2NO_2^- \qquad \text{III.33}$$

which has a calculated weight loss of 19.97% on the basis of bismuth trichloride.

Bismuthates are usually produced by dry methods, on heating a mixture of bismuth III oxide and alkali oxide or peroxide in the oxygen atmosphere and in a range of temperature of 500°C to 800°C, but neither sodium hydroxide nor bismuth trichloride have even been used in a dry method. However, in this investigation lithium bismuthate was formed only in presence of a high concentration of sodium hydroxide, the time required (48 hours) to oxidize bismith III to bismuth V at a temperature of 500°C. Scholder et al(71), produced the lithium bismuthate by heating a mixture of bismuth III oxide and lithium oxide at 600°C in an oxygen atmosphere for 6 hours.

3.2.3.4 Reaction in the presence of sodium peroxide

Observation of the reaction of bismuth trichloride in the lithium nitrate-potassium nitrate eutectic containing sodium peroxide-potassium nitrate eutectic containing sodium peroxide, (the ratio of bismuth trichloride to sodium peroxide being 1:1) showed a white precipitate and suspension at 200°C. By 280°C nitrogen dioxide was evolved which increased in quantity at 350°C.

The reaction mixture was kept at 400°C until the nitrogen dioxide was no longer visible. The quenched melt was dissolved in water and the water insoluble residue filtered off and dried. Qualitative analysis of this product showed the presence of both bismuth and chloride, while quantitative analysis gave 80.2% Bi and 13.2% Cl (claculated for BiOCl, 80.2% Bi and 13.6% Cl). X-ray diffraction of this product gave d-spacings as shown in Table (19).

In another experiment,(the ratio of bismuth trichloride to sodium peroxide being 1:3.6) observation showed a mixture of white and brown precipitates and suspension which at 300°C changed to yellowish-brown. By 400°C, the product was a pale yellow precipitate and colourless liquid. This experiment was kept at 500°C for two days, when the colour of the precipitate changed to orange, but after cooling it changed back to pale yellow. The quenched melt was dissolved in water and the insoluble residue filtered off and dried. During the washing and drying, the colour became brown. X-ray diffraction of this product gave three "d"-spacings at 2.99 (100), 4.47 (73) and 8.92 (58) which, although these cannot be assigned to any possible compound listed in the J.C.P.D.S. Index, are similar to those reported in Table (16).

When the experiment was reported with a ratio of 1:6 and kept at 450°C for 4 hours, the colour of precipitate was orange. This product was filtered off from the remaining melt in the oven at 200°C when the colour changed to yellow. X-ray diffraction of this product gave "d"-spacings as shown in Table (20). A number of the "d"-values were similar to those reported in Table (16).

Table (19) X-ray results of product obtained from reaction of $BiCl_3$ in the melt containing Na_2O_2 (with the ratio of $BiCl_3:Na_2O_2$ = 1:1)

White product at 400°C		BiOCl from J.C.P.D.S. Index (A.S.T.M.)	
d-spacings	I/Io	d-spacings	I/Io
7.39	100	7.38	40
3.70	38.7	3.69	16
3.47	25.5	3.44	100
2.77	16	2.75	75
2.68	35.7	2.67	95
2.59	2	2.57	10
2.46	31.6	2.45	12
2.21	8	2.20	30
1.95	6	1.94	35
1.83	9	1.83	25
1.69	5	1.69	25
1.66	11	1.66	18
1.57	9	1.57	30

Table (20) X-ray diffraction of unwashed product obtained from the reaction of $BiCl_3$ in the melt containing Na_2O_2

Pale yellow product filtered in the oven		From J.C.P.D.S. Index (A.S.T.M.)			
		Li_3BiO_4		KNO_3	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
8.98	92	-	-	-	-
6.19	36	6.17	100	-	-
4.50	87	-	-	-	-
3.91	100	3.91	100	-	-
3.79	87	3.80	100	-	-
3.49	41	3.48	60		
3.35	57	-	-	3.37	4
2.99	100	-	-	3.08	100
2.81	28	-	-	-	-
2.77	30.6	2.76	40	2.78	95
2.64	14.6	-	-	-	-
2.59	25	-	-	-	-
2.49	45.5	2.49	50	2.49	95
2.42	20	2.42	30	2.42	14
2.40	37.4	2.39	50	-	-
2.31	17.3	2.31	25	2.31	35
2.24	12	-	-	-	-
2.18	49.5	2.18	100	2.21	70
2.11	24	2.10	100	-	-
2.06	8	-	-	2.07	8
1.99	7	1.99	10	-	-
1.95	17.3	-	-	-	-
1.90	28	1.89	40	-	-
1.85	28	1.85	50	1.84	12
1.79	15	1.77	5	-	-
1.67	10.7	1.67	20	1.65	10
1.65	25.3	1.61	40	-	-
1.59	23	1.59	30	1.57	12
1.54	15	1.54	60	-	-
1.51	25.5	1.51	60		
1.49	12				
1.47	7				

Thermogravimetric analysis of bismuth trichloride in lithium nitrate-potassium nitrate eutectic containing sodium peroxide (ratio of bismuth trichloride to sodium peroxide being 1.06:1), showed the weight loss started at 150°C with the maximum rate of reaction at 340°C, giving 11.9% weight loss calculated on the bismuth trichloride at 440°C, Fig. (9). Chemical analysis of the water insoluble product gave 79.9% Bi and 13.4% Cl (calculated for BiOCl, 80.2% Bi and 13.6% Cl).

Thermogravimetric analysis was repeated with the ratio of bismuth trichloride to sodium peroxide being 1:4.3. The weight loss started at 150°C with the maximum rate of reaction at 290°C. This experiment heated to 600°C gave a total of 49.6% weight loss, but 37.2% weight loss at 470°C, Fig. (9), both weight losses were calculated on the bismuth trichloride. After dissolving the quenched melt in the water, the light-brown insoluble residue was filtered off and dried in the oven; during the drying colour changed to dark brown.

3.2.3.5 Discussion

In a melt containing sodium peroxide as the basic species, bismuth oxychloride was formed initially, when the ratio of bismuth trichloride to sodium peroxide was close to unity, suggesting:-

$$BiCl_3 + Na_2O_2 \rightarrow BiOCl + 2NaCl + \tfrac{1}{2}O_2 \qquad \text{III.34}$$

with a theoretical weight loss of 5.07% on the basis of bismuth trichloride. Any remaining bismuth trichloride (the exact ratio used was 1.06:1) was reacted with the nitrate melt to give bismuth

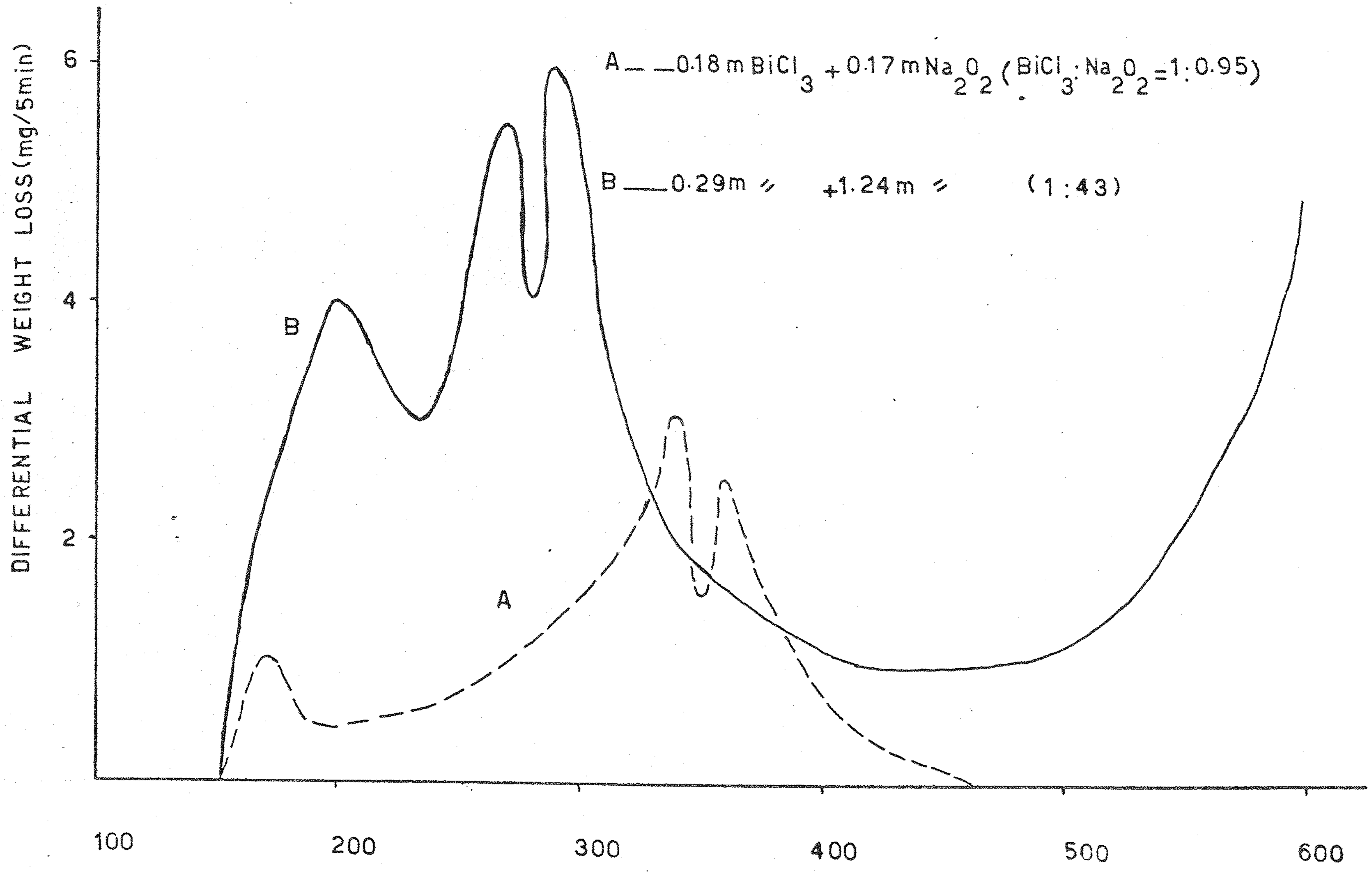


Fig 9 Thermogravimetric analysis of $BiCl_3$ in the melt containing Na_2O_2.

oxychloride, nitrogen dioxide and oxygen as in the equation III.12.

In the reaction with a higher concentration of sodium peroxide (with the larger ratio of 1:3.6) the bismuth trichloride probably first reacted with sodium peroxide to give bismuth oxychloride, according to equation (III.34), then at higher temperatures the bismuth III as BiOCl, oxidized to bismuth V (probably as lithium bismuthate) as in equation:-

$$BiOCl + 2Na_2O_2 + 2NO_3^- + 3Li^+ \rightarrow Li_3BiO_4 + NaCl + 3Na^+ + 2NO + 2O_2 + O^{2-} \qquad III.35$$

which has a theoretical weight loss of 47.6% on the basis of bismuth oxychloride. Thus, overall reaction would be as in equation:-

$$BiCl_3 + 3Na_2O_2 + 2NO_3^- + 3Li^+ \rightarrow Li_3BiO_4 + 3NaCl + 3Na^+ + 2NO + \frac{5}{2}O_2 + O^{2-} \qquad III.36$$

which has a theoretical weight loss of 44.37% on the basis of bismuth trichloride. The lower experimental weight loss of 37.2% at 470°C was probably due to an incomplete reaction of oxidation of bismuth III to bismuth V as in the equation III.35 and the higher experimental weight loss at 600°C possibly due to the self decomposition of melt as equation III.16.

X-ray examination of the unwashed final product after filtering in the oven gave d-spacings which corresponded to both lithium bismuthate and potassium nitrate, while the x-ray examination of the washed final product gave d-spacings of which the three largest peaks were similar to those found for product of the reaction of bismuth trichloride in the presence of hydroxide, (Table 16), and attributed to the lithium metabismuthate ($LiBiO_3$). This lithium metabismuthate has been reported by Scholder(71) and co-workers to be formed by hydrolysing compounds like Li_3BiO_4, Li_5BiO_5 and Li_7BiO_6 with water and the product having a formula of $LiBiO_3.XH_2O$ where X may be 1 to 1.74. Finally, we have not found any further report concerning lithium bismuthate compounds, thus it would appear that further work in this area is necessary to supplement the available data. For example, the use of lithium peroxide or lithium monoxide in the nitrate melt instead of sodium compounds might be expected to give a purer compound and a higher yield.

3.2.3.6 Reaction in the presence of potassium nitrite

Reaction of bismuth trichloride in lithium nitrate-potassium nitrate eutectic containing potassium nitrite, (the ratio of bismuth trichloride to potassium nitrate being 1.3:1) began with the evolution of nitrogen dioxide from 100°C, continuing up to about 400°C, with formation of a white precipitate and a colourless liquid and white froth from 200°C.

The white solid obtained by quenching the melt was dissolved in water and the white insoluble product was filtered off and dried in the oven for two hours at 120°C. Qualitative analysis showed only the presence of bismuth and chloride while quantitative analysis gave 79.5% Bi and 12.9% Cl (calculated for BiOCl, 80.2% Bi and 13.6% Cl).

When the experiment was repeated with a ratio of 1:4, observation showed the evolution of nitrogen dioxide at 100°C the rate decreasing at about 200°C, but nitrogen dioxide was still being evolved slightly up to 450°C, at which temperature the experiment was kept overnight.

Qualitative analysis on the white water-insoluble product gave positive tests for bismuth and chloride and quantitative analysis gave 79.6% Bi and 12.8%Cl.

Thermogravimetric analysis of bismuth trichloride in pure lithium nitrate-potassium nitrate eutectic containing potassium nitrite (ratio of Bi^{3+} : NO_2^- = 1:4), showed a rapid weight loss at 100°C which decreased at 180°C (Fig. 10.A). After keeping the reaction mixture isothermally at 350°C for ten hours the weight loss was 26.2% on the basis of bismuth trichloride (calculated for loss of 2N + 3O is 26.5%).

The white solid obtained by quenching the melt was dissolved in water and the white insoluble product was filtered off and dried at 120°C for two hours. Qualitative analysis gave positive tests for both bismuth and chloride, while quantitative analysis gave 79.8% Bi and 13.1% Cl.

In another thermogravimetric analysis, with the ratio of bismuth trichloride to potassium nitrite being 1:1.2, the first weight loss step started at 100°C with the maximum rate of the reaction at 140°C, giving 49.3% as the first weight loss (Fig. 10.B) on the basis of potassium nitrite. The second step, started at 250°C giving 33.7% weight loss at 400°C, based on the remaining bismuth trichloride. The white water-insoluble product gave positive tests for both bismuth and chloride and quantitative analysis gave 79.9% Bi and 13.2% Cl.

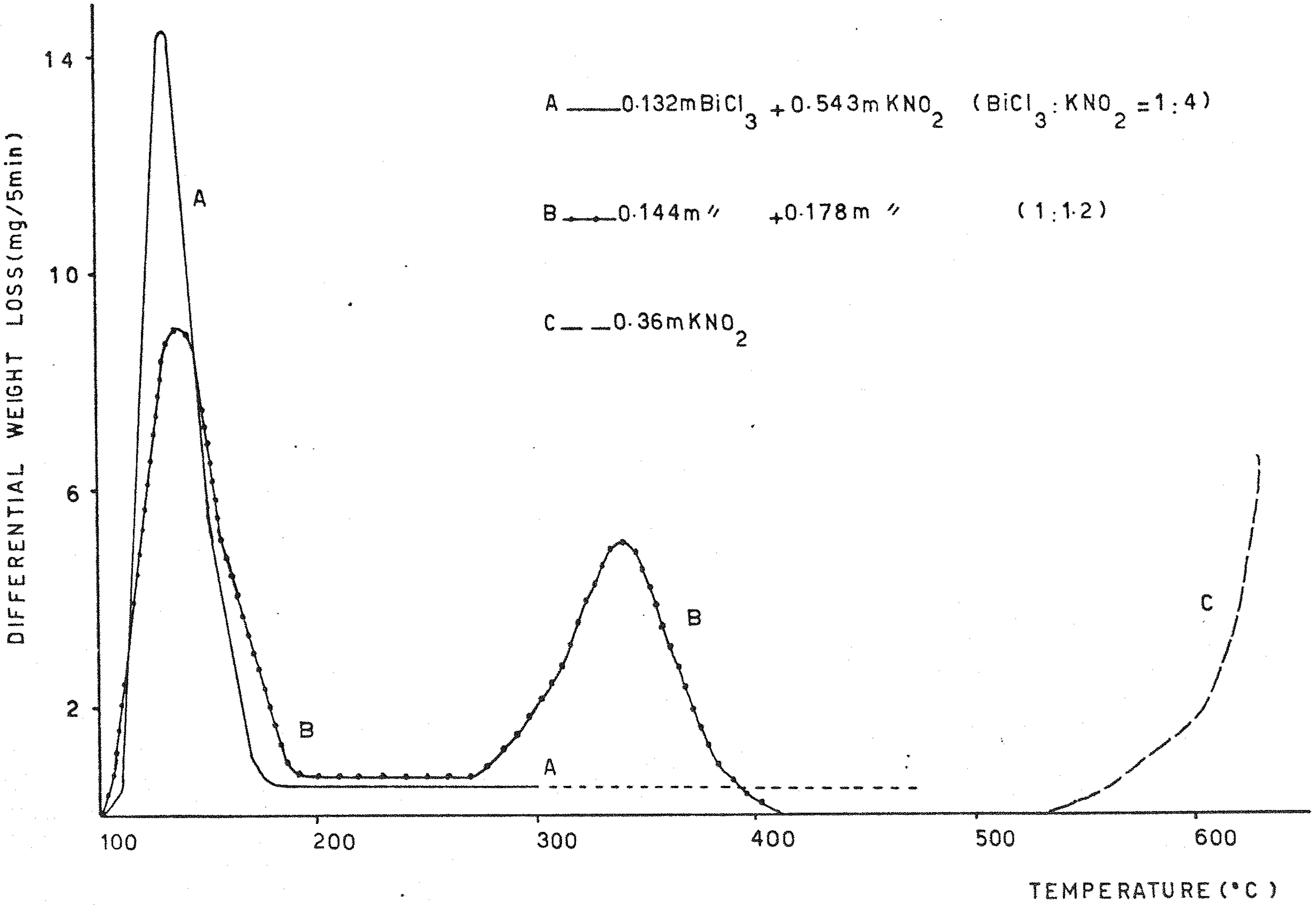


Fig 10 Thermogravimetric analysis of BiCl$_3$ in the melt containing KNO$_2$.

3.2.3.7 Discussion

Bismuth trichloride in the lithium nitrate-potassium nitrate eutectic containing potassium nitrite, rapidly reacted with potassium nitrite at the temperature of 100°C, (as in equation III.37), i.e. a lower temperature than in pure nitrate, due to higher basisity of nitrite and its much large self ionisation as compared with nitrate.

The equation:

$$BiCl_3 + 2NO_2^- \rightarrow BiOCl + NO_2 + NO + 2Cl^- \qquad \text{III.37}$$

has a theoretical weight loss of 26.5% calculated on the basis of bismuth trichloride and 49.2% based on the potassium nitrite.

In the case of a higher ratio of bismuth trichloride to potassium nitrite (1:1.2) than that of 1:2 as in the above equation (III.37), the bismuth trichloride remaining from the reaction with nitrite (as in equation III.37) reacted with the nitrate at a higher temperature than that of bismuth trichloride in pure nitrate, (starting temperature raised from 220°C to 250°C), according to the equation III.12, again to give bismuth oxychloride as a final product. The percentage weight loss of the first step was 49.3 on the basis of potassium nitrite and 33.7 for the second step when calculated on the basis of bismuth trichloride remaining from the first step. In the case of using a lower ratio of bismuth trichloride to potassium nitrate, (1:4) the only reaction occurring was as in the equation III.37. The experimental percentage weight losses of 49.3 (calculated on the potassium nitrite) and 33.7 (calculated on the remaining bismuth trichloride) when the ratio was 1:1.2, and for the ratio of

1:4, 26.2% weight loss (calculated on the bismuth trichloride) were in good agreement with the theoretical percentage weight losses. As shown in Fig. 10, the experimental data, indicated that no stabilization by nitrite acting as a ligand was observed, and the released chloride ion did not have a significant effect on the first peak because of the more rapid reaction when more easily available oxide ions are present. But the chloride ions affected the second peak by stabilizing the reaction of the remaining bismuth trichloride with the nitrate melt for 20°C.

3.2.4 Influence of added compounds acting as ligand

3.2.4.1 Reaction in the presence of potassium chloride

Observation of the reaction of bismuth trichloride in pure lithium nitrate-potassium nitrate eutectic containing potassium chloride (the ratio of bismuth trichloride to potassium chloride being 1:2.3), showed the evolution of nitrogen dioxide to begin at 220°C with the formation of a white suspension. At about 350°C more nitrogen dioxide was evolved, but at 400°C it was no longer visible and the products of the reaction were a white precipitate and colourless liquid. After cooling, the quenched melt was dissolved in water and then the white insoluble residue was filtered off and dried at 120°C. Qualitative analysis showed the presence of bismuth and chloride ions, while quantitative analysis gave 80.4% Bi and 13.1% Cl (calculated for BiOCl, 80.2% Bi and 13.6% Cl). X-ray diffraction of this product gave d-spacings as shown in Table (21).

Thermogravimetric analysis of bismuth trichloride in lithium nitrate-potassium nitrate containing potassium chloride, with a ratio

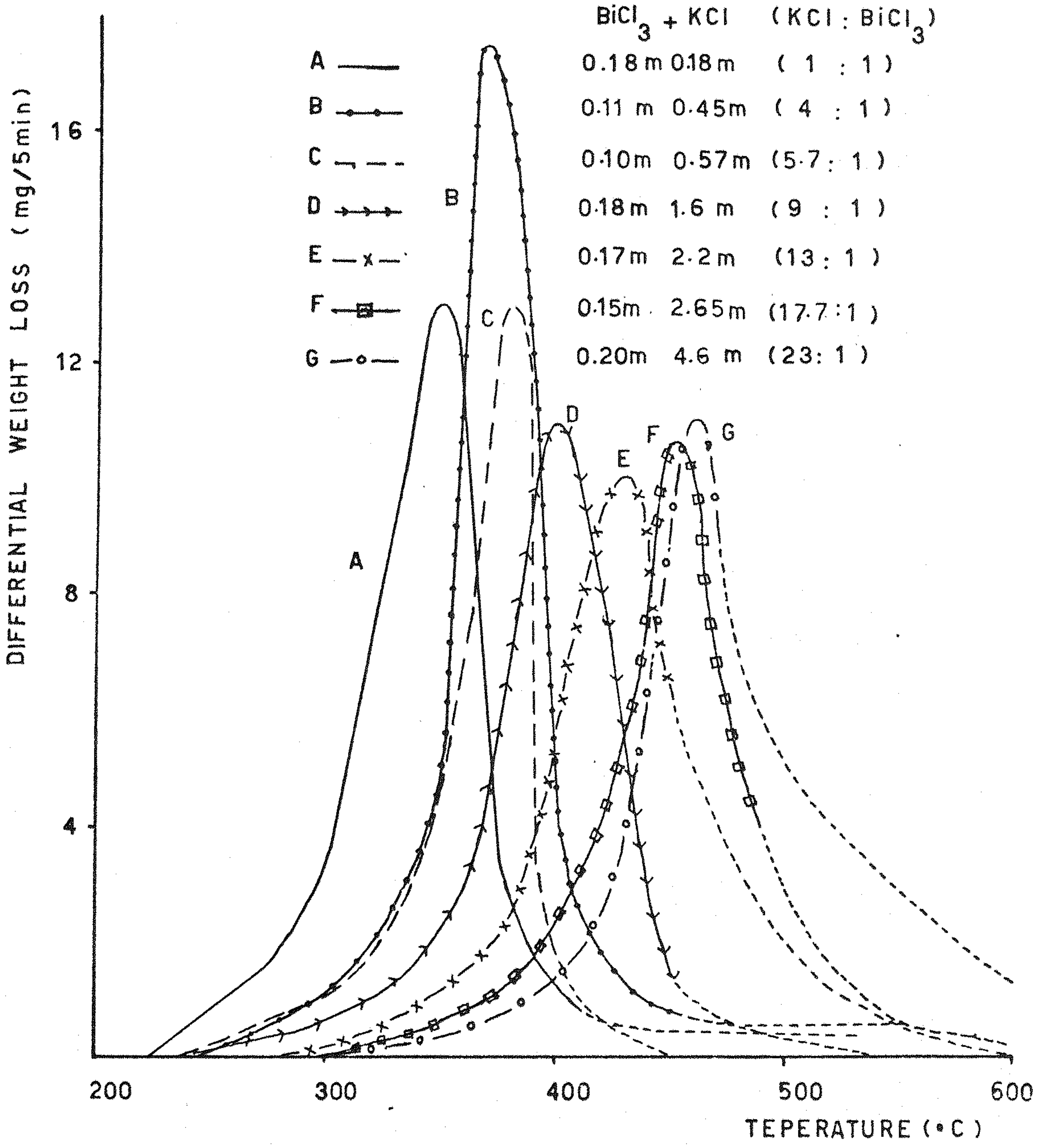


Fig 11 Thermogravimetric analysis of BiCl$_3$ in the melt containing KCl.

of bismuth trichloride to potassium chloride of 1:1, showed the weight loss started at about 230°C (Fig. 11). In order to prevent the decomposition of the melt, the reaction mixture was kept at 410°C for one hour, giving a 32.4% weight loss when an equilibrium weight loss was reached. Qualitative analysis of the white residue after solution in water, showed the presence of both bismuth and chloride, while quantitative analysis gave 79.5% Bi and 13.1% Cl.

Potassium chloride was then added in different molar ratios (i.e. of potassium chloride to bismuth trichloride) these being 4:1, 5.7:1, 9:1, 13:1, 17.7:1 and 23:1. The temperature of maximum rate of weight loss for all of these (shown in(Fig. 11))was found to increase with increasing ratio, the variation being shown in(Fig. 12 and 12A.) The total percent weight loss in each case was close to that found in the reaction of bismuth trichloride alone in the nitrate melt, Table (22).

3.2.4.2 Discussion

In melts containing potassium chloride as a ligand, bismuth trichloride still behaved as a Lux-Flood acid, by abstracting oxide ions from the nitrate to give bismuth oxychloride according to equation III.12, but the reaction started at a higher temperature than with bismuth trichloride alone in pure nitrate, and the temperature of maximum rate of weight loss increased progressively from 350°C to 460°C ± 10 with increasing ratios of potassium chloride to bismuth trichloride from 1:1 to 23:1 (Fig. 11). This indicates a stabilization of the bismuth cation towards the basic oxide ions formed by self ionisation of the melt which is probably due to the formation of chloro complexes such as $BiCl_4^-$.

Table (21) X-ray diffraction of product obtained from reaction of $BiCl_3$ in the melt containing KCl with a ratio of KCl to $BiCl_3$ = 2.3:1.

White product		BiOCl from J.C.P.D.S. Index	
d-spacings	I/Io	d-spacings	I/Io
7.36	100	7.38	40
3.67	71.5	3.69	16
3.43	43	3.44	100
2.72	21.5	2.75	75
2.67	64	2.67	95
2.57	4	2.57	10
2.45	57	2.45	12
2.25	8	2.20	30
1.94	6	1.94	35
1.83	8	1.83	25
1.69	6	1.69	25
1.66	28.5	1.66	18

Table (22) Some thermogravimetric results of the reaction of bismuth trichloride in melt containing various concentrations of potassium chloride

$BiCl_3$		KCl		Molar ratio	Weight loss		Temp. of max rate
g	molar m	g	molar m	KCl:$BiCl_3$	mg	%	°C
0.2094	0.18	0.0493	0.18	1:1	71	33.9	350
0.2195	0.11	0.2081	0.45	4:1	73	33.3	370
0.1811	0.10	0.2502	0.58	5.7:1	60	33.1	380
0.1884	0.18	0.3923	1.6	8.9:1	63	33.4	400
0.1947	0.17	0.6016	2.2	13:1	66	33.9	430
0.1889	0.2	1.0112	4.6	23:1	65	34.4	460

Similar effects of potassium chloride on the reaction of compounds of cobalt (11) with the lithium nitrate-potassium nitrate have been reported by Frozanfar and Kerridge (54). They found that potassium chloride stabilized the cobalt II nitrate hexahydrate and cobalt II chloride in the nitrate melt and by increasing the concentration of potassium chloride, the temperature of maximum reaction rate was also increased. While more recently Shakir (50) has reported a similar stabilization of indium trinitrate in the same nitrate eutectic in the presence of potassium chloride.

The nature of the insoluble bismuth product formed even in the higher temperature reaction,was however the same, i.e. bismuth oxychloride as found when no additional chloride was added. However, it should be noted that some free chloride ion is produced whenever bismuth trichloride reacts and hence some stabilization is presumably possible. Thus towards the end of the reaction, the bismuth species is in all cases probably the same bismuth chloro complex, e.g. $BiCl_4^-$. As shown in Figures 12 and 12A, this chloro complex is not easily formed, because the curve does not reach a constant temperature with the chloride to bismuth ratios used. This might be due to a fairly strong association of the bismuth III coordinated with nitrate ions. By increasing the chloride to bismuth ratios, the nitrate ions will however be replaced by the chloride ions. In Fig. 12A, zero chloride corresponds to the reaction of bismuth nitrate pentahydrated in pure melt and the experimental temperature of maximum reaction rate agrees with that obtained by extrapolating the curve back to zero chloride. This supports the idea that the bismuth III dissociated in the melt to a cation which was then coordinated by nitrate and/or chloride anions

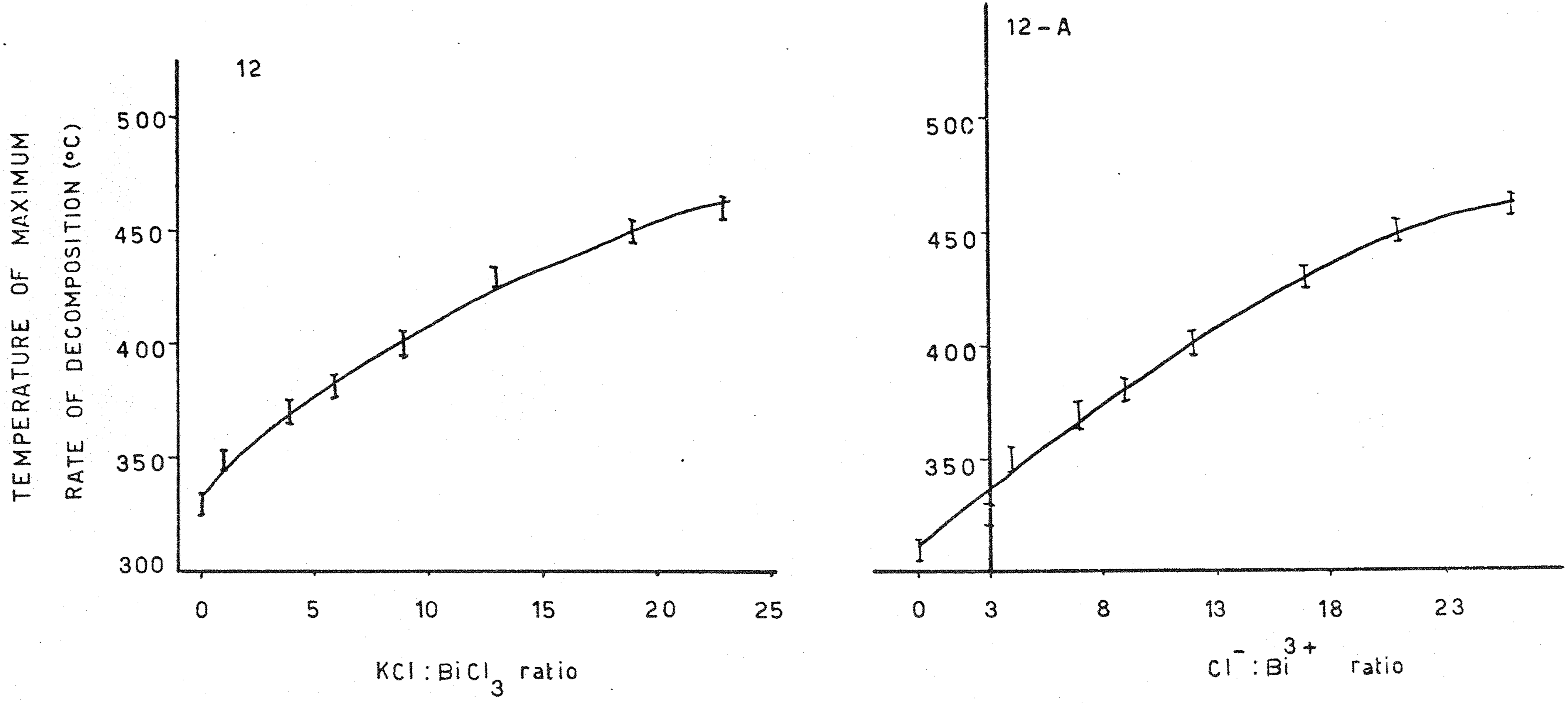


Fig (12) Variation of temperature rate of weight loss of bismuth trichloride in nitrate melt with different molar ratios of potassium chloride to bismuth trichloride.

and chloro coordination increasing with the concentration of latter, rather than the alternative possibility that the bismuth trichloride was largely undissociated in solution and only coordinated to one additional nitrate or chloride anion to take up the fourth coordination position.

3.3 Bismuth nitrate pentahydrate

In view of the effect of chloride ions in stabilizing bismuth cations and it being a constituent of the usual initial product (BiOCl) which when formed from bismuth trichloride results in the release of free chloride ions which can then take part in stabilization, the effect of a zero ratio was studied, i.e. of bismuth III reacting when no chloride was present.

3.3.1 Reaction alone in air and in pure nitrate melt

Hydrated bismuth nitrate alone began to lose water and nitric acid at 100°C, at 200°C nitrogen dioxide started to evolve and at above 400°C the colour of the solid started to change from white to pale yellow. The product formed at 500°C was analysed quantitatively, after cooling, for bismuth giving 89.5% Bi (calculated for Bi_2O_3 is 89.7%).

Thermogravimetric analysis (Fig. 13.A) showed the first weight loss started at about 100°C with maximum rate of reaction at 180°C while the second weight loss began at 200°C finishing at 550°C, giving a total 51.8% weight loss including 40.1% for the first step. Quantitative analysis of this final product gave 89.6% Bi.

Bismuth nitrate pentahydrate was observed to lose an acidic vapour at 120°C in lithium nitrate-potassium nitrate eutectic. At 250°C nitrogen dioxide started to be evolved continuously up to a temperature of 450°C, when the colour of the precipitate started to change from white to pale yellow. After keeping the reaction mixture at this temperature until nitrogen dioxide was no longer visible, and then cooling, the quenched melt was dissolved in water and the yellow water insoluble product filtered off and dried in the oven for two hours. Qualitative analysis of this product gave a positive test for bismuth but negative for lithium and potassium, whereas quantitative analysis gave 89.5% Bi.

Thermogravimetric analysis of bismuth nitrate pentahydrate in the lithium nitrate-potassium nitrate eutectic (Fig. 13.B), showed the first weight loss started at 80°C and the second weight loss at 170°C with the maximum rate of reaction at 320°C, giving a 52.9% weight loss at 480°C. After cooling and dissolving the quenched melt in water, the yellow insoluble product was filtered off and dried in the oven. Qualitative analysis gave positive tests for bismuth, while quantitative analysis gave 89.4% (calculated for Bi_2O_3 is 89.7% Bi).

3.3.2 Reaction in the melt in presence of sodium hydroxide

The observation of the reaction of bismuth nitrate pentahydrate in the pure lithium nitrate-potassium nitrate eutectic containing sodium hydroxide (the ratio of bismuth nitrate pentahydrate to sodium hydroxide being 1:27), showed a mixture of white and yellow

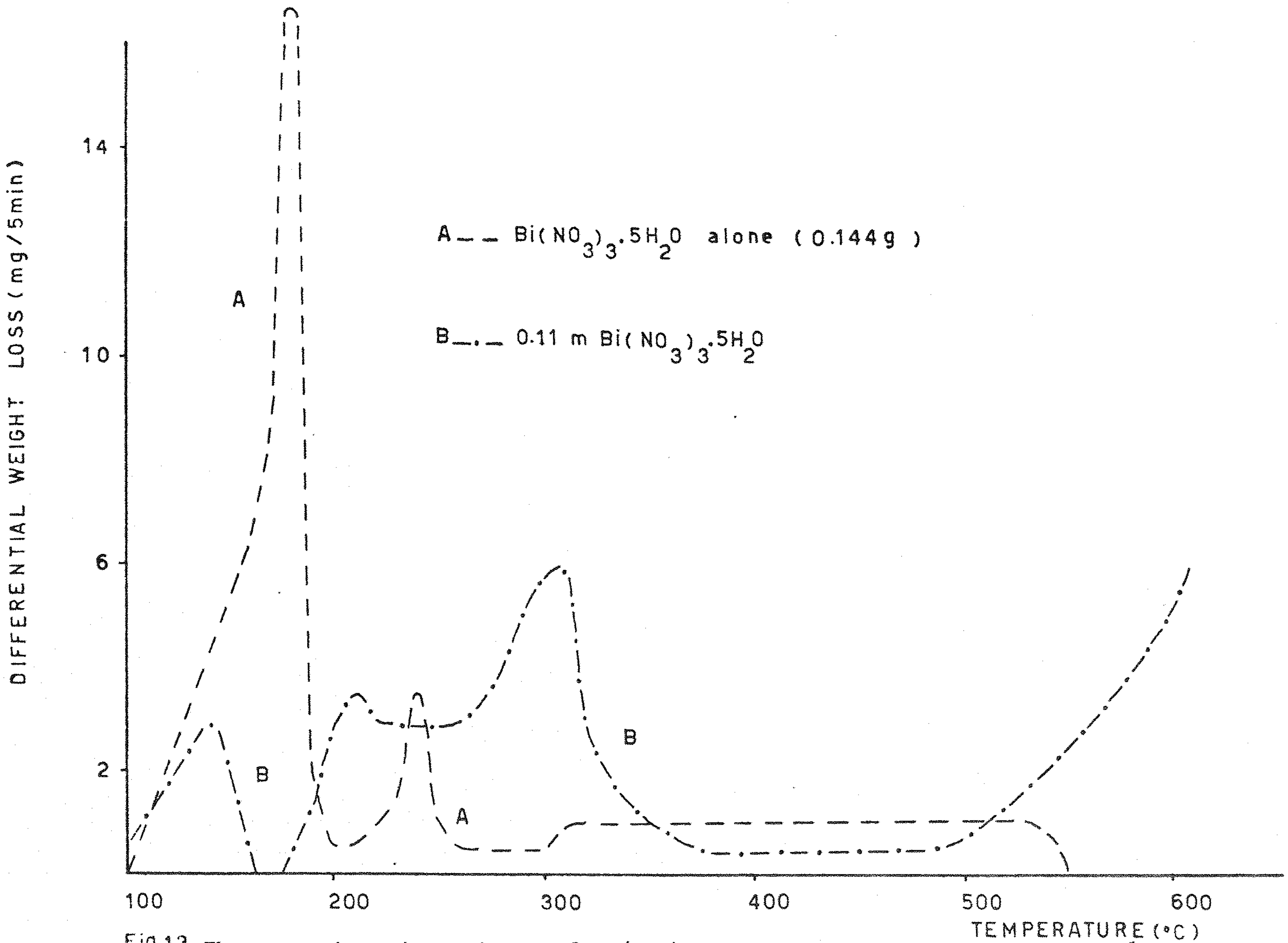


Fig 13 Thermogravimetric analysis of $Bi(NO_3)_3.5H_2O$ alone in air and in pure melt.

precipitates at 200°C. On keeping the reaction mixture at 250°C for 20 hours, the product was a pale yellow precipitate and colourless liquid. After cooling, the quenched melt was dissolved in water and the yellow insoluble product filtered off and dried in the oven at 120°C. Qualitative analysis gave a positive test for bismuth and quantitative analysis gave 89.4% Bi.

When the above experiment with the same ratio was repeated but at 400°C, the product was also a pale yellow precipitate and colourless liquid, though by keeping the reaction at 470°C for four hours, the colour of the precipitate changed to orange which on cooling changed back to pale yellow. The quenched melt was dissolved in water and the yellowish brown water insoluble residue, filtered off and dried in the oven at 120°C. Qualitative analysis of this product showed the presence of bismuth and lithium, while quantitative analysis gave 79.5% Bi and 3.1% Li. X-ray diffraction gave d-spacings corresponding to bismuth III oxide and lithium bismuthate, as shown in Table (23).

This experiment was repeated with the ratio of bismuth nitrate pentahydrate to sodium hydroxide of 1:34.5, but kept at 450°C for 24 hours. After cooling, the quenched melt was dissolved in water and the light brown insoluble product was filtered off and dried in the oven at 120°C. Quantitative analysis of this product gave 70.9% Bi and 5.5% Li, while analysis for oxidizing power gave 1.9 (calculated for Li_3BiO_4, 71.1% Bi, 7.1% Li and oxidizing power 2.0). X-ray diffraction of above product gave d-spacings as shown in Table (24).

Thermogravimetric analysis (Fig. 14-A) (the ratio of $Bi^{3+}:OH^{-}=1:27.6$), Table (23) X-ray diffraction of product obtained from reaction of $Bi(NO_3)_3.5H_2O$ in the nitrate melt containing NaOH (the ratio of $Bi^{3+}:OH^- = 1:27$).

Yellowish brown product at 470°C		From J.C.P.D.S. Index			
		Bi_2O_3		Li_3BiO_4	
d-spacing	I/Io	d-spacing	I/Io	d-spacing	I/Io
6.16	48	-	-	6.17	100
3.90	100	-	-	3.91	100
3.79	52	-	-	3.80	100
3.61	8	3.62	100	-	-
3.49	32	-	-	3.48	60
3.45	20	3.45	20	-	-
3.30	26	3.31	35	-	-
3.24	60	3.25	100	-	-
3.17	18	3.18	25	-	-
2.76	20	2.76	6	2.76	40
2.69	32	2.69	40	-	-
2.63	6	2.64	6	-	-
2.54	10	2.53	10	-	-
2.49	30	-	-	2.49	50
2.44	18	-	-	2.42	30
2.39	24	-	-	2.39	50
2.31	14	-	-	2.31	25
2.24	4	2.24	6	-	-
2.18	36	-	-	2.18	100
2.10	14	-	-	2.10	100
2.05	6	2.04	2	-	-
1.99	4	1.99	4	1.99	10
1.95	8	1.96	25	-	-
1.89	18	1.88	10	1.89	40
1.87	12	1.87	18	-	-
1.85	20	1.84	6	1.85	50
1.65	12	-	-	1.67	20
1.63	12	-	-	1.62	20
1.61	20	-	-	1.61	40
1.59	20	-	-	1.59	30

Table (24) X-ray diffraction of product obtained from reaction of $Bi(NO_3)_3.5H_2O$ in the melt containing NaOH (the ratio of $Bi^{3+}:OH^- = 1:34.5$)

light brown product		Li_3BiO_4 from J.C.P.D.S.	
d-spacings	I/Io	d-spacings	I/Io
6.14	48	6.17	100
3.89	100	3.91	100
3.78	75	3.80	100
3.47	38	3.48	60
2.76	19	2.76	40
2.49	30	2.49	50
2.42	15	2.42	30
2.39	25	2.39	50
2.30	11	2.31	25
2.18	37	2.18	100
2.10	14	2.10	100
1.99	3	1.99	10
1.89	18	1.89	40
1.85	19	1.85	50
1.65	7	1.67	20
1.63	10	1.62	20
1.61	18	1.61	40
1.59	20	1.59	30

showed the weight loss started at 190°C with the maximum rate of reaction at 240°C and by keeping the reaction at 250°C for 20 hours, gave an overall 24.5% weight loss calculated on the basis of bismuth nitrate pentahydrate. Quantitative analysis of the yellow water insoluble residue gave 89.5% Bi.

In another thermogravimetric analysis with the ratio of $Bi^{3+}:OH^{-}$ = 1:26, the weight loss started at 180°C with the maximum rate of reaction at 255°C. This reaction kept at 450°C for 24 hours gave a 40.6% weight loss on the basis of bismuth nitrate pentahydrate. Quantitative analysis of the light brown residue after solution in water, gave 70.7% Bi and 5.2% Li while analysis for oxidizing power gave 1.8. X-ray diffraction of this product gave d-spacings as shown in Table (25).

3.3.3 Discussion

When bismuth nitrate pentahydrate was heated alone in air, the first step gave bismuth oxynitrate as equation:-

$$Bi(NO_3)_3.5H_2O \rightarrow BiONO_3 + 4H_2O + 2HNO_3 \qquad \text{III.38}$$

with the theoretical weight loss of 40.8% and the second step was decomposition of the bismuth oxynitrate to bismuth III oxide as in equation:-

$$BiONO_3 \rightarrow Bi_2O_3 + 2NO_2 + \tfrac{1}{2}O_2 \qquad \text{III.39}$$

which has a theoretical weight loss of 11.1%. The experimental weight loss of 40.1% and 11.7% were in reasonable agreement with the theoretical weight loss.

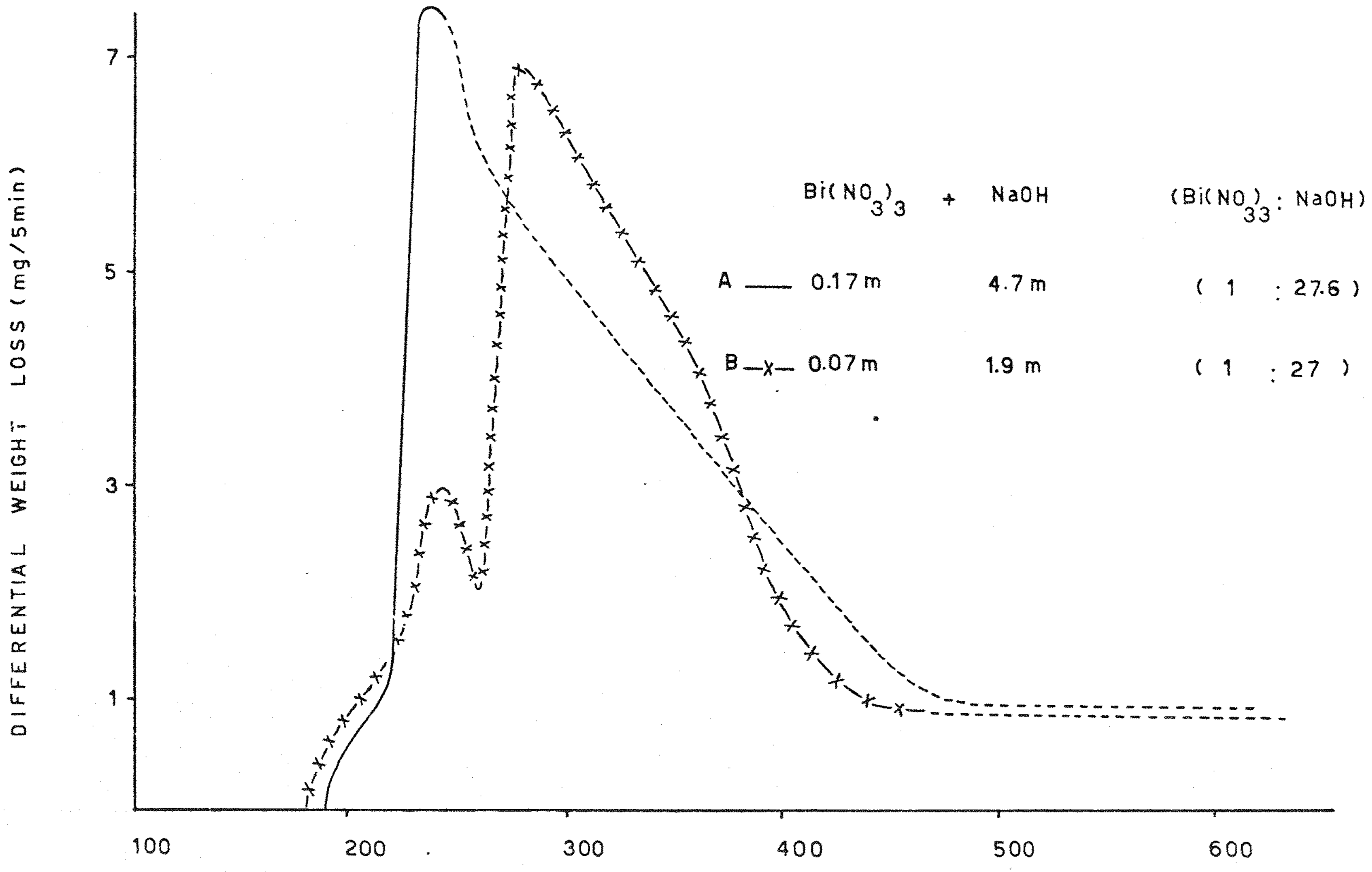


Fig 14 Thermogravimetric analysis of $Bi(NO_3)_3 \cdot 5H_2O$ in the melt containing NaOH.

Table (25) X-ray diffraction of product obtained from reaction of $Bi(NO_3)_3.5H_2O$ in the melt containing NaOH (the ratio of Bi^{3+} : OH^- = 1:26)

light brown product		Li_3BiO_4 from J.C.P.D.S. Index	
d-spacings	I/Io	d-spacings	I/Io
6.16	41.5	6.17	100
3.90	100	3.91	100
3.79	87.6	3.80	100
3.47	40.5	3.48	60
2.76	18	2.76	40
2.48	32.6	2.49	50
2.41	14.6	2.42	30
2.39	28	2.39	50
2.30	14.6	2.31	25
2.18	37	2.18	100
2.10	18	2.10	100
1.99	3	1.99	10
1.89	18	1.89	40
1.85	26	1.85	50
1.67	8	1.67	20
1.62	8	1.62	20
1.61	18	1.61	40
1.58	16	1.59	30
1.54	9	1.54	60

Several workers have reported that they obtained bismuth III oxide as a final product when bismuth nitrate pentahydrate or bismuth oxynitrate were heated, but they have reported different temperatures for conversion into the bismuth III oxide ranging from 450-650°C(107-110). For example, Duval reported the temperature of 600°C for conversion of bismuth nitrate pentahydrate to bismuth III oxide while Battow and Kiel reported the temperature of 450°C for the conversion of bismuth oxynitrate to the bismuth III oxide. Here the reaction was completed at 550°C though the major weight loss was finished by 300°C.

In lithium nitrate-potassium nitrate eutectic, bismuth nitrate pentahydrate started to lose a mixture of water and nitric acid at about 100°C, in accordance with the equation III.38. This step had not gone to completion when the eutectic started to melt, but the second step started at 170°C which was followed by a third reaction to give bismuth III oxide, nitrogen dioxide and oxygen as in equation III.39.

The experimental data and comparison of this reaction with that of bismuth nitrate pentahydrate alone in air (Fig.13) indicated that the first step, which was formation of bismuth oxynitrate from bismuth nitrate pentahydrate, was stabilized by nitrate melt. In comparing the reaction of bismuth trichloride alone with pure nitrate,(which gave BiOCl at 400°Cand later at 500°C a mixture of several bismuth oxychlorides like $Bi_{12}O_{15}Cl_6$, $Bi_{24}O_{31}Cl_{10}$) with the reaction of bismuth nitrate pentahydrate in the melt which gave a bismuth III oxide as a final product at 450°C-500°C, it was found that bismuth trichloride is more stable in nitrate melt than bismuth nitrate pentahydrate. Therefore adding sodium hydroxide to this reaction may result in the formation of lithium bismuthate at a lower temperature than that necessary for the reaction of bismuth trichloride in the basic melt.

In the melt containing sodium hydroxide, the evolution of water started at about 180°C, probably due to the combination of bismuth nitrate pentahydrate with sodium hydroxide. Bismuth III oxide was formed at 200°C, a lower temperature than in pure nitrate, as in the equation:-

$$2Bi(NO_3)_3.5H_2O + 6NaOH \rightarrow Bi_2O_3 + 13H_2O + 6NaNO_3 \qquad III.40$$

which has a theoretical weight loss of 24.1% (calculated on the basis of two molecules of bismuth nitrate pentahydrate. This reaction was followed by reaction of bismuth III oxide with hydroxide in the melt to give lithium bismuthate as in the equation III.41:

$$Bi_2O_3 + 8NaOH + 2NO_3^- + 6Li^+ \rightarrow 2Li_3BiO_4 + Na_2O + 4H_2O + 6Na^+ + 2NO_2^- \qquad III.41$$

with a theoretical weight loss of 15.4% on the basis of bismuth III oxide and 7.4% based on the two molecules of bismuth nitrate pentahydrate. The experimental weight loss of 24.5% is in good agreement with the theoretical weight loss of 24.1% for the formation of bismuth III oxide and the higher experimental weight loss of 40.6% (compared with the overall theoretical weight loss of 31.5%) is probably due to the self decomposition of melt as equation III.17. X-ray results and the chemical analyses of 70.9% Bi, 5.5%Li, oxidizing power of 1.90 and 70.7% Bi, 5.2% Li and 1.85 oxidizing power, obtained from the products heated to 450°C for 24 hours, from both reactions in a basic melt, indicated that in such a melt bismuth III was oxidized to bismuth V. By comparing this reaction with the reaction of bismuth trichloride in a basic melt (Section 3.2.3) it can be shown that the lithium bismuthate was formed at a lower temperature and shorter time (24 hours at 450°C) than that of 60 hours at 500°C of the reaction of bismuth trichloride in the melt containing sodium hydroxide.

More recently, Vallaly(111) has reported the formation of lithium bismuthate from reaction of bismuth nitrate pentahydrate and bismuth III oxide in lithium nitrate-potassium nitrate eutectic containing basic species. He reported a quantitative analysis of 70.4% Bi, 5.1% Li and 1.95 oxidizing power for the reaction product obtained from heating the bismuth nitrate pentahydrate in the melt containing sodium hydroxide (ratio of $Bi^{3+}:OH^- = 1:36$) at 450°C for 20 hours, which is similar to the results found here from the product obtained from the same reaction. When sodium peroxide was used, he found a slightly different percentage of bismuth and lithium (71.1% Bi and 2.8% Li) but similar oxidizing power (1.94), calculated for Li_3BiO_4, 71.1% Bi, 7.1% Li and oxidizing power of 2. In both experiments (in presence of NaOH and Na_2O_2 respectively) he found the bismuth III oxide as an intermediate product, and therefore began with bismuth III oxide instead of bismuth nitrate pentahydrate in the melt containing sodium hydroxide, but found a rather lower percentage of bismuth in the end product (67.9% Bi, 5.8% Li and 1.89 oxidizing power). Finally, that chemical analysis on the final products obtained from reaction of bismuth III compounds in the melt containing sodium hydroxide and peroxide gave a lower percentage of lithium (ranging from 5.1% - 5.8%), than the theoretical value of 7.1%,is probably due to the washing out of the lithium as lithium hydroxide during dissolution of the quenched melt.

It would appear that further work in this area is necessary to completely characterise the product. Also the effect of different reaction conditions could be investigated, for example the use of lithium peroxide or monoxide in the nitrate melt instead of sodium compounds might be expected to give a purer compound and a higher yield. Moreover, using cold water or alkaline hydroxide solution and fast powdering the reaction product, a fast dissolution may be achieved, thus reducing hydrolysis and giving a higher yield of the lithium bismuthate V.

3.4 Sodium metabismuthate

3.4.1 Reaction of sodium metabismuthate alone in air and in pure melt

Sodium metabismuthate alone in air showed evolution of water at 120°C which increased at 170°C. By 350°C the colour had changed from yellowish brown to dark brown, at 450°C to yellow, and at 500°C to dark red. On cooling the colour changed back to yellow. A sample of the yellow product was dissolved in concentrated nitric acid and quantitative analysis on the solution gave 78.3% Bi (calculated for a mixture of Bi_2O_3 + Na_2O_2 (one to one) is 76.8% Bi and for Bi_2O_3 + Na_2O is 79.1% Bi). By dissolving another sample of this product in water, sodium oxide was dissolved and a yellow water insoluble product was filtered off and dried at 120°C for two hours. Qualitative analysis on this product and on the aqueous filtrate gave positive tests for bismuth and sodium respectively, while quantitative analysis on the yellow product gave 89.4% Bi (calculated for Bi_2O_3 is 89.7% Bi).

In another experiment, quantitative analysis of the dark brown product formed after heating only to 380°C gave 76.7% Bi (calculated for a one to one mixture of Bi_2O_3 + Na_2O_2).

Thermogravimetric analysis of sodium metabismuthate ($NaBiO_3$) showed the first weight loss started at 80°C with the maximum rate of weight loss at 170°C, the second weight loss by 200°C and the third weight loss at 420°C, (Fig. 15-A) giving for the first, second and the third stages weight losses of 7.2%, 4.3% and 1.5% respectively. X-ray diffraction of water insoluble product gave d-spacings as shown in Table (26).

Sodium metabismuthate in pure lithium nitrate-potassium nitrate eutectic, began to lose water below 100°C. At 180°C, there was a yellowish-brown precipitate and suspension, while by 220°C the colour of the precipitate had changed to dark brown. By 400°C the colour of the precipitate changed to pale yellow and until 500°C there was no further change. After dissolving the quenched melt in water, a pale yellow insoluble product was filtered off and dried at 120°C for two hours. Qualitative analysis of this product gave positive tests for bismuth and lithium while quantitative analysis gave 86.8% Bi and 0.65% Li (calculated for Bi_2O_3 is 89.7% Bi and for $LiBiO_2$, 84.3% Bi and 2.8% Li). X-ray diffraction of the above product gave d-spacings as shown in Table (27).

Thermogravimetric analysis of sodium metabismuthate in pure nitrate melt showed that the first weight loss started below 100°C, the second weight loss at 170°C with the maximum rate of reaction at 230°C and a third weight loss at 475°C (Fig. 15-B), giving 6.7% weight loss of the first step and 9.4% weight loss for the second step. After dissolving the quenched melt from heating to 600°C in

Table (26) X-ray diffraction of product obtained from reaction of $NaBiO_3$ alone in air, heated to 420°C

Yellow insoluble product after dissolving in water		J.C.P.D.S. Index Bi_2O_3		Yellow insoluble product after dissolving in water		J.C.P.D.S Index Bi_2O_3	
"d"	I/Io	"d"	I/Io	"d"	I/Io	"d"	I/Io
4.50	3	4.49	4	2.42	6	2.42	6
4.07	3	4.08	4	2.38	14	2.39	14
3.61	10	3.62	8	2.24	6	2.24	6
3.44	28	3.45	20	2.16	6	2.17	6
3.30	39	3.31	35	2.15	6	2.15	6
3.25	100	3.25	100	2.12	7	2.13	8
3.17	29	3.18	25	2.00	6	2.00	6
2.75	6	2.76	6	1.95	21	1.96	25
2.71	50	2.71	40				
2.69	64	2.69	40	1.90	3	1.90	4
2.63	6	2.64	6	1.87	17	1.87	18
2.55	14	2.56	16	1.84	6	1.84	6
2.53	8	2.53	10	1.75	12.5	1.75	10
2.49	7	2.50	8				

Table (27) X-ray diffraction of product obtained from reaction of $NaBiO_3$ in pure melt heated to 500°C

Pale yellow product		From J.C.P.D.S. Index (A.S.T.M.)			
		Bi_2O_3		Li_3BiO_4	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
6.27	38.5	-	-	6.17	100
5.90	10	-	-	-	-
5.02	10	-	-	-	-
4.37	21	-	-	-	-
4.31	32.5	-	-	3.91	100
3.87	19	-	-	3.80	100
3.73	10	-	-	-	-
3.64	13.5	3.62	8	-	-
3.58	27	-	-	-	-
3.45	8	3.45	20	3.48	60
3.29	23	3.31	35	-	-
3.25	100	3.25	100		
3.17	13.5	3.18	25		
3.13	23	-	-		
3.08	10	-	-		
3.03	88.5	-	-		
2.89	23	-	-		
2.70	23	2.71	40	2.76	40
2.68	52	2.69	40		
2.62	31	2.64	6		
2.57	8	2.56	16	2.49	50
2.38	8	-	-	2.42	30
2.35	10	-	-	2.35	50
2.19	19	2.00	6	2.18	100
2.12	8	-	-	2.10	100
1.98	14	1.99	4	1.99	10
1.97	14	-	-		
1.96	10	1.96	25		
1.88	9	1.88	10	1.89	40
1.87	9	1.87	18	1.85	50
1.74	10	1.75	10		
-	-	-	-	1.67	20
-	-	-	-	1.62	20
-	-	-	-	1.61	40
-	-	-	-	1.59	30

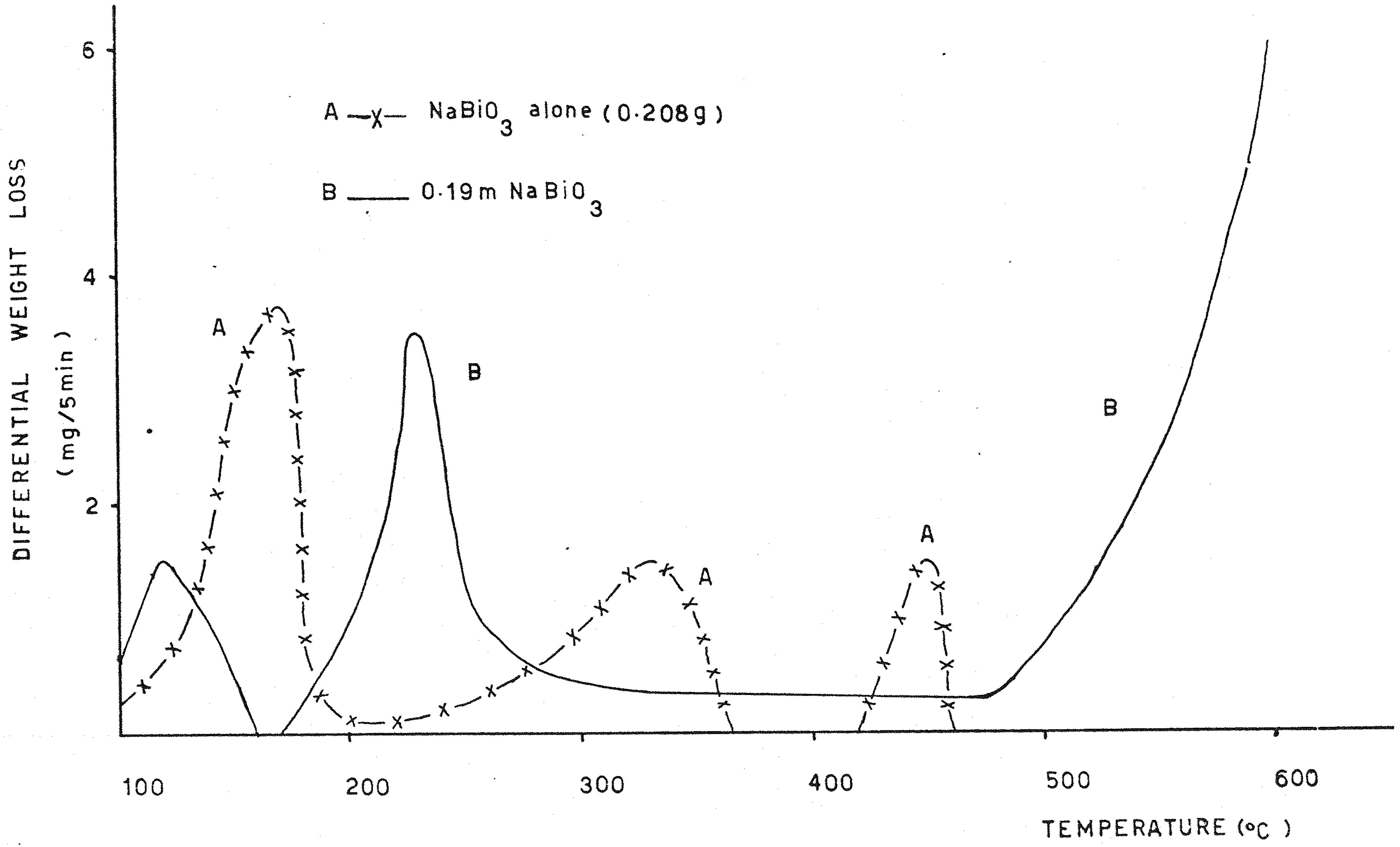


Fig 15 Thermogravimetric analysis of $NaBiO_3$ alone in air and in pure melt.

water, the mixture of white and yellow water insoluble products was filtered off and dried in the oven. Qualitative analysis gave positive tests for both bismuth and lithium while the aqueous filtrate was basic (PH = 12-14).

3.4.2 Discussion

When sodium metabismuthate was heated alone in air, it lost water which amounted to 7.2% by weight in the first step, and later decomposed in two further stages to a mixture of bismuth III oxide with sodium peroxide (at 360°C) while the peroxide at higher temperatures decomposed to sodium monoxide (at 460°C), as in equations:-

$$2NaBiO_3 \rightarrow Bi_2O_3 + Na_2O_2 + \tfrac{1}{2}O_2 \qquad \text{III.42}$$

$$Na_2O_2 \rightarrow Na_2O + \tfrac{1}{2}O_2 \qquad \text{III.43}$$

Each of these equations shows a theoretical weight loss of 2.8% when calculated on the basis of the initial sodium metabismuthate. Thus the final product would be a mixture of bismuth III oxide with sodium monoxide as in equation:-

$$2NaBiO_3 \rightarrow Bi_2O_3 + Na_2O + O_2 \qquad \text{III.44}$$

with a theoretical weight loss of 5.7%. The higher experimental weight loss of 4.3% for the second step is probably due both to equation III.42 and to some extent to equation III.43, but this equation III.43 does not go to completion at temperatures 210°C to 360°C because of the formation of some sodium monoxide on the surface of the sodium peroxide and that this surface layer eventually became thick enough to protect the peroxide at the centre of the mixed particles from decomposition at the temperature of 360°C, but the third stage then resulted from decomposition of the "protected" peroxide which occurred at higher temperatures (420°C-460°C). Therefore, the experimental weight loss of 1.5% for the third step was lower than the theoretical of 2.8%. X-ray results and the chemical analysis of 76.7% and 78.3% for bismuth obtained from the product heated to 380°C and 500°C respectively, suggested that the final product probably would be a mixture of bismuth III oxide with sodium peroxide and sodium monoxide (calculated for bismuth in a one to one mixture of Bi_2O_3 + Na_2O_2 and Bi_2O_3 + Na_2O, 76.8% and 79.1% respectively).

The reaction of sodium metabismuthate in the pure lithium nitrate-potassium nitrate eutectic initially occurred below 100°C by loss of water which amounted to 6.8% by weight, and the second step occurred at 170°C, with the weight loss of 9.6%. X-ray examination of the water insoluble product obtained from the product heated to 500°C showed the presence of bismuth III oxide with other unidentified lines and the chemical analysis of 86.8% Bi and 0.65% Li on the same product suggested that the reaction product is at least a mixture of two bismuth compounds, probably bismuth III oxide with lithium bismuthate III ($LiBiO_2$)(calculated for a one to one mixture of Bi_2O_3 + $LiBiO_2$ is 87.8% Bi and 0.98% Li). Since the product gave a negative test for oxidizing power, therefore the reduction of bismuth V to bismuth III and substitution of lithium cations for sodium may occur as in the following equation:-

$$3NaBiO_3 + Li^+ \rightarrow Bi_2O_3 + LiBiO_2 + Na_2O + \frac{3}{2} O_2 + Na^+ \qquad III.45$$

which has a theoretical weight loss of 5.7%. Though the higher percent weight loss found in the thermogravimetric experiment may perhaps be due to an impurity in sodium metabismuthate, it is more probable that further reactions initiating weight loss have also taken place.

CHAPTER FOUR

Reaction of some chlorides of platinum metals in pure nitrate melt and in the melt containing basic species.

4.1 Introduction

In the previous chapter we investigated the behaviour of bismuth compounds in lithium nitrate-potassium nitrate eutectic and in melts containing acidic and basic species. Bismuth has been among the elements little studied in molten nitrates, also included in this list of relatively unknown elements of platinum metals particularly those of the second row of the transition metals. Therefore, this chapter will deal with the behaviour of some chlorides of the three ruthenium, rhodium and palladium in pure nitrate eutectic and in the presence of basic species and the absorption spectra of the resultant complex species will also be discussed.

The chemistry of rhodium has been little studied in molten nitrates, and no details have so far been published on the behaviour of palladium and ruthenium in nitrate melts. So it is useful to review certain physical and chemical properties of these metals and their different compounds in order to more fully understand the behaviour of these compounds in nitrate melt.

The platinum metals in various forms are currently used as catalysts for a wide variety of hydrogenation, dehydrogenation, oxidation, isomerization, cyclization, dehydration and dehalogenation reactions. Products produced by these reactions include high-octane gasoline, nitric acid, vitamins, hydrogen peroxide and many other products. Precious metals catalysts are also used to remove trace impurities such as acetylene in ethylene and oxygen in hydrogen.

Because of their high melting point and stability, platinum metals have found applications as thermocouples, resistance thermometers, electrodes and high temperature furnace windings. Frequently for these applications platinum and palladium are alloyed with rhodium, ruthenium or osmium to increase their strength, hardness and corrosion resistance.

The first metal in this investigation which will be reviewed is ruthenium. The chemistry of this metal is still poorly understood, but interactions with molten salts have frequently been recorded during the course of preparative investigation or separations. For example, ruthenium is unaffected by mineral acids and is also insoluble in fused sulphates. But it can be got into solution by fusion with sodium peroxide which oxidizes it to sodium ruthenate (vi), (Na_2RuO_4). Sodium ruthenate (vi) is also reported to be obtained either by fusion of ruthenium (iv) oxide with sodium hydroxide or with sodium peroxide at the temperature of 540°C-560°C, in a stream of oxygen. Potassium ruthenate (vi) has been claimed to have been prepared by the fusing of ruthenium metal with potassium nitrate and potassium hydroxide. Rubidium and cesium ruthenate (vi) have also been claimed to have been produced.(112) Other alkali and alkaline earth ruthenate with ruthenium in various oxidation states have also been reported to be formed(113-115). For example, sodium ruthenate (v) was prepared by a solid state reaction between ruthenium (iv) oxide and sodium peroxide. Ruthenium (iv) oxide is itself can be made by heating the metal(116) or trichloride(117) in a stream of oxygen below 600°C and 1000°C respectively.

The most commonly encountered compound of ruthenium is the trichloride. Like many trichlorides it exists in both water-soluble (hydrated) and water-insoluble (anhydrous) forms. Hydrated ruthenium trichloride ($RuCl_3.3H_2O$), the usual commercial form can be formed by evaporation of a solution of ruthenium tetroxide in aqueous hydrochloric acid in a stream of hydrogen chloride. Aqueous solution of the trichloride are straw coloured in dilute solution and red-brown in concentrated solution. Anhydrous ruthenium trichloride occurs in two forms. The dark brown β form has been reported by K.R. Hyde(142) and co-workers to be formed by heating ruthenium sponge at 330°C in a mixture of carbon monoxide and chlorine (1:3). The black α form was prepared by heating the β form in a chlorine atmosphere to 700°C and this transition is reported to occur at 450°C and to be irreversible.

The second metal in this investigation which will be reviewed is rhodium. Compact rhodium is almost insoluble in all acids at 100°C, including aqua regia. Hot concentrated sulphuric acid will slowly dissolve the finely divided metal. The metal is attacked by fused hydrogen sulphates. Rhodium compounds exhibit oxidation states of 2,3,4 and 6. The trivalent form is by far the most stable. Rhodium sesquioxide (Rh_2O_3) may be prepared by heating the finely divided metal, nitrate or chloride(118) in air or oxygen. This oxide has been found to occur in two forms.(119,137) A low temperature hexagonal form which is obtained by precipitating a hydrated rhodium III oxide and then heating it in air at 700°C. But on heating this oxide above 750°C a high temperature orthorhombic form is obtained. Rhodium sesquioxide pentahydrate can be made by action of alkalis on solutions of rhodium trichloride.(120) The aqueous chemistry of rhodium trichloride is very complicated.(121) Two forms of rhodium trichloride are known. The trichloride formed by high temperature combination of the elements is a red crystalline, nonvolatile compound, insoluble in water(122). A water soluble form of the hydrated rhodium trichloride, wine red crystals of $RhCl_3.3H_2O$(123), can be made by treating rhodium hydroxide with hydrochloric acid, and evaporating the solution to dryness on a steam bath. If an aqueous solution of rhodium trichloride is treated with sodium nitrite the very soluble sodium hexanitritorhodate III is formed, and which on heating is said to form a mixed oxide(124) ($Na_2O.8RhO_2$).

Many oxyanions of rhodium in various oxidation states have been made. Potassium rhodate (vi), $K_2(RhO_4)$, is formed by passing chlorine into a solution of rhodium dioxide or sesquioxide dissolved in concentrated potassium hydroxide solution.(125) Sodium and lithium rhodate IV, Na_2RhO_3, Li_2ThO_3, are claimed to have been obtained by heating the metal with sodium or lithium carbonate for 20 hours at 600-1000°C. The compounds first formed to rhodite III, $LiRhO_2$,$NaRhO_2$, being later converted into rhodite IV.(126)

Finally the last metal in this investigation which will be reviewed is palladium. The finely divided metal is quite soluble in mineral acids. When it is heated in air at red heat, the black monoxide, PdO, is formed. This oxide can be formed by fusing palladium II chloride with sodium nitrate at 600°C, and then leaching out the salts with water. The oxide is a strong oxidizing agent and is easily reduced to the metal by hydrogen. It is insoluble in water and acids, including aqua regia, but dissolves in molten potassium hydrogen sulphate. The hydrated oxide, $PdO.nH_2O$ can be prepared as a yellowish-brown precipitate by the hydrolysis of palladium II nitrate. Unlike the anhydrous oxide it is soluble in acids. It initially loses water in air and goes brown, and loses more water on being heated but cannot be completely dehydrated without loss of oxygen.

The commonest compound of palladium is palladium II chloride. This compound is formed by direct combination of the elements at 500°C, but at about 600°C it begins to sublime and dissociate into the elements. It can also be prepared by heating aqueous hydrogen tetrachloropalladate II, which is obtained by dissolving palladium in aqua regia. The anhydrous compound prepared in this way, is insoluble in water and dissolves only with difficulty in hydrochloric acid. The hydrated palladium II chloride can be obtained from aqueous solution as dark red hygroscopic crystals. Palladium II chloride has been claimed to be the only stable solid chloride over the range 500°C to 1500°C(127), and it is also reported that it is decomposed in current of hydrogen chloride to metal at 800°C and in an oxygen current to form palladium II oxide and metal at 780°C and 920°C respectively(128).

The above discussion has briefly introduced the physical and chemical behaviour of platinum metal compounds in various aqueous solutions. However, the chemistry of ruthenium and palladium metals in molten nitrates is largely unknown, but to a certain extent the behaviour of palladium compounds in various molten nitrites and their spectra in these melts have been investigated. For example, N.I.Al-Salim(129) has reported that palladium dichloride dissolved in nitrite melts yielding a yellow solution of hexanitropalladate II complex, the spectrum of this solution giving a band at 27000 cm^{-1}. However, the final residue obtained from reaction of palladium dichloride in nitrite, was reported to be palladium metal.

The behaviour of rhodium trichloride in the molten sodium nitrate-potassium nitrate eutectic (45.5 mole% $NaNO_3$) at 330°C has been investigated$^{(130)}$. In particular, its spectrum in pure nitrate melt and in melts containing sodium nitrite or potassium chloride has been measured and compared with those in fused lithium chloride-potassium chloride at 440°C. Rhodium trichloride dissolved in molten sodium nitrate potassium nitrate eutectic at 300°C forming a yellow solution, the spectrum of this solution showing a strong absorption band with a maximum at 28200 cm^{-1}, very similar to a spectrum of potassium hexanitrorhodate III in this melt, but with a higher absorption edge from 15000 cm^{-1} to 25000 cm^{-1}, though without a maximum. In the presence of nitrite in the melt, this lower energy absorption was reduced until the spectrum approached that of potassium hexanitrorhodate III in molten nitrate. However, in a melt containing a high concentration of potassium chloride, the strong band which was attributed to $Rh(NO_2)_6^{3+}$ had become small, while two new bands appeared at 18800 cm^{-1} and 24000 cm^{-1}, where were attributed to the hexachlororhodate III anion.

The present investigation was concerned with the reaction of 'monohydrated' ruthenium trichloride, 'monohydrate' rhodium trichloride and anhydrous palladium dichloride in lithium nitrate-potassium nitrate eutectic melt. Monohydrated ruthenium trichloride and monohydrated rhodium trichloride have been found to gain 0.5 to 1 molecules of water during a one year period even though they were stored in a desicator.

These compounds were kindly supplied by the Johnson Matthey Research Centre, Sonning Common Reading, and some of the reaction products were also examined by them, using x-ray photoelectron spectroscopy or ESCA (Electron Scattering Chemical Analysis) in an endeavour to determine the oxidation states of the metals. In this technique when monoenergetic x-ray impinge upon a compound, the kinetic energy of the ejected electrons (E_k) is determined by the difference between the binding energy of the electron (E_b) and the energy of the x-ray photon ($h\nu$). If the kinetic energy of the ejected electron is determined, the binding energy of the electrons can be evaluated by the relationship:-

$$E_b = h\nu - E_k \qquad \text{(iv-1)}$$

The ESCA method of analysis is primarily suitable for surface analysis because the ejected electrons are easily stopped by even a minute thickness of solid. Thus the analysis is characteristic of the top few monolayers of a surface. All elements except hydrogen may be identified,and the oxidation state and bonding of the element is usually determinable. The binding energy increases with oxidation state, for example, there is a 1.7 eV increase in the binding energy of the 3d 3/2 and 3d 5/2 electrons ejected from the Mo(vi)oxide as compared to Mo(iv) oxide. The 3d 3/2 electrons have a binding energy about 3.1 eV higher than do 3d 5/2 electrons. Similarly on increasing the atomic number, the binding energy of the core electrons should increase, due to the increase the nuclear charge. This effect is seen in the present work, the binding energy of the Ru 3d 5/2 electrons and Rh 3d 5/2 electrons increased with increasing atomic number, from 282 eV to 309.5 eV.

4.2 Hydrated ruthenium trichloride

4.2.1 Reaction alone in air and in pure nitrate

When hydrated ruthenium trichloride was heated alone in air the formation of an acidic vapour was noticed at 120°C and evolution of chlorine gas started at about 400°C, the final solid product being ruthenium (IV) oxide. Thermogravimetric analysis showed the first weight loss started at 80°C giving 16.6% weight loss at 280°C. above this temperature the weight loss started to increase again, giving 47.2% as a total weight loss (30.6% for the second step). X-ray diffraction of the product gave d-spacings of 3.20, 2.56 and 1.70 with 100, 89 and 40 intensities. The J.C.P.D.S. Index gave 3.17, 2.55 and 1.69 with 100, 50 and 30 intensities for ruthenium (IV) oxide.

Reaction of hydrated ruthenium trichloride in pure lithium nitrate-potassium nitrate eutectic melt in a tube produced an acidic vapour at about 100°C and evolution of nitrogen dioxide at around 200°C. This evolution was no longer visible at 350°C, and after keeping the reaction at 400°C for four hours and then dissolving the quenched melt in water, an insoluble dark blue product was filtered off and dried in the oven to constant weight. Qualitative analysis of this product gave negative flame tests for both lithium and potassium, while x-ray diffraction gave the d-spacings as shown in Table (1). The pattern shows that the ruthenium (IV) oxide produced is not perfectly crystalline.

In another experiment hydrated ruthenium trichloride was heated in pure nitrate melt, but the reaction temperature was increased to 600°C, when x-ray diffraction of dark blue water insoluble product gave d-spacings as shown in Table (1) and the pattern showed that this product was more perfectly crystalline.

When the reaction was repeated in pure melt, and the reaction temperature was increased to 500°C, x-ray diffraction of the water insoluble product gave only three lines of d-spacings of 2.08, 1.48 and 1.47 with 100, 40 and 40 intensities. The reported d-value and intensities for lithium ruthenate (IV) from J.C.P.D.S. Index are 2.07 (100, 1.47 (60) and 1.46(60.

Thermogravimetric analysis of hydrated ruthenium trichloride in pure nitrate eutectic, showed a first weight loss at 100°C giving 6.7% by 180°C, the temperature at which the weight loss started to increase again, with a maximum rate of reaction at 300°C. Fig.(1). This reaction mixture was kept at 340°C for two hours, giving an overall 89.3% (82.6% for the second step) weight loss based on the hydrated ruthenium trichloride, (6.7% weight loss for the first step).

4.2.2 Reaction in basic melts

4.2.2.1 Reaction in the presence of sodium hydroxide

Observation of the reaction of hydrated ruthenium trichloride in a tube with lithium nitrate - potassium nitrate eutectic containing sodium hydroxide, the ratio of ruthenium to hydroxide being 1:4, showed an acidic vapour to be evolved at about 120°C, which was yellowish orange in colour, which on cooling became a dark blue solid. Qualitative analysis of this sublimation product (which was produced only in small amounts) gave a positive test for chloride ion. This sublimation increased at about 300°C, but by 400°C the tube contained a dark blue precipitate and a colourless liquid. The reaction mixture was kept not higher than 450°C, to avoid the decomposition of nitrate melt. After dissolving the quenched melt in water, the dark blue insoluble product was filtered off and dried at 120°C to constant weight. This product was examined by x-ray, giving d-spacings as shown in Table 2 (column a). The aqueous filtrate gave a positive test for nitrite ion.

When the experiment was repeated with a ratio of ruthenium to hydroxide of 1:16, and the temperature was kept at 450°C for two hours, the quenched melt after dissolving in water yielded a yellowish-orange solution and a dark blue precipitate. The yellowish-orange solution had absorption bands at 21500 cm^{-1} and 27000 cm^{-1}, the spectrum being shown in Fig.(2), and the examination of the dark blue insoluble product by x-ray diffraction gave the d-spacings as shown in Table 2(column b).

In another experiment with the ratio of ruthenium to hydroxide being 1:26, reaction kept at 450°C for two hours, the quenched melt, after dissolving in water again gave a yellowish-orange solution, and the dark blue insoluble product was filtered off quickly and dried. This product gave a positive test for sodium but negative for lithium and potassium and dissolved in both dilute aqueous sodium hydroxide and hydrochloric acid, giving yellowish-orange and amber-red solutions respectively. X-ray diffraction of this dark blue solid product gave no sign of any maxima.

Thermogravimetric analysis of ruthenium trichloride in lithium nitrate - potassium nitrate eutectic containing sodium hydroxide, with a ratio of ruthenium:hydroxide of 1:4, showed a first weight loss at about 120°C and a second weight loss at 180°C, Fig.(1). After keeping the reaction at 400°C isothermally for two hours, the total weight loss was 34.6%(based on the hydrated ruthenium trichloride), with a 3.0% weight loss for the first step.

4.2.2.2 Reaction in the presence of lithium hydroxide

In the previous section, x-ray examination of the reaction product at 500°C showed some x-ray lines of lithium ruthenate (IV). Thus in

Table (1): X-ray diffraction of solid products obtained from reaction of hydrated $RuCl_3$ in pure melt.

Dark blue product produced by melt reaction at 400°C		RuO_2 from J.C.P.D.S. (A.S.T.M.) Index		Dark blue product produced by melt reaction at 600°C	
d-spacings	I/I	d-spacings	I/I	d-spacings	I/I
3.17	100	3.17	100	3.17	100
2.55	100	2.55	50	2.55	77
2.24	27	2.24	10	2.24	16
-	-	2.22	4	2.21	6
-	-	2.00	1	2.00	2
1.68	65	1.68	30	1.68	50
1.59	20	1.58	9	1.58	12
1.55	15	1.55	4	1.55	6
1.42	17	1.42	5	1.42	7

order to see if more conclusive results could be obtained, lithium hydroxide monohydrate was used to increase the concentration of lithium as well as of the hydroxide anions in the reaction melt.

The reaction of hydrated ruthenium trichloride in lithium nitrate - potassium nitrate eutectic containing lithium hydroxide monohydrate with the ratio of ruthenium to hydroxide being 1:2 gave an evolution of water continuously from 150°C to 500°C, while at 450°C there was formed a dark blue precipitate and a colourless liquid. The quenched melt was dissolved in water and the dark blue insoluble product was filtered off and dried in the oven at 120°C to constant weight. This product was examined by x-ray diffraction, giving the d-spacings as shown in Table (3), while qualitative analysis of the aqueous filtrate gave a positive test for nitrite ion.

4.2.3 Discussion

When hydrated ruthenium trichloride was heated alone in air, the first stage of reaction was the loss of water of hydration as in equation (IV-2):-

$$RuCl_3.H_2O \rightarrow RuCl_3 + H_2O \qquad \text{(IV-2)}$$

which has a theoretical weight loss of 8.0%. The higher experimental weight loss of 16.6% at 280°C was probably due to the presence of impurities and in particular to the evolution of the excess water slowly absorbed during storage. Therefore if in the above equation we hadtwo molecules of water instead of one, the theoretical weight loss for the above equation would be 14.8%. Moreover the presence of acidic vapour at 210°C was probably due to partial hydrolysis of hydrated ruthenium trichloride to water, hydrogen chloride and a ruthenium (III) oxide chloride.

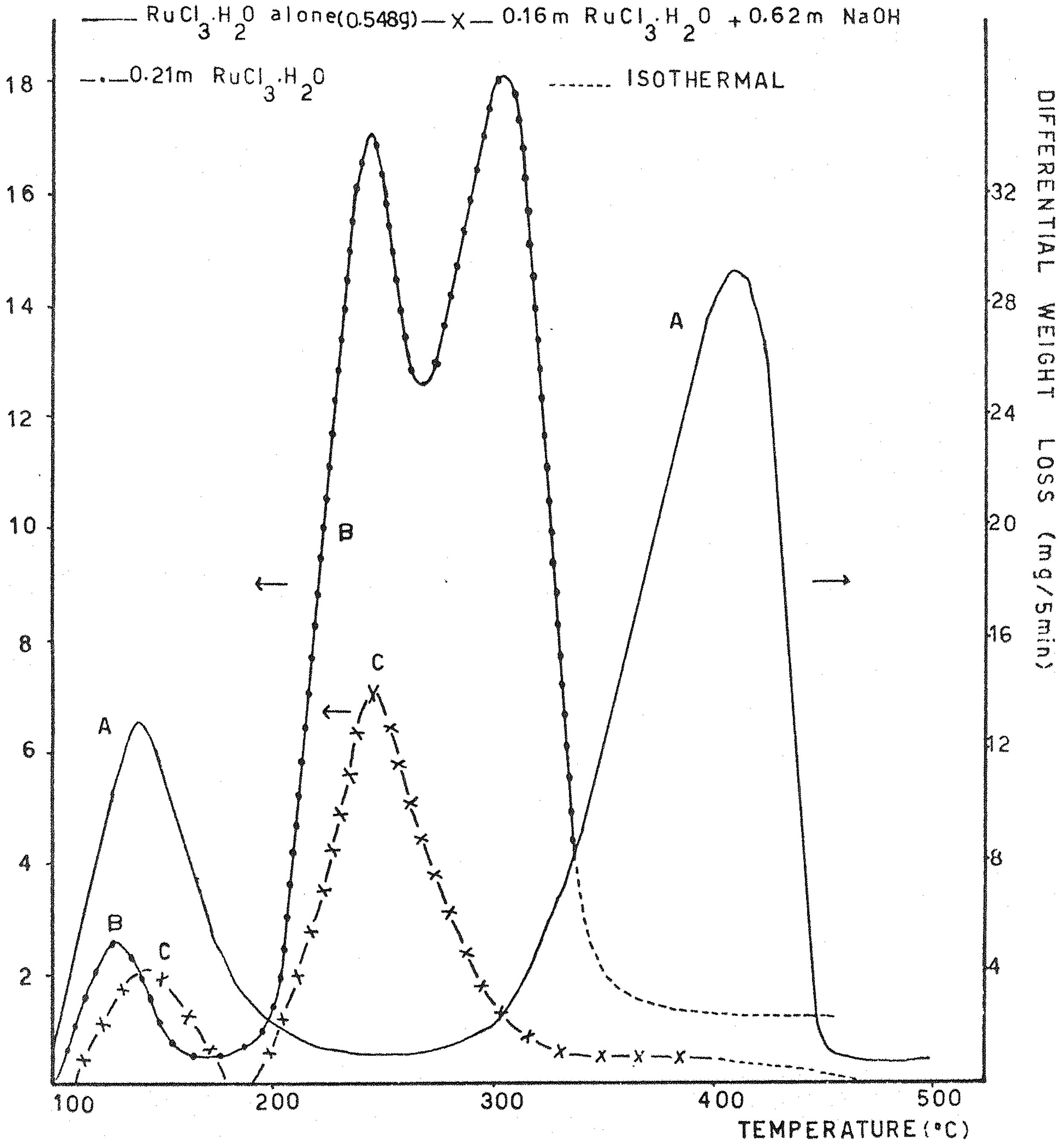
At higher temperatures ruthenium trichloride and any ruthenium (III)

Table (2) X-ray diffractions of products obtained from reactions of hydrated $RuCl_3$ in the melt containing different concentrations of NaOH.

a) Dark blue product (ratio of $\frac{Ru^{3+}}{OH^-} = \frac{1}{4}$)		RuO_2 from J.C.P.D.S. (A.S.T.M.) Index		b) Dark blue product (Ratio of $\frac{Ru^{3+}}{OH-} = \frac{1}{16}$)	
d-spacings	I/I	d-spacings	I/I	d-spacings	I/I
3.17	100	3.17	100	3.17	100
2.54	100	2.55	50	2.55	87
2.24	25	2.24	10	2.24	20
2.20	25	2.22	4	2.22	18
-	-	2.00	1	2.00	2
1.68	65	1.68	30	1.68	55
1.58	15	1.58	9	1.58	15

Table (3): X-ray diffraction of product obtained from reaction of hydrated $RuCl_3$ in the melt containing $LiOH.H_2O$.

Dark blue product		From J.C.P.D.S. (A.S.T.M.) Index			
		RuO_2		$LiRuO_3$	
d-spacings	I/I	d-spacings	I/I	d-spacings	I/I
3.17	100	3.17	100		
2.55	90	2.55	50		
2.24	23	2.24	10		
2.21	16	2.22	4		
2.08	10	2.00	1	2.07	100
1.68	60	1.68	30		
1.58	17.5	1.58	9		
1.55	9	1.55	4		
1.47	4	-	-	1.47	60
1.42	3	-	-	1.46	60



Fig(1) Thermogravimetric analysis of $RuCl_3.H_2O$ alone in air, in pure melt, and in the melt containing NaOH.

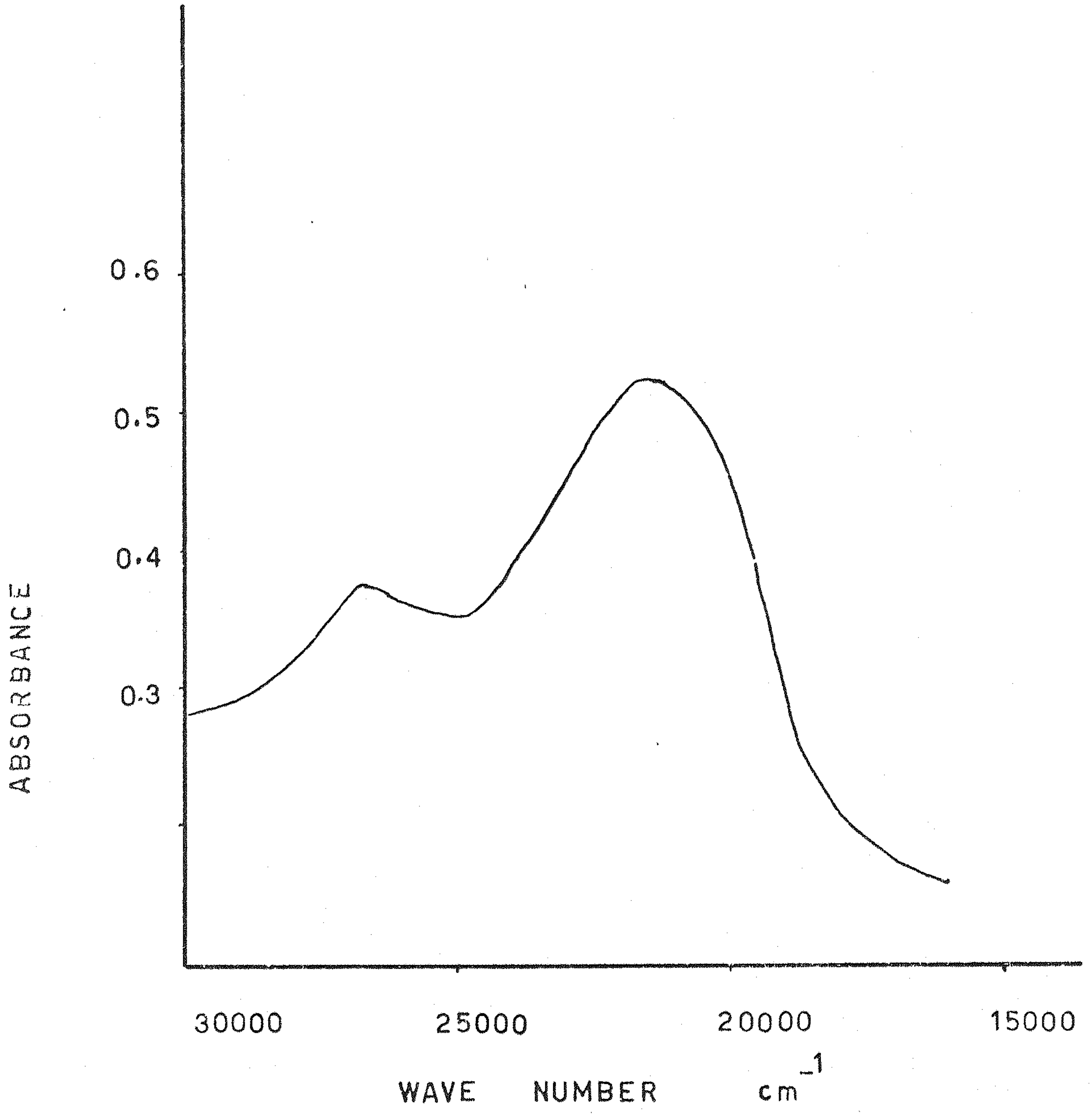


Fig (2) Absorption spectra of aqueous ruthenate (VI) obtained from reaction of $RuCl_3.H_2O$ in a high concentration of NaOH.

oxide chloride resulting from the first stage, e.g. Ru_2OCl_4 as in equation (IV-3):-

$$2RuCl_3.H_2O \rightarrow Ru_2OCl_4 + 2HCl + H_2O \qquad (IV-3)$$

decomposed in air to ruthenium (IV) oxide as equations (IV-4) and (IV-5):

$$RuCl_3 + O_2 \rightarrow RuO_2 + \frac{3}{2} Cl_2 \qquad (IV-4)$$

$$Ru_2OCl_4 + \frac{3}{2} O_2 \rightarrow 2RuO_2 + 2Cl_2 \qquad (IV-5)$$

Theoretical weight loss for reaction (IV-4) is 41.0% and for reaction (IV-5) is 20.8%, on the basis of hydrated ruthenium trichloride and this latter reaction probably caused the lower experimental weight loss of 30.6%. Gutbier and Schieferdecker(117) reported that ruthenium (IV) oxide was formed by decomposition of ruthenium trichloride in a stream of oxygen at 1000°C.

In the lithium nitrate - potassium nitrate eutectic, hydrated ruthenium trichloride started from 100°C to lose water of hydration as in equation (V-2), and hydrogen chloride by partial hydrolysis of hydrated ruthenium trichloride. These reactions had not gone to completion (Fig.1.B) because the reaction rate did not drop to zero before the second reaction began, which caused the lower experimental weight loss of 6.7%.

This second stage is considered to be the reaction of the ruthenium trichloride with the nitrate melt. The former behaved as a Lux-Flood acid (i.e. by abstracting an oxide ion from the nitrate) and at the same time the trichloride was oxidized to form ruthenium (IV) oxide as in equation (IV-6):-

$$RuCl_3 + 3NO_3^- \rightarrow RuO_2 + 3NO_2 + \tfrac{1}{2}O_2 + 3Cl^- \qquad (IV-6)$$

which has a theoretical weight loss of 74.2% on the basis of ruthenium trichloride. The higher experimental weight loss of 82.6% was probably also due both to impurities and to the evolution of the water slowly absorbed during storage, which had not been completely evolved during the first stage. As Fig.(1) shows, an unusual double peak with maxima at 245°C and 305°C was obtained indicating that probably the additional chloride obtained (at 245°C via equation (IV-5)) stabilized the remaining ruthenium trichloride by forming a ruthenium complex such as $RuCl_6^{3-}$. Similarly, Kerridge and Khudhari have reported the formation of tetrachloroferrate (III) in the reaction of ferric trichloride in nitrate melt(88) and more recently Shakir has reported the formation of chloro complexes of aluminium in the reaction of aluminium trichloride in nitrate melt(50), when multiple thermogram peaks were also obtained.

In a comparison between reactions of hydrated ruthenium trichloride alone in air and in nitrate melt, their thermograms show (Fig.1) that because of greater availability of oxide ions in the melt, reaction occurs at a lower temperature than in air.

According to the x-ray results, the reaction product formed at 500°C in pure nitrate melt probably contained lithium ruthenate (IV). Formation of this compound could have occurred by reaction of ruthenium (IV) oxide with the lithium nitrate, as in the equation (IV-7):-

$$RuO_2 + 2LiNO_3 \rightarrow Li_2RuO_3 + 2NO_2 + \tfrac{1}{2}O_2 \qquad \text{(IV-7)}$$

This additional weight loss was not evident on the thermogram because of melt decomposition at this temperature.

Since, according to the x-ray results (Table 1), at higher temperatures (600°C), this product was not found, it probably decomposed at the higher temperature to ruthenium (IV) oxide and lithium oxide, the latter being leached out when the reaction products were dissolved in water. Lithium ruthenate (IV) has been claimed to be prepared by heating a mixture of ruthenium (IV) oxide either with lithium carbonate at 1000°C for 24 hours or with lithium oxide at 750°C in a nitrogen atmosphere(135).

In the melt containing sodium hydroxide (ratio of ruthenium to hydroxide being 1:4), both the first and second weight losses started at the same temperatures as for reaction in pure melt, but with a single maximum at 245°C, in contrast with the double peaks at 245°C and 305°C obtained from the reaction in pure melt (Fig.1), indicating that the high basicity and higher availability of oxide ions in this reaction probably nullified the probable formation of chloro-complexes of ruthenium, e.g. $(RuCl_6)^{3-}$. Moreover, in the reaction with sodium hydroxide, nitrogen dioxide was not seen to be evolved, though the end product was still ruthenium(IV) oxide,as shown in Table 2(column a). The yellow-orange acidic sublimation at low temperatures is again probably due to the vaporizoration of a mixture of hydrogen chloride and one or more ruthenium oxide chlorides such as Ru_2OCl_4,produced by partial hydrolysis of hydrated ruthenium trichloride.

However, the first weight loss is attributed to the equation (IV-2) and the lower experimental weight loss of 3.0% is probably due to the absorption of the hydration water of ruthenium trichloride by sodium hydroxide. Later, at higher temperature, a yellow-orange acidic sublimation product also started to be evolved which would cause a higher experimental weight loss for the second stage. However, the reaction at this stage seems to be mainly as in the equation (IV-8) which has a theoretical weight loss of 23.5% based on the hydrated ruthenium trichloride:

$$2RuCl_3.H_2O + 6NaOH + 2NO_3^- \rightarrow 2RuO_2 + 6NaCl + 2NO_2^- + \tfrac{1}{2}O_2 + 5H_2O \quad \text{(IV-8)}$$

The higher experimental weight loss of 31.6% was probably due also in part to the evolution of the water slowly absorbed during storage which had not been completely evolved during the first stage because of absorption by sodium hydroxide at low temperatures; and also in part due to the sublimation of any ruthenium oxide chlorides such as Ru_2OCl_4 and Ru_2OCl_6.

With a higher concentration of sodium hydroxide, for example with a ruthenium to hydroxide ratio of 1:16, the final reaction product was a mixture of ruthenium (IV) oxide and a water soluble ruthenium compound. The sbsorption spectra of the yellowish-orange solution obtained from dissolving the above mixture in water showed bands at 21500 cm^{-1} and 27000 cm^{-1}(Fig.2), which corresponds to those of ruthenate (VI). This solution was observed to be unstable over long periods, decomposing to form dark blue ruthenium (IV) oxide. The absorption spectra of ruthenate (VI aqueous solution has been reported by several workers(131-134) to give bands at 21500 cm^{-1} and 27000 cm^{-1}. The presence of the ruthenium (VI) in the reaction product is probably attributable to an oxidation such as in equation (IV-9):-

$$RuO_2 + 2NaOH + NO_3^- \rightarrow Na_2RuO_4 + H_2O + NO_2^- \qquad (IV-9)$$

The formation of high oxidation state compounds in nitrate melts has been reported by several workers and particularly when in the presence of hydroxide. For example, Krot and co-workers(100) have claimed the formation of neptunium (VII), probably NpO_6^{5-}, in sodium nitrate - potassium nitrate eutectic in the presence of sodium hydroxide and potassium bromate at 300°C. Brough, Habboush and Kerridge(87) have reported that potassium manganate (VI) is quickly decomposed in lithium nitrate - potassium nitrate at 210°C, but in the presence of sodium hydroxide, the manganate (VI) ion is stabilized. In the present investigation, (Chapter III), we have reported the formation of lithium bismuthate (V) from the bismuth (III) compound, when hydroxide was present.

All x-ray results on insoluble products obtained from reaction of hydrated ruthenium trichloride in the pure melt and in the melt containing sodium hydroxide indicated that these products were ruthenium (IV) oxide, in some cases mixed with ruthenate (VI). To supplement these results and in order to attempt to have more evidence of the oxidation state of ruthenium in these products, unwashed samples of these reaction products were examined by ESCA (Electron Scattering Chemical Analysis) by courtesy of Johnson Matthey Research Centre, Sonning Common, Reading. All the samples were found to have one nm surface layer of carboneous material. This was mostly removed by Ar^+ bombardment before the ESCA analysis. However, the carbon 1S peak was observed on all the spectra. Unfortunately, the oxidation states of ruthenium could not be well defined, probably due to the obscuring of ruthenium 3d peaks by carbon 1S and also because of the similar binding energies of chloride compounds of ruthenium in oxidation state three with oxygen compounds of ruthenium in oxidation states of three and higher.

Finally in melts containing lithium hydroxide, ruthenium trichloride oxidized to ruthenium (IV) oxide as in the equation (IV-10):-

$$2RuCl_3.H_2O + 6LiOH.H_2O + 2NO_3^- \rightarrow 2RuO_2 + 6LiCl + 2NO_2^- + 12H_2O \quad \text{(IV-10)}$$

while the formation of some ruthenate (IV) was probably due to a reaction similar to equation (IV-7). Increasing the concentration of lithium by adding lithium hydroxide monohydrate to the melt had only little effect in producing lithium ruthenate (IV). This was probably due to a reaction similar to the higher stability of lithium hydroxide in the melt at 500°C as compared to sodium hydroxide(100) and thus the lower availability of oxide. Possibly higher temperature may have been more effective in the forming such ruthenate (IV), but time did not allow investigation of this possibility.

4.3 Hydrated rhodium trichloride

4.3.1 Reaction alone in air and in pure nitrate

Thermogravimetric analysis of hydrated rhodium trichloride alone in air, Fig.(3), showed the first weight loss started at about 100°C, giving 10.9% weight loss at 400°C and a second weight loss started at about 550°C with a maximum rate of reaction at 760°C, giving 37.7% weight loss at 860°C (48.6% total weight loss). X-ray diffraction of this product gave d-spacings as shown in Table (4).

Hydrated rhodium trichloride was observed to dissolve in pure lithium nitrate - potassium nitrate eutectic at about 200°C forming a yellow solution which on increasing the temperature changed to red, and from which at 250°C nitrogen dioxide started to be evolved. At 300°C there was a dark brown precipitate which at 400°C changed to black, and there was no further change up at 450°C, though on cooling the colour changed back to dark brown. After dissolving the quenched melt in water, a dark brown aqueous insoluble product was filtered off then dried in the oven for two hours. Flame photometry on this product gave a positive test for potassium. This product on x-ray diffraction gave only one d-spacing at 2.55 indicating a largely amorphous nature, but when the product alone was heated up to 940°C for four hours, it gave an average of 18.5% weight loss and x-ray diffraction of this product gave the series of d-spacings as shown in Table 5 (column a).

Thermogravimetric analysis of hydrated rhodium trichloride in pure nitrate melt, showed the first weight loss started at about 100°C and the second weight loss at 200°C with a maximum rate of reaction at 375°C (Fig. 4). When the experiment was kept isothermally at 450°C for five hours, in order to avoid decomposition of the nitrate melt, it gave overall a 156.8% weight loss based on the hydrated rhodium trichloride (12.8% weight loss for the first step). Qualitative analysis of water insoluble dark brown product gave a positive test for potassium,but negative for lithium. X-ray diffraction of above product again gave only the one d-spacing of 2.55 and again, when this product was heated for four hours at 950°C giving 15.8% weight loss, qualitative analysis of the product gave a negative test for potassium.

4.3.2 Reaction in the melt containing potassium chloride

Hydrated rhodium trichloride in nitrate eutectic containing potassium chloride (ratio of hydrated rhodium trichloride to potassium chloride being 1:11) was again soluble at 200°C, but giving a red solution which at 300°C changed to deep red. Nitrogen dioxide started to evolve at 350°C. After dissolving the quenched melt in water, a dark brown insoluble product was filtered off and dried to constant weight. Qualitative analysis of this product gave a positive test for potassium. X-ray diffraction showed that the product was completely amorphous, as no lines were obtained, but after heating at 950°C for four hours, it gave a 18.5% weight loss and x-ray diffraction of this product gave the d-spacings as shown in Table 5 (column b).

Thermogravimetric study of hydrated rhodium trichloride in lithium nitrate - potassium nitrate eutectic, containing potassium chloride (ratio of hydrated rhodium trichloride to potassium chloride being 1:10.5) showed the first weight loss started at 100°C and the second weight loss at about 200°C with a maximum rate of reaction at 435°C (Fig.4). This reaction was kept at 470°C isothermally for 6 hours giving 166.7% as a total weight loss. (14.1% weight loss for the first step.) After dissolving the quenched melt in water, the dark brown residue was filtered off and dried in the oven to constant weight. Qualitative analysis of this product gave a positive test for potassium.

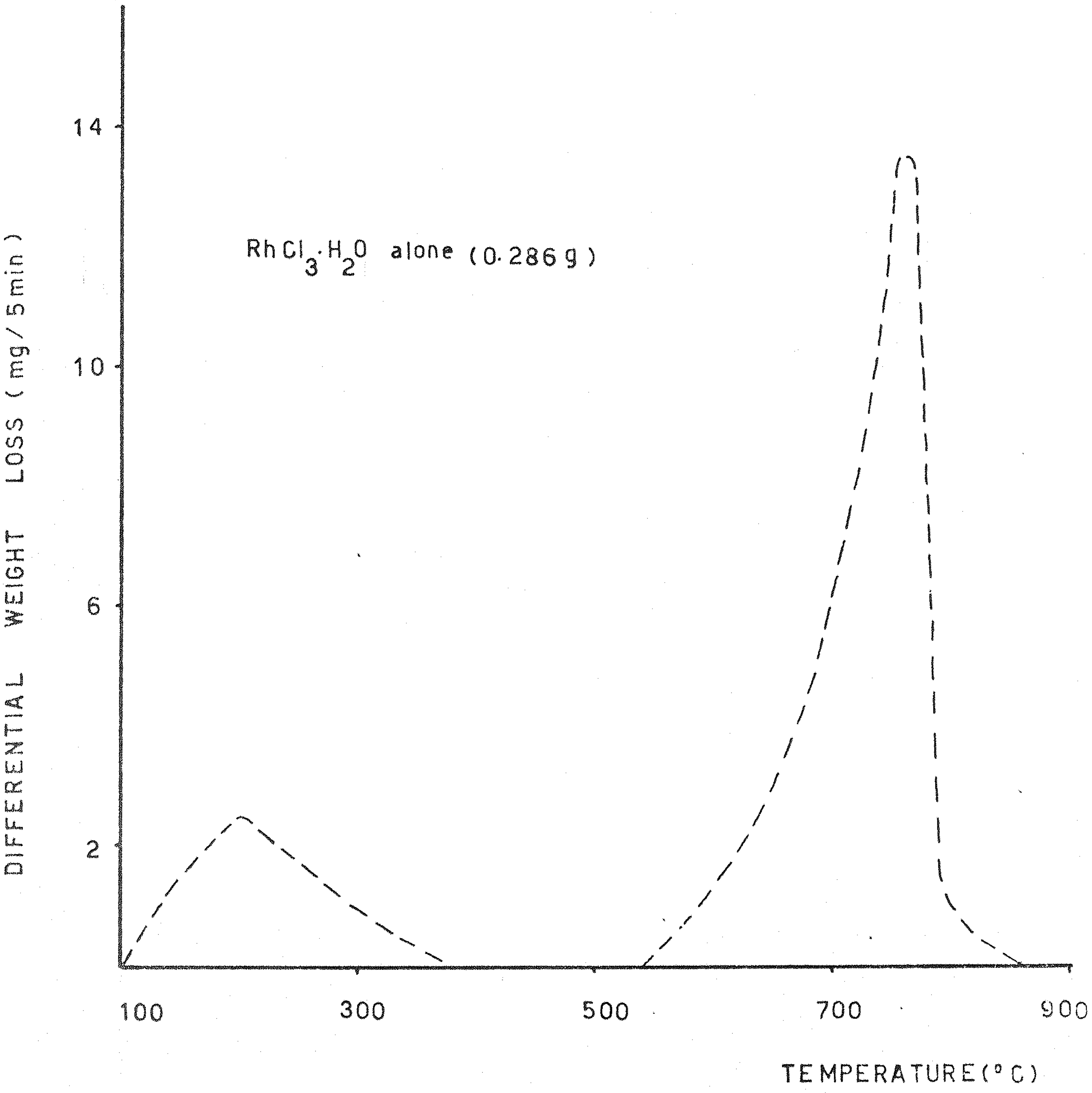


Fig (3) Thermogravimetric analysis of RhCl$_3$.H$_2$O alone in air.

Table (5): X-ray diffraction of products obtained from reactions of hydrated $RhCl_3$ in pure melt and in the melt containing KCl, heated to 950°C.

a) Product obtained from reaction in pure melt		Rh_2O_3 (low temperature form) (137)		b) Product obtained from reaction in the presence of KCl	
d-spacings	I/I	d-spacings	I/I	d-spacings	I/I
3.70	50	3.68	53	3.72	50
2.71	75	2.73	88	2.72	77
2.55	100	2.55	100	2.55	100
2.30	11	2.30	11	2.30	9
2.23	7	2.23	7	2.25	6
2.11	12	2.11	6	2.11	17
1.86	39	1.87	37	1.87	36
1.71	56	1.72	53	1.72	50
1.50	30	1.50	33	1.51	28
1.47	86	1.48	30	1.47	23

4.3.3 A spectroscopic study of a melt solution of hydrated rhodium trichloride in pure melt and in the presence of ligands

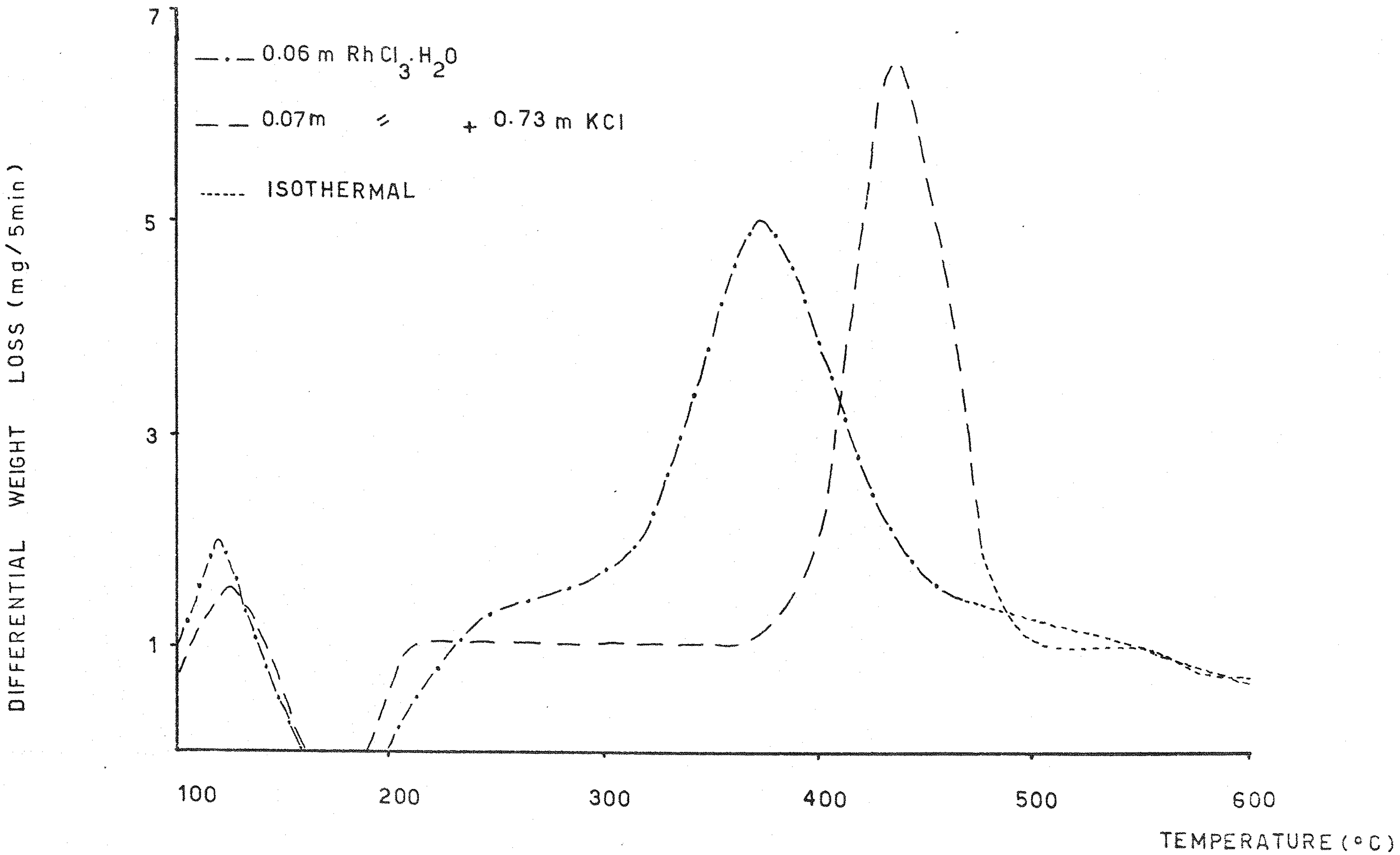
A yellow solution formed when hydrated rhodium trichloride started to dissolve in lithium nitrate - potassium nitrate eutectic at 200°C. This solution gave an absorption band at 27500 cm^{-1} with an extinction coefficient of 3400 L mol^{-1} cm^{-1}, Fig.(5-A). By adding potassium nitrite to the nitrate melt, the rate of solution of hydrated rhodium trichloride was increased. The absorption spectrum of hydrated rhodium trichloride in lithium nitrate - potassium nitrate eutectic containing potassium nitrite at 200°C, as shown in Fig.(5-B), gave a band at 27500 cm^{-1} with an extinction coefficient of 3600 $Lmol^{-1}$ cm^{-1}. The spectrum of hydrated rhodium trichloride in the melt containing potassium chloride (ratio of hydrated rhodium trichloride to potassium chloride being 1:310) at 200°C gave a band at 27500 cm^{-1} with an extinction coefficient of 1600 mol^{-1} cm^{-1} (Fig. 5-C).

4.3.4 Discussion

When hydrated rhodium trichloride was heated alone in air, lost its water of hydration as in equation (IV-11) similar to that of hydrated ruthenium trichloride at the first stage:-

$$RhCl_3.H_2O \rightarrow RhCl_3 + H_2O \qquad (IV-11)$$

which has a theoretical weight loss of 7.9%. The higher experimental weight loss of 10.9% is probably due to the impurities and to the evolution of the excess water slowly absorbed during storage. Thus, if in the above equation we had 1.5 molecules of water instead of one per rhodium trichloride molecule, the theoretical weight loss would be 11.4% for the loss of 1.5 molecules of water.



Fig(4) Thermogravimetric analysis of $RhCl_3.H_2O$ in pure melt and in the melt containing KCl.

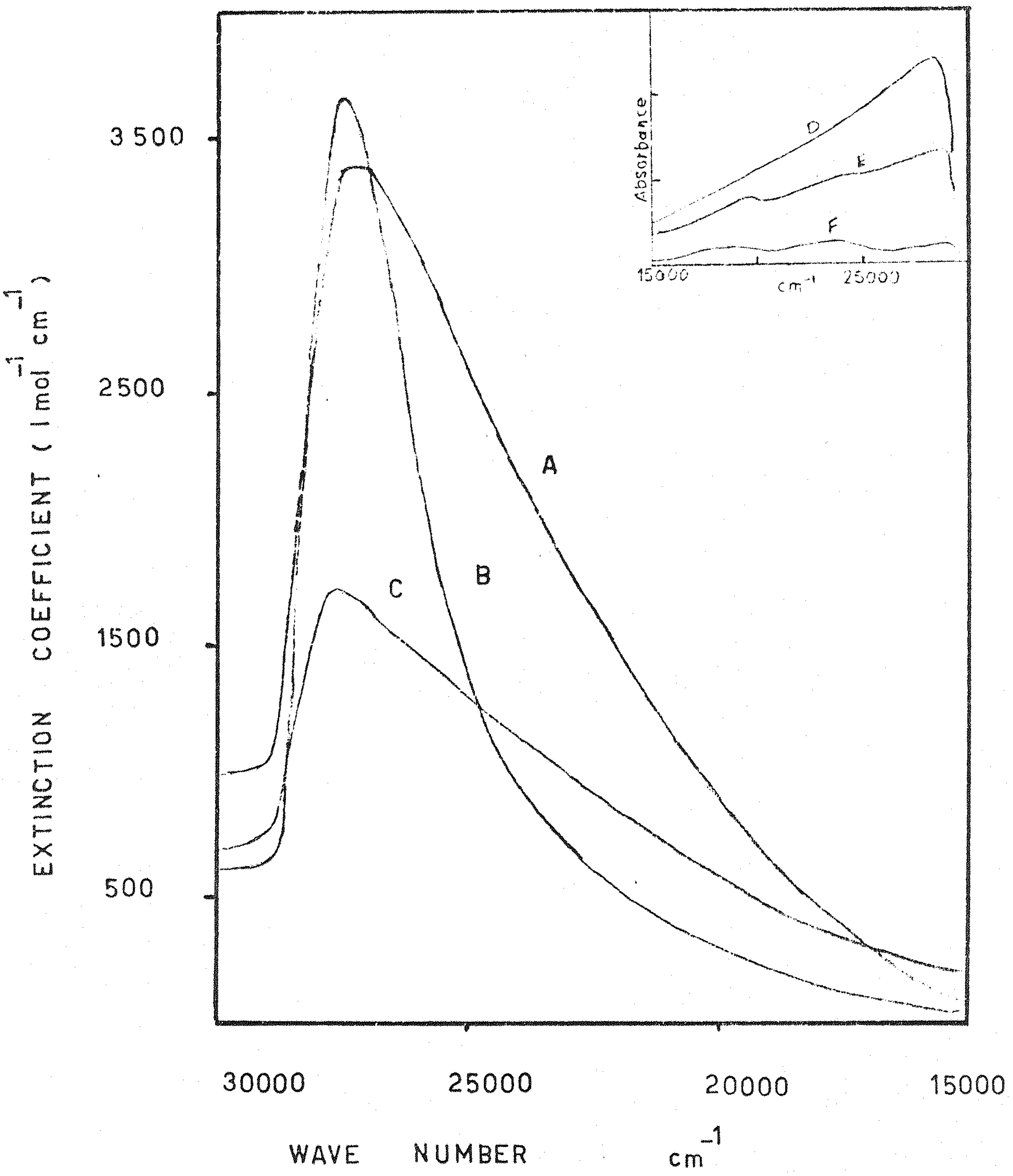


Fig (5) Absorption spectra of (A) $RhCl_3.H_2O$ solution in pure melt, (B) in the melt containing KNO_2, (C) in the melt containing KCl.

The second stage loss occurred at higher temperature and reaction is thought to be as in equation (IV-12):-

$$2RhCl_3 + \frac{3}{2}O_2 \rightarrow Rh_2O_3 + 3Cl_2 \qquad \text{(IV-12)}$$

which has a theoretical weight loss of 36.2%, calculated on the basis of hydrated rhodium trichloride. The higher experimental weight loss of 37.9% is probably due to the presence of impurities.

Rhodium trichloride has been reported to be oxidized by oxygen at the temperature of 440°C-500°C to rhodium III oxide(118) (Rh_2O_3). This oxide has been reported to occur in two forms. Lunde(136) obtained a low temperature form with a hexagonal structure, by heating rhodium trichloride in oxygen at 600°C, while Wold and co-workers(119) have reported that this form of the oxide was prepared by precipitating hydrated rhodium III oxide and then heating it in air at 700°C, though on heating this oxide above 750°C, a high temperature orthorhombic form was obtained. The latter workers also reported that the high temperature form could be prepared by heating finely divided rhodium metal at 1000°C in air. However, the x-ray diffraction pattern of the final product obtained from reaction of hydrated rhodium trichloride alone in air indicated that it was largely the low temperature form of rhodium III oxide (137).

In lithium nitrate - potassium nitrate eutectic, hydrated rhodium trichloride started to lose its water of hydration as in equation (IV-11) at 100°C, similarly to that when heated alone in air. The higher experimental weight loss of 12.8% was again probably due to the evolution of the water slowly absorbed during storage. This indicated that the molecules of the hydration water would be between 1.5 and 2, which would then give a theoretical weight loss of 11.4% - 14.7%. By a temperature range of 200°C - 300°C, rhodium trichloride was partially soluble in the melt (probably due to the formation of $Rh(NO_2)_6^{3-}$) forming a yellow solution, then above these temperatures, this complex and the undissolved rhodium trichloride probably reacted with the melt to give a mixture of rhodium III oxide and potassium rhodate III, as in the following equations:-

$$RhCl_3 + 6NO_3^- \rightarrow Rh(NO_2)_6^{3-} + 3O_2 + 3Cl^- \qquad (IV-13)$$

$$Rh(NO_2)_6^{3-} + 2NO_3^- + K^+ \rightarrow KRhO_2 + 6NO_2 + 2NO + 2O^{2-} \qquad (IV-14)$$

$$2RhCl_3 + 6NO_3^- \rightarrow Rh_2O_3 + 6NO_2 + \frac{3}{2}O_2 + 6Cl^- \qquad (IV-15)$$

which have a theoretical weight loss of 42.3%, 189.8% and 71.3% respectively, based on the hydrated rhodium trichloride. Due to the dissolution of an unknown amount of rhodium trichloride in the melt a theoretical weight loss is impossible to calculate without more information, in addition some part of the experimental weight loss is due to the self decomposition of the melt, possibly catalysed by chloride(80).

The x-ray result for the end product showed it was largely amorphous with only one peak with a d-value of 2.55 which corresponded to the strongest line of rhodium III oxide in the low temperature form(137), but may of course be due to a similar Rh-O spacing in a related compound. The presence of potassium in the water insoluble product strongly suggests the latter and this may have been formed by the decomposition of, say, the nitrite complex, to potassium rhodate III as in equation (IV-14).

Finally, by heating the original end product to 950°C, rhodium III oxide was obtained crystalline in the hexagonal form(137), i.e. now without contamination by any potassium oxide. The 18.5% experimental weight loss obtained in this process is thus probably due to the decomposition of the potassium rhodate III as in equation (IV-16):-

$$2KRhO_2 \rightarrow Rh_2O_3 + K_2O \qquad (IV-16)$$

which has a theoretical weight loss of 27.0%, for loss of K_2O. The lower experimental weight loss is probably due to the presence of some rhodium III oxide in the product at 500°C, as the x-ray patterns showed only one peak with a d-value of 2.55 which corresponds to the strongest line of this oxide in the low temperature form(137). Dissociation of potassium oxide to potassium and oxygen has been reported to occur above 830°C(143) and may provide a convenient mechanism for this weight loss.

In order to obtain more evidence of the oxidation state of rhodium in the reaction product at 450°C, unwashed samples (which would thus not have lost any potassium oxide by reaction with water) were examined by using ESCA techniques and a washed sample was analysed quantitatively by hydrogen reduction of the rhodium compound to the metal. This work was carried out in the laboratories of the Johnson Matthey Research Centre, Sonning Common, Reading. The rhodium ESCA result of 309.5 ± 0.3 indicated an oxidation state of three and quantitative analysis gave 57.6% rhodium for the final product at 450°C (calculated for $KRhO_2$ 59.2% Rh). A sample of the end product after heating to 950°C was also analysed quantitatively giving 73.9% rhodium (57.6 and 73.9) which may well have been due to impurity possibly caused by the reaction with melt and the high temperature treatment respectively, but the x-ray results for the end product at 950°C gave a series of d-spacings corresponding to the rhodium III oxide.

In the melt containing potassium chloride, hydrated rhodium trichloride started to lose water at about 100°C as in the equation (IV-9). The higher experimental weight loss of 15.2% was again probably due to the evolution of the water slowly absorbed during storage. Therefore, in equation (IV-11), if we had two molecules of water instead of one, the theoretical weight loss would be 14.7% for loss of two molecules of water. By 200°C, the rhodium trichloride similarly to that in pure melt, dissolved in melt as in the equation (IV-13) to form a yellow solution. However, addition of chloride ion stabilized the rhodium trichloride in the nitrate, probably due to the formation of chloride containing complexes such as $(Rh(NO_2)_xCl_y)^{3-}$ (with $x + y = 6$), as in equation (IV-17):

$$RhCl_3 + xNO_3^- \rightarrow (Rh(NO_2)_xCl_y)^{3-} + \frac{x}{2}O_2 + (\frac{x}{2} - \frac{y}{2})Cl^- \qquad (IV\text{-}17)$$

Because the temperature of the maximum reaction rate was raised from 400°C (for reaction in pure melt) to 435°C, more rhodium trichloride would be able to dissolve in the melt to form such complexes, which would at higher temperatures react with nitrate as in equation (IV-18):

$$(Rh(NO_2)_xCl_y)^{3-} + yNO_3^- \rightarrow RhO_2^- + yCl^- + O^{2-} + (y + x)NO_2 + (\frac{y - x}{4})O_2 \qquad (IV\text{-}18)$$

while the undissolved rhodium trichloride would react as in the equation (IV-15). The higher experimental weight loss of this reaction (166.7%) compared with that of reaction in pure melt (156.8%) is probably due to this greater dissolution of rhodium trichloride which later at the higher temperature caused more weight loss. The x-ray diffraction pattern of the original end product gave only a single peak with a d-value of 2.55 which corresponds to the strongest line of rhodium (III) oxide in the low temperature form(137), but by heating this product to 950°C, the hexagonal crystalline form of rhodium III oxide was obtained and the experimental weight loss (after heating to 950°C) was probably due to the decomposition of potassium rhodate (III) as in the equation (IV-16).

The absorption spectra of hydrated rhodium trichloride in pure melt and in the melt containing potassium nitrite and potassium chloride at the temperature of 200°C are given in Fig.(5). The spectrum of hydrated rhodium trichloride was characterized by one strong band with a maximum at 27000 cm^{-1} and an extinction coefficient of 3400 l mol^{-1} cm^{-1}. This band was assymmetric with a long absorption tail on the low energy side. The addition of potassium nitrite to this solution gave a more symmetric band at 27000 cm^{-1} and an extinction coefficient of 3600lmol^{-1} cm^{-1} as did hydrated rhodium trichloride in the melt containing potassium chloride when the absorption maximum occurred at 27000 cm^{-1} with an extinction coefficient of 1600lmol^{-1} cm^{-1}.

The spectra of rhodium trichloride and potassium hexanitritorhodium (III) in the sodium nitrate - potassium nitrate eutectic at 300°C have been reported. Ogilvie and Holmes(138) claimed that the rhodium trichloride in this nitrate melt and in presence of nitrite ion, gave a maximum at 28200 cm^{-1} a ($\varepsilon = 2100$) which was similar to that of the rhodium (III) nitrite complex in sodium nitrate - potassium nitrate eutectic. In the melt containing a high concentration of potassium chloride (ratios of rhodium trichloride to potassium chloride used were 1:260 and 1:600), the band which was attributed to $Rh(NO_2)_6^{3-}$ became very small while two new bands appeared at 18800 cm^{-1} and 24000 cm^{-1}, which were considered to be due to the formation of $RhCl_6^{3-}$ (due to the increasing concentration of chloride ion). Their reported absorption spectra of rhodium (III) in pure melt and in the melt containing sodium nitrite and potassium chloride are given in the inset to Fig.(5).

The results found in the present investigation when compared to those reported by Ogilvie and Holmes, indicated that when rhodium trichloride dissolved in pure lithium nitrate - potassium nitrate eutectic and in the melt containing potassium chloride with a ratio of hydrated rhodium trichloride to potassium chloride of 1:310, there was no evidence of bands at 18800 cm^{-1} and 24000 cm^{-1} (reported by Ogilvie and Holmes to be due to $RhCl_6^{3-}$). Possibly high chloride to rhodium ratios are needed for formation of the chloro-complex in the more acidic nitrate melt containing lithium cation.

4.4 Palladium dichloride

4.4.1 Reaction alone in air and in pure nitrate

Thermogravimetric analysis of palladium dichloride alone in air showed the first weight loss started at 400°C with maximum rate of weight loss at 715°C. The second weight loss began at 800°C with a maximum rate at 850°C (Fig. (6)). The first weight loss was 30.8% and the second 8.9%. Quantitative analysis of the end product gave 98.5% Palladium (calculated for PdO, 86.97% Pd). When the experiment was repeated, but heated only to 750°C, giving 30.9% weight loss, quantitative analysis of the product gave 85.8% Palladium. The x-ray diffraction lines of these products are shown in Table (7).

Palladium dichloride was observed to dissolve in lithium nitrate - potassium nitrate eutectic to give a yellow solution at about 200°C. On increasing the temperature to 300°C, the colour of the solution changed to red and a brown suspension formed. By 310°C a small amount of nitrogen dioxide was evolved, at about 400°C this evolution increased, but ceased at 450°C. After three hours at this temperature a black precipitate was formed and the bottom of the tube was mirror-like. After solidification, the solid was dissolved in water and a dark brown insoluble product filtered off, then dried at 120°C for two hours. The filtrate was analysed qualitatively and gave positive tests for chloride, potassium and lithium ions, but negative for palladium. The dark brown water insoluble product was examined by x-ray diffraction, giving the d-spacings shown in Table (8-a).

Thermogravimetric analysis of palladium dichloride in pure nitrate melt showed weight loss started at about 300°C, with maximum rate of reaction at 380°C, Fig. (7). In order to avoid decomposition of melt, the reaction was kept at 450°C isothermally for one hour giving 62.3% weight loss in total. Quantitative analysis of the water insoluble product gave 85.5% palladium (calculated for PdO, 86.9% Pd), and x-ray diffraction of the end product gave d-spacings as shown in Table (8-b).

4.4.2 Reaction in the presence of potassium chloride

In the presence of potassium chloride in the nitrate melt, palladium dichloride was also observed to dissolve and at 200°C gave a red-brown solution which on increasing the temperature became deep red in colour. Nitrogen dioxide was evolved from 350°C when the ratio of palladium dichloride:potassium chloride was 1:1, and at an increased rate at 400°C. Whereas, when the ratio was 1:11, the evolution of nitrogen dioxide was first observed at 400°C. However, both the reaction mixtures were kept at 450°C until nitrogen dioxide was no longer evolved when there was a dark brown precipitate and colourless liquid. The dark brown insoluble product was filtered off after dissolving the quenched melt in water, and dried in the oven to constant weight. Quantitative analysis of

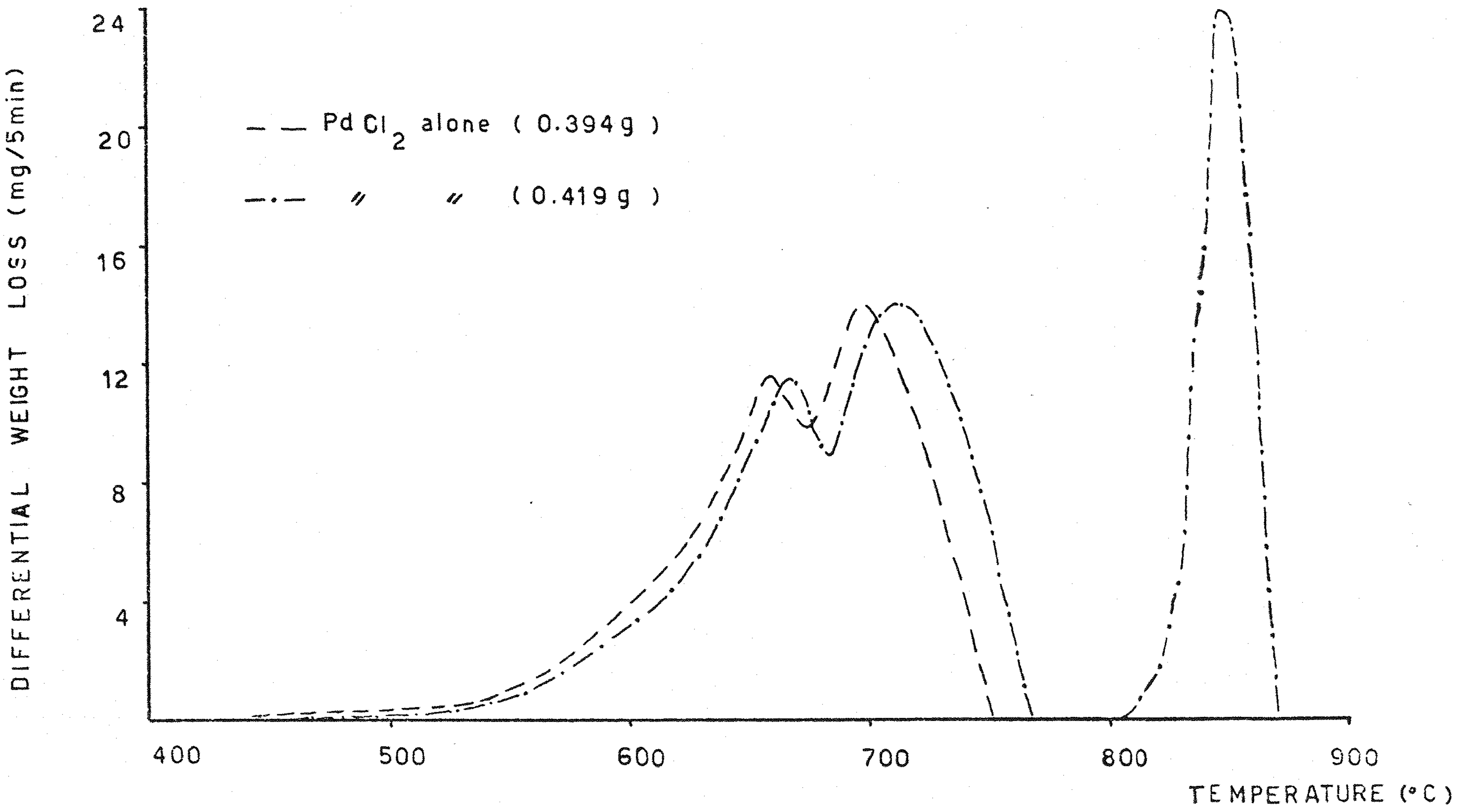


Fig (6) Thermogravimetric analysis of $PdCl_2$ alone in air.

Table (7) X-ray diffraction of products obtained from heating $pdCl_2$ alone in air at 750°C and 860°C

Product at 750°C		PdO from J.C.P.D.S. Index		Product at 860°C		Pd from J.C.P.D.S. Index	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
3.04	4	3.04	4	2.24	100	2.24	100
2.65	30	2.66	35	1.94	38	1.94	42
2.64	100	2.64	100	1.37	22	1.37	26
2.14	13	2.15	20				
1.67	22	1.67	30				
1.54	15	1.54	18				
1.52	13	1.52	12				

Table (8) X-ray diffraction of products obtained from reaction of $PdCl_2$ with melt. (a) in a tube. (b) on the thermobalance.

(a) Product reaction of tube		PdO from J.C.P.D.S. Index		(b) Product of thermobalance reaction	
d-spacings	I/Io	d-spacings	I/Io	d-spacings	I/Io
3.04	4	3.04	4	3.03	4
2.66	30	2.66	35	2.66	22
2.64	100	2.64	100	2.64	100
2.15	17	2.15	20	2.14	15
1.67	19	1.67	30	1.67	18
1.53	11	1.53	18	1.54	10
1.52	13	1.52	12	1.52	13

the water insoluble products obtained from the second thermogravimetric analysis gave 85.6% palladium, (calculated for PdO, 86.9%).

4.4.3 A spectroscopic study of a melt solution of palladium dichloride in pure melt and in the presence of potassium chloride

The absorption spectra of palladium dichloride in pure melt and in the melt containing potassium chloride, (ratio of palladium dichloride to potassium chloride being 1:33.5) at 200°C is shown in Fig. (8-a) giving bands at 28300 cm^{-1}, 24000 cm^{-1} and 28300 cm^{-1}, 22500 cm^{-1} respectively. After solidification of these melts, the solids were dissolved in water giving yellow aqueous solutions, the absorption spectra of which are shown in Fig. (8-b). The maxima were found to be at 25000 cm^{-1} for the reaction product of pure melt but at 24500 cm^{-1} in the presence of potassium chloride.

4.4.4 Discussion

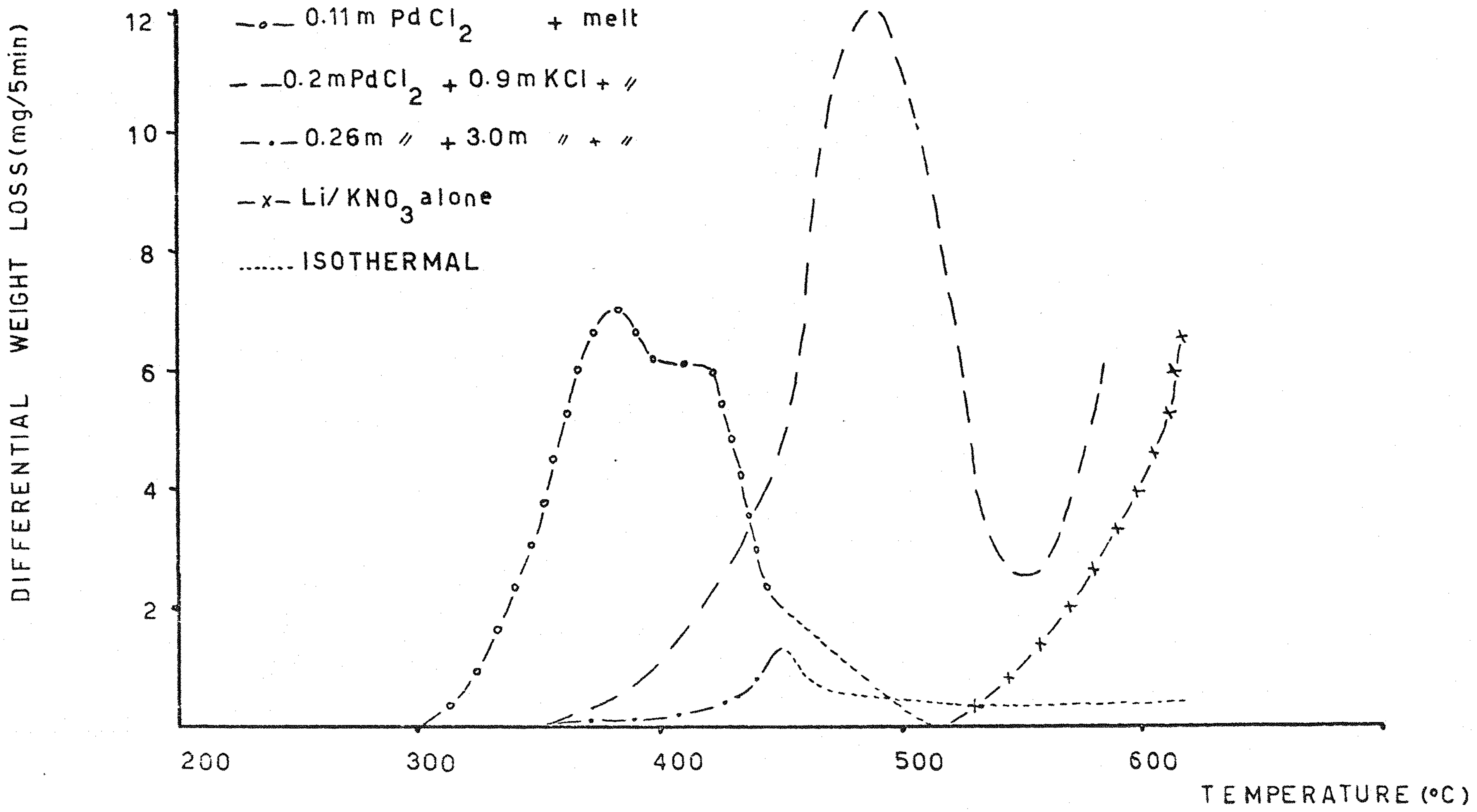
When palladium dichloride was heated alone in air, at the first step it decomposed to palladium monoxide, according to the equation:-

$$PdCl_2 + \tfrac{1}{2}O_2 \rightarrow PdO + Cl_2 \qquad \text{(IV-19)}$$

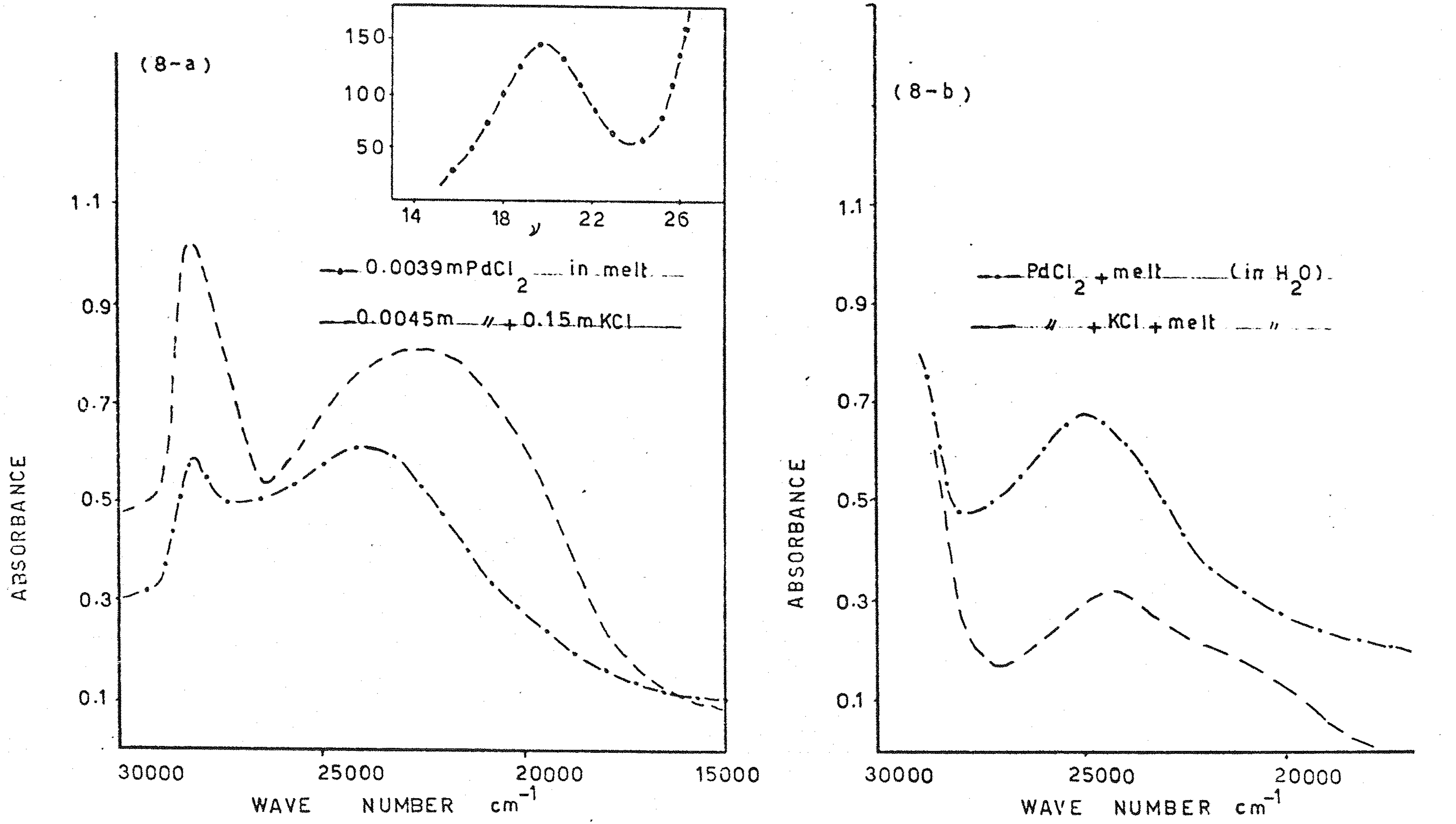
which has a theoretical weight loss of 31.0%. At higher temperature a second reaction occurred which is considered to be decomposition of palladium monoxide to metal, according to the equation:-

$$PdO \rightarrow Pd + \tfrac{1}{2}O_2 \qquad \text{(IV-20)}$$

with a theoretical weight loss of 9.0%. The experimental results are



Fig(7) Thermogravimetric analysis of $PdCl_2$ in pure melt and in the melt containing KCl.



Fig(8) Absorption spectra of PdCl$_2$ solution in pure melt and in the presence of KCl, and absorption spectra of aqueous PdCl$_2$ obtained from dissolution of above reaction products in water.

in good agreement with the above theoretical values. The chemical analysis and x-ray examination also indicated that the end products were palladium monoxide and palladium metal. It has recently been reported that palladium dichloride was decomposed in an oxygen current to palladium oxide and to palladium metal at 780°C and 920°C, respectively(128).

By a temperature of 200°C - 300°C, palladium dichloride dissolved in lithium nitrate - potassium nitrate melt to give a fairly dilute solution, probably due to the formation of complexes such as $(Pd\ (NO_3)_4\ Cl_2)^{4-}$. Above 300°C palladium dichloride began to react with nitrate melt and behaved as a Lux-Flood acid, i.e., abstracting oxide from nitrate melt to form palladium monoxide, as in equation (IV-21):

$$PdCl_2 + 2NO_3^- \rightarrow PdO + 2NO_2 + 2NO_2 + \tfrac{1}{2}O_2 + 2Cl^- \qquad \text{(IV-21)}$$

which has a theoretical weight loss of 60.9% based on the palladium dichloride. The product was shown by x-ray diffraction to be palladium monoxide and the weight loss on the isothermal thermogram at 450°C was found to agree reasonably with the calculated weight loss. The observed formation of a metallic mirror of palladium metal indicates that some decomposition of the oxide occurred and this further reaction would give a slightly higher weight loss and may account for some of the larger loss observed. However, the slight decomposition of nitrate at 450°C could also be responsible for this slightly higher weight loss.

In the melts containing potassium chloride, palladium dichloride behaved similarly as it did in the pure melt, dissolving and forming a yellow solution which, on increasing the temperature, changed to deep red. The start of the evolution of nitrogen dioxide in this reaction was raised from 300°C, in the reaction with pure melt, to 350°C, and the temperature of maximum rate of reaction from 380°C to 490°C when the ratio of palladium dichloride to potassium chloride was 1:4.5. When the ratio was 1:11.5, by 450°C a 59.8% weight loss was recorded, compared with the first experiment (ratio of 1:4.5) which by 530°C gave a 66.6% weight loss. Thus, the higher concentration of potassium chloride, tended to decrease the rate of the reaction of palladium dichloride with the nitrate, probably by the formation of more stable chloro complexes, possibly of a type such as $(Pd(NO_3)_x\ (Cl)_{6-x})^{4-}_{x=1-4}$. These complexes would eventually react as in the general equation (IV-22) but at successively higher temperatures as the proportion of chloride increased:

$$(Pd(NO_3)_x(Cl)_{6-x})^{4-}_{x=1-4} + 2NO_3^- \rightarrow PdO + 2NO_2 + xNO_3^- + 6-x(Cl^-) + \tfrac{1}{2}O_2 \qquad \text{(IV-22)}$$

which of course also has a theoretical weight loss of 60.9% on the basis of palladium dichloride. The higher experimental weight loss of 66.6% is probably due to the self decomposition of the melt, possibly catalysed by chloride.(80)

Dissolution of palladium dichloride in pure nitrate probably occurs with formation of nitrato-chloro palladium (II) complexes possibly of type $(Pd(NO_3)_4\ Cl_2)^{4-}$. In the presence of potassium chloride, (ratio of palladium dichloride to potassium chloride being 1:4.5, 1:11.5 and 1:33.5) probably there could be complexes formed containing more chloride, e.g. $(Pd(NO_3)_2Cl_4)$ and $(Pd(NO_3)Cl_5)^{4-}$ where replacement of two or three more nitrates by chlorides have occurred. The absorption maximum of palladium dichloride in the melt containing potassium chloride showed a shift to 22500 cm^{-1} Fig(8-a) as compared with the band at 24000 cm^{-1} in the pure melt. The absorption maximum of the aqueous solutions formed by the solidified melts from the above experiments were also shifted from 25000 cm^{-1} to 24000 cm^{-1} by the addition of chloride ion (Fig. 8-b).

The shift in the position of the absorption maximum in nitrate melt on addition of chloride is consistent with the results reported by Dickinson and Johnson(139-140) for palladium dichloride in potassium chloride - lithium chloride eutectic though their results were necessarily at the higher temperature of $450^{\circ}C$ (shown in the inset to Fig. 8-a) in which $PdCl_6^{4-}$ was suggested to be formed and where the absorption band was found at approximately 20000 cm^{-1}, though in the present work this value with the high chloride ratio used was not reached (ratio of palladium dichloride to potassium chloride of 1:33.5). This probably because the chloride concentration in the nitrate melt, although close to saturation, was still too low, resulting in the replacement of some but not all nitrate by chloride giving complexes such as $(Pd(NO_3)_2Cl_4)^{4-}$ or $(Pd(NO_3)Cl_5)^{4-}$. Dickinson and Johnson treated their results on the basis of square planar and octahedral geometries and concluded that palladium (II) in the chloride melt exists as an octahedral $PdCl_6^{4-}$ complex with some degree of tetragonal distortion.

Support for the shifting of the aqueous spectrum maximum is also given by the work of Sundaram and Sandell(141) who found that in aqueous palladium (II) perchlorate solutions of increasing chloride concentration, the absorption band showed a shift from 26000 cm^{-1} (no chloride present) to 21000 cm^{-1} (ratio of palladium to chloride of 1:54.3).

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