STUDIES IN REACTIONS BETWEEN METAL OXIDES AND FLUORIDES

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Studies in Reactions between Metal Oxides and Fluorides.

Abstract.

No systematic investigation of the reactions between metal oxides and fluorides has been previously reported. An attempt has been made to study these reactions on two distinct lines which are described separately.

The first section deals with the silicofluoride and ferric fluoride processes for the decomposition of natural beryl. Modified preparations and chemical analyses of the reactants are given. The constituent oxides of beryl have been separately sintered with the individual complex fluorides and the course of the reactions of the type represented by the equation

$$2BeO + 2Na_2SiF_6 \longrightarrow 2Na_2BeF_4 + SiO_2 + SiF_4$$

studied by X-ray methods. It has been found possible to correlate the individual reactions with the decomposition processes of beryl. Some experiments have been carried out on the controlled oxidation of potassium and sodium ferric fluorides and a probable mechanism discussed.

The second section deals with the investigations of the reactions between the alkali metal fluorides and some oxides of Group II metals. The preparation and chemical and X-ray analysis of the reactants are described. The lattice constants of all the reactants have been re-determined, several with greater accuracy than before.

The investigations of these reactions show that two types of reaction occur (a) reactions the progress of which may be formulated by an equation representing simple double decomposition,

e.g. $2NaF + MgO \rightarrow Na_2O + MgF_2$

and (b) those which result in the formation of double fluorides of the general formula $A^{I}B^{II}F_3A$,

e.g. $3KF + CaO \rightarrow KCaF_3 + K_2O$.

The courses of the reactions have been followed by X-ray methods and it has been found that several of the slower reactions involve an intermediate stage of limited mixed crystal formation between the oxide and fluoride prior to and during the initial stages of reaction.

The separate syntheses of all the double fluorides formed as reaction products are detailed. Several double fluorides are being reported for the first time. The complete crystallographic powder data of these fluorides are given and their structures discussed. Only two have been previously investigated crystallographically. Evidence is detailed for a unique structure postulated for the new compound barium lithium fluoride.

C O N T E N T S

	Pages
Introduction and Historical Survey	1 – 8
SECTION I.	
Investigations of the Reactions between Metal Oxides and Complex Metal Fluorides.	
Part I: Some industrial processes used in the decomposition of natural beryl.	
(a) The silicofluoride process for the decomposition of natural beryl.....	9 – 11
(b) The ferric fluoride process for the decomposition of natural beryl.	12 – 13
Part II: Experimental Methods.	
A. The preparation and analysis of reactants.....	14 – 26
B. Experimental techniques employed in:	
1. Reactions in the temperature range 600° – 750°	26 – 29
2. Analysis of reaction products by X-ray methods	29 – 30
C. Investigations of the reactions between:	
1. Sodium silicofluoride and	
(a) beryllium oxide	31 – 34
(b) aluminium oxide	35 – 39
(c) silicon dioxide	39 – 40
2. Natural cryolite and beryllium oxide	40 – 41
3. Sodium silicofluoride and natural beryl	41 – 46

C O N T E N T S

(Contd.)

Pages

4. Potassium ferric fluoride and

(a) beryllium oxide ..... 46 - 47
(b) aluminium oxide ..... 47 - 49
(c) silicon dioxide 49
(d) natural beryl ..... 50 - 51

Part III: General Discussion of Results ..... 52 - 54

Part IV : Some experiments on the controlled oxidation of potassium and sodium ferric fluorides.

(a) Introduction and Experimental Methods ..... 55 - 58

(b) Discussion of results ..... 59 - 63

SECTION II.

Investigations of the reactions between the alkali metal fluorides and some oxides of Group II metals.

Part I: General Introduction ..... 64 - 69

Part II: Experimental Methods:

(a) The preparation and chemical and X-ray analysis of reactants ..... 70 -102

(b) Experimental techniques employed in:

1. Reactions in the temperature range 600° - 1300° 103-111

2. Use of X-ray methods for the accurate determination of lattice constants and the crystallographical characterisation of new compounds 111-118

C O N T E N T S

(Contd.)

Page

(c) Investigations of the reactions between:

I Magnesium oxide and the alkali metal fluorides ..... 119 - 159
II Calcium oxide and the alkali metal fluorides ..... 160 - 178
III Strontium oxide and the alkali metal fluorides ..... 179 - 190
IV Barium oxide and the alkali metal fluorides ..... 191 - 206
V Zinc oxide and the alkali metal fluorides ..... 207 - 226
VI Ferric oxide and magnesium fluoride ..... 227 - 233
VII Zirconium dioxide and calcium fluoride ..... 234 - 237

Part III: Discussion of the reactions between the alkali metal fluorides and the Group II metal oxides ..... 238 - 250

Part IV: The crystallography of the compounds of general formula $A^{I}B^{IV}F_3$.

(a) Methods employed for indexing monoclinic crystals of the type $a = b = c$ and $\beta = 90^{\circ}$ from powder data ..... 251 - 263

(b) The crystallography of the double fluorides of the "Perovskite" type ..... 264 - 271

(c) The structure of barium lithium fluoride ..... 272 - 276

Part V: General Discussion ..... 277 - 283

Acknowledgments 284

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Introduction and Historical Survey.

Introduction and Historical Survey.

The first recognition of the occurrence of solid reactions between two inorganic compounds is generally attributed to Spring (Bull. Soc. Chim., France 1883, 44, 166), who investigated the reaction of barium carbonate with sodium sulphate. The nature of inorganic solid reactions was however hardly recognised till about 1912. Intensive investigations in this field, thereafter, could be evidenced by the monographs of Hedvall (J.A. Hedvall, Reaktionsfähigkeit fester Stoffe, Barth, Leipzig 1938) and Jost (W. Jost, Diffusion und Chemische Reaktion in festen Stoffen, Steinkopff, Dresden und Leipzig, 1937).

The thermodynamic relations have been elucidated by Tammann (Z. anorg. u. allgem. Chem., 1925, 149, 21). The criterion governing these reactions is that reactions in systems composed entirely of solids must be exothermic. Reactions between oxides and sulphides, phosphides, carbides and silicides have been studied in fair detail by Hedvall (Hedvall and Hermtren, Z. anorg. u. allgem. Chem., 1926, 154, 1), but the work done with halogenides is surprisingly small. A few isolated double decomposition reactions such as those of barium oxide with lead chloride, bromide and iodide appear to be the only form of investigations made (Hedvall, Gerging, Lindekranta and Nelson, Z. anorg. u. allgem. Chem., 1951, 197, 399). Reactions involving fluorides are less common. Indeed the only investigation reported is

that of thallium fluoride and barium oxide by Hedvall, Gerping et alia (loc. cit.). This reaction is referred to in greater detail in the introduction to Section II of this thesis.

Some attempts to dissolve 0.1% to 0.2% by weight of magnesium oxide in secondary and tertiary eutectics of various alkali and alkaline earth metal fluoride melts have been made by Ruff (Ruff and Ipsen, Z. anorg. u. allgem. Chem., 1925, 144, 87). This was for the purpose of trying to obtain a suitable electrolyte for the electrolytic production of magnesium. The reported thermal analyses of the possible alkali and alkaline earth metal fluoride binary systems are also comparatively few, though extensive work is now being done in this direction in Russia by Bergmanov, Bergmann and co-workers with the idea of obtaining fluoride fluxes for the purification of non-ferrous metals.

Most of the double fluorides established in the thermal analyses have not been subjected to any further investigations. Potassium magnesium fluoride has been investigated crystallographically by van Arkel (Physica, 1925, 5, 167) and potassium zinc fluoride by Goldschmidt (Geochem. Vert. d. Elem., 1927, VIII). These compounds have been indexed as cubic and assigned to the perovskite (calcium titanate) class of compounds. Harasy-Szabo (Magyar Tud. Kozlemenyek, 1947, No.1, 36) listed these two fluorides as monoclinic with $a=b=c$ and $\beta = 90^0$ but no further data were supplied. It is

of interest to note that while the double oxides of the perovskite class have evoked particular attention in recent years by the discovery of the anomalous dielectric properties of barium titanate (e.g. Farrington, Planer and Boswell, Phil. Mag., 1949, 40, 157), no research whatsoever has been reported in connection with the double fluorides of this class.

The silicofluoride process for the decomposition of natural beryl is one of the better known industrial processes utilising complex fluorides. Considerable work resulting in the evolution of a highly efficient process has been carried out by the Siemens-Konzern ("Beryllium" Siemens-Konzern, translated by Finbach and Michel, Chemical Catalog Co., New York, 1932). The process itself is discussed in some detail in the relevant section of this thesis, but it is important to note that no stage of the decomposition process has been studied at any time by X-ray methods. Perhaps more empirical is the ferric fluoride process described by Kawecki (Trans. Electrochem. Soc., 1946, 89, 233). The success of this process depends on the fact that it requires only the theoretical quantity of sodium ferric fluoride necessary to react with the beryllium oxide content of the ore. It is claimed to be applicable to ores containing only 2% beryllium oxide by weight with success.

The claims of this process prompted a more thorough investigation of some of the reactions between metal oxides and fluorides. It appeared, for instance, very probable that the oxide constituents of beryl react preferentially with sodium ferric fluoride in such a way that under the conditions of experiment only the beryllium oxide reacted with the complex fluoride. It was therefore decided to investigate the sintering reactions of sodium silicofluoride and sodium ferric fluoride with the individual constituent oxides of beryl and to attempt to correlate the results obtained with the actual decomposition processes of the mineral. An understanding of such processes would be of considerable importance in the possible application of fluorides to other minerals such as ilmenite, for which no very satisfactory method of decomposition is known. These investigations are detailed in the first section of this thesis.

The conversion of some fluorides to oxides by ignition in air or oxygen is often reported in the literature. This fact has apparently always been taken for granted in the use of fluorides and has never been investigated from any aspect. Its general acceptance can be judged by the work of Demange (Ann. Chim., 1937, I, 225), who has analysed ferric, nickel and chromium fluorides prior to the determinations of their heats of formation, by ignition to constant weight in air. Sidgwick (N.V. Sidgwick, The Chemical Elements

and their Compounds, Clarendon Press, Oxford, 1950, Vol. I, page 251) lists strontium and barium fluorides as being converted into their respective oxides by ignition in air above 1000°C. The mechanism of these conversions appeared to be of considerable interest in that the question arises how the fluorine is lost; it may be liberated in the form of hydrogen fluoride by hydrolysis with the water vapour of the atmosphere. Alternatively, the fluorine might be evolved in the form of a less reactive oxide such as fluorine monoxide. It was therefore proposed to heat a complex fluoride such as potassium ferric fluoride, which is apparently easily converted to a mixture of potassium fluoride and ferric oxide at as low a temperature as 600°C, in a controlled atmosphere of dry oxygen. The results of these investigations are detailed in the latter part of the first section of this thesis.

It appeared necessary, however, that for a better understanding of the reactions between metal oxides and fluorides, some investigations of a more fundamental character were needed. The obvious choice lay in the utilisation of the fluorides of the alkali metals. These fluorides are of exceptional stability compared to those of metals of other groups. Their comparatively low melting points appeared suitable for their being used as successful reactants in the temperature range 600°C - 1000°C. Moreover, a survey of

their lattice constants showed the existence of close similarity in values with those of the oxides of some Group II metals, e.g.

$a_{NaF} = 4.617$ X-units; $a_{MgO} = 4.202$ X-units.

In addition, the similarities were further maintained in the lattice type (face-centred cubic) and in the sizes of the metal ions, e.g.

$Na^{+} = 0.95A$; $Ca^{++} = 0.99A$.

The similarity in the ion sizes of fluorine and oxygen is better known ($F^{-} = 1.36A$; $O^{--} = 1.40A$). It was therefore of extreme interest to investigate whether any extensive range of mixed crystal formation was possible between a carefully chosen alkali metal fluoride and an alkaline earth metal oxide. Conversely, the possible existence of mixed metal-oxygen-fluorine compounds in this range of oxides and fluorides has not been investigated to date.

Prior to such investigations a technique of making intimate powder mixtures and subjecting them to suitable heat treatment had to be evolved. The chief difficulty lay in the extreme hygroscopic nature of potassium, rubidium and caesium fluorides. Some of the German workers have prepared such mixtures by grinding the components under petroleum. This method, however, did not appear particularly promising for use with light powders such as magnesium oxide. The cost and availability of rubidium and caesium salts further demanded investigations on a semi-micro scale. The details of the

techniques ultimately employed and the reactions investigated are described in the second section of this thesis. Such reactions appeared to be, in addition, particularly well suited for study by X-ray powder methods in view of the high crystallinity of the reactants. Apart from the more routine X-ray analysis of the reaction products, there appeared to be the possibility of keeping a constant check on the structures and cell constants of the reactants by more precise methods. It was also noticed that though considerable powder data were available for the alkali metal fluorides and Group II oxides, values published for particular compounds differed to a greater extent than could be accounted for by normal experimental error. The apparent inconsistencies are most probably due to the small dimensions of the powder cameras used by workers up to about 1955. Some of the results of earlier workers have yet to be taken as standards for lack of more modern work. The standard interplanar spacings published by the A.S.T.M. are not as complete as they could be, both from the point of view of providing all the spacings normally attributed to a substance and in the inclusion of all the compounds known. Some work, therefore, appeared to be necessary in the preparation and chemical and X-ray analysis of the reactants to be employed.

It was anticipated that compounds of the type $A^{+}B^{++}F_3$ would probably result in some of these reactions. Reference has already been made to the data published for potassium

magnesium fluoride and potassium zinc fluoride, which at their best may be described as approximate.

Excellent work has however been done by Megaw (Proc. Phys. Soc., 1946, 58, 133) on the crystallographic interpretation of powder photographs of some double oxides of the perovskite type. The synthesis and elucidation of the structures of the double fluorides, and thereby comparison with oxide structures, were therefore of comparative importance. The latter part of the second section of this thesis deals with these investigations.

The possible extension of the investigations of reactions between oxides and fluorides to reactants derived from other groups of the periodic table, e.g. magnesium fluoride and ferric oxide, appeared to be commendable. Apart from the study of the individual reactions, it appeared necessary to collect information from as many sources as possible before any involved discussion or coordination of the preceding results was made.

S E C T I O N I

Investigations of the Reactions between Metal Oxides and Complex Metal Fluorides

PART I

Some Industrial Processes used in the Decomposition of natural Beryl.

A Historical Survey and Introduction to the present Research.

Some industrial processes used in the decomposition of natural beryl - a historical survey and introduction to the present research.

(a) The silicofluoride process for the decomposition of natural beryl.

At the present day beryllium is of growing importance, especially in the production of alloys and in nuclear research. Its extraction is complicated by the difficulty of attacking beryl, the only ore available in considerable quantities, followed by the difficulty of separating the beryllium from the accompanying aluminium. Beryl is an aluminosilicate of the empirical formula $3\,BeO, Al_2O_3, 6SiO_2$. Its detailed structure has been given by Wahl (Z. Krist, 1927, 66, 433).

In 1919 Copaux (Compt. rend. 1919, 168, 610) showed that beryl could be decomposed by melting the ore with twice its weight of sodium silicofluoride at 850°. The method is apparently based on the assumption that at 750° the sodium silicofluoride dissociates into sodium fluoride and silicon tetrafluoride, and the latter attacks the beryllium oxide as formulated by the equation

$$2BeO + SiF_4 \rightarrow SiO_2 + 2BeF_2$$

followed by the conversion of the beryllium fluoride into the double fluoride sodium beryllium fluoride (Na_2BeF_4). Thus

$$2\,NaF + BeF_2 \rightarrow Na_2BeF_4$$

The alumina is analogously converted into artificial cryolite (Na_3AlF_6). No experimental evidence is, however, available to justify this assumption (J. Newton Friend, A Textbook of Inorganic Chemistry, Griffin, London, 1926, Vol.III, part II, page 9). Boiling water extracts the soluble double fluoride of beryllium from the relatively insoluble cryolite. The metal is then obtained electrolytically from the sodium beryllium fluoride.

Illig, Rosenfeld and Fischer of the Siemens-Konzern ("Beryllium", Siemens-Konzern, translated by Rinbach and Michel, Chemical Catalog Co., New York, 1932) later found that a practically quantitative reduction of beryl could be obtained by sintering it with an equal weight of sodium silicofluoride at 650°. The chief advantages claimed over Copaux's method were (a) the reaction vessels could be lined with a cheap refractory like fire-clay in contrast to the expensive graphite used in Copaux's method; (b) the end product was in the form of a friable mass, and (c) the yield was higher as any free beryllium fluoride produced at a higher temperature was less soluble. A most comprehensive literature survey and flow sheets for the decomposition processes of beryl are given by Besson (Bull. Soc. Chem., France, 1949, (V), 16, D 18).

Though the technicalities of the silicofluoride process have been brought to a high state of efficiency, very little

has been reported of its chemistry. Cryolite, for instance, is normally quoted as a reaction product but no data are available for the extent of its formation under varying conditions.

The plan of research proposed was to sinter the constituent oxides of beryl with sodium silicofluoride, individually, and to correlate the results obtained with similar experiments conducted on beryl itself.

(b) The ferric fluoride process for the decomposition of natural beryl.

The aim of the silicofluoride process was apparently to convert the beryllium oxide into soluble sodium beryllium fluoride and the aluminium oxide into soluble cryolite, thus enabling a separation of the beryllium content by leaching. More modern methods are designed to extract the beryllium as a soluble fluoride, leaving the aluminium oxide and silica from the ore substantially unattacked.

Such a process is due to Kawecki (Trans. Electrochem. Soc., 1946, 89, 233). In this process sodium ferric fluoride (Na_3FeF_6) is used as the attacking re-agent. The finely ground ore is made into wet briquettes with the theoretical amount of sodium ferric fluoride required to react with the beryllium oxide content of the ore, as given by the equation

$$3BeO + 2Na_3FeF_6 \rightarrow 3Na_2BeF_4 + Fe_2O_3$$

and heated for half an hour at 750°. The soluble sodium beryllium fluoride is leached from the insoluble alumina and silica of the ore and the ferric oxide formed as a reaction product. Of particular interest is the claim of its applicability with advantage to a new low-grade beryllium ore of about 2% by weight of beryllium oxide. This ore consists of magnetite with small quantities of helvite, a beryllium iron aluminium silicate. The sodium beryllium fluoride is subjected to one of the usual metallurgical

processes for obtaining the metal.

It would be seen that processes of this type, in which the desired ore constituent is selectively attacked without consumption of re-agents by unwanted materials, are of special value in the utilisation of low-grade mineral deposits. The methods are apparently dependent on the fact that under suitable working conditions a re-agent can be made to attack preferentially a particular oxide constituent of an ore.

No details of the chemistry of this process have been reported and it was of interest to investigate whether aluminium oxide, for example, had no reaction with sodium ferric fluoride when heated separately from beryllium oxide and silica. It was decided to investigate these reactions by sintering the constituent oxides of beryl separately with an alkali metal ferric fluoride and to attempt to correlate the results of these investigations with similar experiments conducted on beryl. By way of modification, it was decided to employ potassium instead of sodium ferric fluoride. Apart from ascertaining the validity of this compound as an attacking re-agent, it was hoped that an appreciably lower working temperature could be arrived at by this means.

PART II

Experimental.

Experimental Methods.

A. The preparation and analysis of reactants.

In view of the fact that X-ray analytical methods were to be applied to the reactions to be investigated, it was of importance that the reactants were of dependable purity and in relatively well crystallized forms. It was fortunate that supplies of pure oxides were available. The beryllium oxide employed was the "pure" form supplied by Hopkin and Williams Ltd. Similarly, "Analar" grade aluminium oxide was at hand. In the reactions involving silica, selected crystals of natural quartz were utilised. This sample was known to contain only traces of iron as an impurity. The oxides were all ignited to constant weight in platinum at 900° immediately before the preparation of the mixtures. They were ground to a fine powder in an agate mortar before ignition. In the experiments with cryolite and beryllium oxide a finely ground sample of highly crystalline pure natural cryolite was employed.

Sodium silicofluoride was, however, only obtainable as a commercial product and its synthesis and analysis were therefore attempted. Sodium and potassium ferric fluoride were also prepared and analysed.

The preparation and analysis of sodium silicofluoride.

A method of preparation which appeared most suitable for obtaining a pure sample of this substance was by its precipitation from a solution of hydrofluosilicic acid by the addition

of sodium chloride. Adoption of this procedure resolved the preparation into (a) the preparation of a solution of hydrofluosilicic acid followed by the estimation of its concentration; and (b) the precipitation of sodium silicofluoride by the addition of pure sodium chloride, followed by the isolation and analysis of the complex fluoride.

The preparation of a solution of hydrofluosilic acid.

Preliminary experiments for obtaining a solution of hydrofluosilicic acid exploited the conventional method of leading into water gaseous silicon tetrafluoride produced by the interaction of silica, fluorite and concentrated sulphuric acid. The purification of the tetrafluoride gas was attempted by passing it through two U-tubes packed with glass wool to remove most of the hydrogen fluoride, and then through a third U-tube containing glass wool with finely powdered dry sodium fluoride to remove the remaining hydrogen fluoride. The method was, however, not found convenient for the preparation of any appreciable volumes of the pure acid solution in that:

(a) The method was satisfactory when natural fluorite and finely powdered natural quartz were employed. Mixtures of calcium fluoride and "Neosyl" silica had, however, to be previously heat treated by drying at 200° for a smooth and complete reaction to ensue.

(b) It was desirable that the temperature be maintained below 160° to eliminate the possibility of fluorosulphonic

acid being formed and passing into the solution of hydrofluosilicic acid. This was difficult in practice.

(c) Frequent agitation of the absorption flask was found to be necessary to prevent the blocking of the delivery tube in spite of the fact that the end of the tube dipped below a mercury surface.

A complete departure was therefore made from this method for the preparation of a hydrofluosilicic acid solution. Weighed quantities of "Neosyl" silica were placed in a platinum vessel of about 800 ml. capacity and about 250 ml. of distilled water added for every 15g. of silica. This mixture was stirred electrically by means of a glass stirrer protected by a polythene cave. The requisite volume of hydrogen fluoride solution (40% by weight) to react completely with the silica was then introduced at the rate of a drop about every five seconds into the suspension of silica. Admission of the acid was through a length of polythene tubing attached at one end to a platinum funnel with the aid of picein wax and drawn out to a jet at the other. Conditions were so arranged that a slight excess of silica was present when all the acid had run in. This was to avoid the presence of excess hydrofluoric acid which would have prevented storage of the solution in a glass flask at a later stage. The silica was found to be dissolved at an extremely rapid rate. The stirring was nevertheless continued for about thirty minutes after all the hydrofluoric acid had run in. The solution was

then filtered twice through No.42 filter paper to remove the excess of silica. Storage was in a three litre Pyrex flask.

By this procedure the hydrofluosilicic acid is obtained directly as given by the equation

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O.$$

The estimation of the concentration of a solution of hydrofluosilicic acid.

The method employed for this estimation was based on the principle outlined by Penfield (Chem. News 1879, 39, 179). This makes use of the reaction given by the equation

$$H_2SiF_6 + 2KCl \rightarrow K_2SiF_6\downarrow + 2HCl.$$

The hydrochloric acid formed could be easily estimated by titration against standard sodium hydroxide. Penfield's method has been shown to be simple and accurate provided an excess of alcohol is added (Anosov and Chirkov J. Applied Chem. U.S.S.R. 1932, 5, 1097). The potassium silicofluoride formed is comparatively insoluble in alcohol and is therefore almost completely precipitated. This is essential for the prevention of a possible hydrolysis of the silicofluoride. Thus

$$K_2SiF_6 + 2H_2O \rightarrow 2KOH + H_2SiF_6.$$

This would otherwise be followed by reaction of the potassium hydroxide with the hydrochloric acid

$$KOH + HCl \rightarrow KCl + H_2O,$$

leaving free hydrofluosilicic acid in solution. Any appreciable quantities of this acid complicate the choice of a suitable

indicator for the titration.

The procedure finally adopted was to effect the precipitation by the addition of a 1% solution of "Analar" potassium chloride in excess, followed immediately by a volume of rectified spirits equal to that of the solution. Subsequent titrations using methyl red as indicator gave sharp end points and concordant results when the solutions were allowed to stand for about fifteen minutes prior to titration, after the addition of the alcohol. Approximately decinormal, sodium hydroxide solutions were employed which had been standardised against potassium hydrogen phthalate. The results showed that the acid solution contained approximately 8% by weight of hydrofluosilicic acid.

The precipitation of sodium silicofluoride from a solution of hydrofluosilicic acid.

A 20% solution of sodium chloride of "Analar" grade was used for the precipitation. The requisite volume of this solution based on the equation

$$H_2SiF_6 + 2NaCl \longrightarrow Na_2SiF_6 + 2HCl$$

was run into the acid with continuous stirring. A suspension resulted which was further stirred electrically for about an hour. This suspension was allowed to stand overnight when the sodium silicofluoride was found to set into a compact mass. The supernatant liquid was siphoned off and the precipitate transferred to a No.40 filter paper. This precipitate was washed with distilled water until it was chloride free. The

mass was dried in a vacuum desiccator containing silica gel for four days, when a perfectly white micro-crystalline mass resulted. This mass was further dried for four hours in nickel boats in a vacuum furnace at 250°. An approximate yield of 95% was recorded when a correction for the solubility of the sodium silicofluoride was applied (Carter, Ind. Eng. Chem. 1930, 22, 887 and Nikolaev, Ivanov and Koltypin J. Applied Chem. U.S.S.R. 1936, 9, 1183).

The analysis of sodium silicofluoride.

The purity of the sample of sodium silicofluoride obtained was assessed by two methods:

(a) Volumetrically, by the method employed by Carter (Ind. Eng. Chem. 1930, 22, 886). In this method the silicofluoride is quantitatively hydrolysed by a standard solution of sodium hydroxide. Thus

$$Na_2SiF_6 + 4NaOH \rightarrow 6NaF + SiO_2 + 2H_2O.$$

(b) Gravimetrically, by the determination of the sodium content in the form of the sulphate.

In the volumetric method weighed quantities of sodium silicofluoride, which would require about 25 ml. of approximately decinormal sodium hydroxide solution for hydrolysis, were tipped into titration flasks. Solutions were obtained with distilled water and titration against the standard alkali performed with the solution as hot as possible. Phenolphthalein was used as indicator and the first permanent tinge of pink taken as the end point. Under these conditions

concordant results were obtained which gave a purity of 100%.

Analysis of Sodium Silicofluoride

Weight of Na_2SiF_6 in g.	ml. of 0.1043N-NaOH	Weight of Na_2SiF_6 (calculated) in g.	% Purity
0.1262	25.60	0.1260	100
0.1108	22.50	0.1108	100
0.1052	21.25	0.1046	100

This method has been criticized by Worthington and Haring (Ind. Eng. Chem. Anal. Ed. 1931, 3, 7), who point out the possibility of hydrolysis on the lines given by the equations

$$Na_2SiF_6 + 2H_2O \rightarrow 2NaOH + H_2SiF_6 \qquad (1)$$

followed by

$$H_2SiF_6 + 6NaOH \rightarrow 6NaF + SiO_2 + 4H_2O \qquad (2)$$

The extent of the hydrolysis represented by equation (1) would occasion a corresponding error in an analysis based on the equation

$$Na_2SiF_6 + 4NaOH \rightarrow 6NaF + SiO_2 + 2H_2O.$$

The same authors point out that hydrolysis of the alkali metal silicofluoride is only very slight. Aqueous solutions of sodium silicofluoride are however distinctly acid and Hudleston and Bassett (J. Chem. Soc. 1921, 119, 405) have suggested that the mechanism of interaction between sodium

silicofluoride and sodium hydroxide is probably by an initial slow reaction

$$SiF_6^{--} \rightarrow SiF_4 + 2F^-$$

followed by the relatively rapid

$$SiF_4 + 3H_2O \rightarrow 4HF + H_2SiO_3$$

This would make the titration virtually one of hydrofluoric acid against sodium hydroxide; yet conforming to the proportions laid down by the stoichiometric equation

$$Na_2SiF_6 + 4NaOH \rightarrow 6NaF + SiO_2 + 2H_2O$$

Evidence which establishes this postulate on a secure basis has been put forward by Rees and Hudleston (J.Chem. Soc. 1936, 1334)

In the gravimetric method of analysis, the procedure outlined by Rees and Hudleston (J.Chem.Soc.1931, 1648) was employed. A weighed sample of about a gram of sodium silicofluoride was decomposed in a platinum crucible with excess "Analar" grade sulphuric acid. The decomposition is given by the equation

$$Na_2SiF_6 + H_2SO_4 \rightarrow Na_2SO_4 + 2HF + SiF_4$$

Evaporation of the excess sulphuric acid was completed by heating on a sand bath at about 350° to constant weight. The sodium content was thereby determined as the anhydrous sulphate. Any conversion of the sulphate to pyrosulphate was avoided by heating strongly with ammonium carbonate.

$$Na_2B_4O_7 + (NH_4)_2CO_3 \rightarrow Na_2SO_4 + (NH_4)_2SO_4 + CO_2$$

This method gave a purity of 100% to the sodium silicofluoride.

Analysis of Sodium Silicofluoride

Weight of Na_2SiF_6 in G.	Weight of Na_2SO_4 in G.	% Purity.
0.2042	.1538	99.7
0.1864	.1404	100

The preparation and analysis of potassium ferric fluoride.

It was decided to prepare a quantity of potassium ferric fluoride by the conventional method of obtaining it as a precipitate by the addition of a solution of potassium fluoride to one of ferric chloride.

A solution of ferric chloride was obtained by utilising a very pure form of iron powder (Carbonyl Iron, Grade C, supplied by Mond Nickel Co.)A ferrous chloride solution was prepared initially by dissolving a weighed quantity of the iron powder in the theoretical volume of pure concentrated hydrochloric acid required for the complete conversion to ferric chloride at a later stage. The dissolution was facilitated by gently warming the reaction

flask. Oxidation to the ferric state was effected by the addition of a twenty volume solution of hydrogen peroxide, dropwise, to the ferrous chloride solution which was electrically stirred. This was a modification of a method due to Frietag (Pharm.Ztg.1925, 70, 274). The progress of the oxidation was followed by testing drops of the solution against a freshly prepared 2% solution of potassium ferricyanide. The oxidation was complete in about an hour.

The precipitation of the potassium ferric fluoride was effected by the addition of a 40% solution of potassium fluoride to that of ferric chloride. The strength of the solution of potassium fluoride was accurately determined by evaporating a weighed volume to dryness in a platinum crucible; followed by conversion of the potassium fluoride to the sulphate by heating on a sand bath at about 300° with an excess of "Analar" grade sulphuric acid. The estimation of the potassium content as the sulphate was thereby possible.

$$2\,KF + H_2SO_4 \rightarrow K_2SO_4 + 2HF$$

This procedure had to be adopted as the potassium fluoride was supplied in the form of an unspecified hydrate. Accurate weighing was furthermore inconvenient because of the deliquescence of the substance.

The requisite volume of this solution of

potassium fluoride was added dropwise to that of the ferric chloride which was electrically stirred. Potassium ferric fluoride was formed as a white precipitate. The suspension was allowed to stand overnight and the supernatant liquid siphoned off. The precipitate was transferred to a No.40 filter paper and washed with distilled water to which had been added about five drops of 40% hydrofluoric acid solution for every 100 ml. of water employed. The washing was continued till the precipitate was chloride-free. The addition of the few drops of hydrofluoric acid was found to be essential to prevent the potassium ferric fluoride assuming a brownish tinge; this was probably due to slight hydrolysis into hydrated ferric oxide. Thus

$$K_3FeF_6 + 3H_2O \rightarrow 3KF + Fe(OH)_3 + 3HF$$

The potassium ferric fluoride was dried in a vacuum desiccator over silica gel for five days and then in a vacuum furnace at 200° for six hours. A white amorphous powder resulted. The stages of preparation could be represented by the following equations

(a) $Fe + 2HCl \rightarrow FeCl_2 + H_2$

(b) $2FeCl_2 + 2HCl + H_2O_2 \rightarrow 2FeCl_3 + 2H_2O$

(c) $FeCl_3 + 6KF \rightarrow K_3FeF_6 + 3KCl$

A yield of 75% was recorded; the loss was most probably due to the solubility of the potassium ferric fluoride in

the solution and in the water used for washing.

The analysis of the sample of potassium ferric fluoride was based on its decomposition with excess concentrated sulphuric acid followed by a gravimetric estimation of the iron content.

A sample of the potassium ferric fluoride was dried for an hour at 250° in vacuum and a weighed quantity decomposed with excess sulphuric acid of "Analar" grade in a platinum crucible. The decomposition was considerably facilitated by the application of gentle heat. The contents of the crucible were transferred to a 600 ml. beaker quantitatively and the iron content estimated by the procedure detailed by Vogel (A. I. Vogel, Textbook of Quantitative Inorganic Analysis, Longmans, London 1947, p.484). The precaution of a preliminary oxidation with a few drops of concentrated nitric acid was taken.

Analysis by this method gave a purity of 100% to the sample of potassium ferric fluoride.

Analysis of potassium ferric fluoride.

Weight of K_3FeF_6 in g.	Weight of Fe_2O_3 in g.	% Purity.
0.5802	0.1614	100
0.5136	0.1428	100

The analytical procedure could be best represented by the following scheme

$$2K_3FeF_6 + 6H_2SO_4 \longrightarrow 3K_2SO_4 + Fe_2(SO_4)_3 + 12HF$$

$$Fe_2(SO_4)_3 \xrightarrow{NH_4OH} Fe(OH)_3 \longrightarrow Fe_2O_3$$

The preparation and analysis of sodium ferric fluoride.

A sample of about 20g. of sodium ferric fluoride was prepared by a series of reactions strictly analogous to those exploited for the potassium salt. The analysis was effected in a similar fashion. The sodium fluoride utilised was a "pure" sample supplied by Hopkins and Williams Ltd. The requisite quantity of this substance was weighed out directly and dissolved in an excess of distilled water. Analysis gave a purity of 100%.

Analysis of sodium ferric fluoride.

Weight of Na_3FeF_6 in g.	Weight of Fe_2O_3 in g.	% Purity.
0.4088	0.1224	100
0.4372	0.1310	100.

6. Experimental techniques employed in:-

1. Reactions in the temperature range 600° - 750°.

The experimental conditions employed in the investi-

gations of the reactions involving the use of sodium silicofluoride and potassium ferric fluoride were so designed as to simulate those of the actual industrial processes. The apparatus and methods may be best described under the following sections.

(a) Heating arrangements and temperature measurements.

A Gallenkamp nichrome-wound furnace carrying a "sand-finished" silica tube was employed. It was anticipated that long periods of heating, even extending over several days, would have to be resorted to for successful reaction. This discouraged the idea of using any form of energy regulator for the maintenance of the temperature as the failure of such a device would either completely cut off the electrical supply or short circuit the mains directly through the furnace. Instead the furnace was supplied from the 110 D.C. mains through a suitably sensitive heavy duty wire rheostat. An ammeter and subsidiary fuses were also introduced into the circuit as necessary auxiliaries.

The temperature measurements were made with a chromel-alumel thermocouple connected to a Siemens pyrometer indicator. The end of the thermocouple was placed in the upper centre of the annular space between the furnace tube and the furnace. The tube was well lagged in position with asbestos. This appeared to be the most suitable position for recording the temperature as the thermocouple could on no account be placed inside the tube for reason of possible attack by

fluoride vapours. The reaction mixtures were contained in boats placed in the tube and the ends of the tube loosely plugged with woolly asbestos thereby enabling access to the atmosphere. A close check on the temperature variations of this system at different times of the day and night was made. A maximum variation of $\pm 5^{\circ}$ over the range 600-750° was found. It was later found that slight adjustments of the current at certain critical times of the day diminished these fluctuations considerably.

(b) Choice of refractories:-

The choice of refractory materials is normally based on the resistance to attack under particular experimental conditions. It is, however, doubtful whether any refractory is ideally suited for investigations of reactions between oxides and fluorides at high temperatures. In the present research most suitable refractories were found by trial and error for particular series of investigations. A silica furnace tube was preferred in these experiments as the possible attack of other refractories such as mullite and sillimanite by fluoride vapours has not been previously investigated. It was found that the inner surface of the silica tube became sticky with prolonged heating of fluorides in it. The tube had therefore to be lined with asbestos paper to overcome this difficulty. A tube which fractured after some months use showed several radial cracks and an obvious tendency for the silica to devitrify in the hotter regions. Alumina

boats were avoided in these experiments though they were found later to be unattacked by alkali metal fluorides up to about 850°. A few preliminary experiments conducted with mixtures of beryllium oxide and sodium silicofluoride in silica boats showed the tendency of the reaction products to fuse firmly to the boats. Platinum boats were eventually employed in all the experiments described in this section. No instances of adherence of reaction products to platinum were recorded.

2. Analysis of the reaction products by X-ray methods.

X-ray analysis by the powder method was adopted in the study of the reactions to be detailed.

A Metropolitan-Vickers "Raymax" set was used for the production of X-rays. This was of the continuously evacuated type fitted with a de-mountable anticathode. A cobalt target was used in the experiments with complex fluorides as it was most suited for obtaining diffraction patterns of iron compounds. There was the added advantage in this arrangement of iron compounds being self-filtering to cobalt radiation. A 9 cm. diameter powder camera of the type designed by Bradley, Lipson and Petch (J. Sci. Instruments. 1941, 18, 216) was used. Specimens were prepared by grinding the entire reaction mass to a fine powder in an agate mortar and filling suitable lengths of Lindemann glass capillaries. Lindemann glass is a lithium borate glass of low scattering power. Representative sampling was thereby ensured which is an essential pre-

requisite of successful X-ray powder analysis. In the case of the oxidation products of potassium ferric fluoride which contained free deliquescent potassium fluoride, the mass was crushed with a nickel spatula on a porous tile heated to about 100°. The capillaries were filled off this plate and immediately sealed to exclude moisture.

The films were measured with a standard steel rule graduated in millimetres and the interplanar spacings calculated by the method of Bradley and Jay (Proc. Phys. Soc. 1932, 44, 564) which eliminates any errors due to film shrinkage.

Investigations of the reactions between 1. Sodium Silicofluoride and (a) Beryllium oxide.

C. Investigations of the reactions between 1. Sodium silicofluoride and (a) Beryllium oxide.

The procedure adopted for the investigation of this reaction was to sinter intimate mixtures of sodium silicofluoride and beryllium oxide and analyse the reaction products by the powder method. Such an investigation demands the assignment essentially arbitrary, of suitable values to three main controlling factors, namely (a) temperature (b) composition of reaction mixtures and (c) duration of experiments.

The Siemens-Tonnam fluoride process for the decomposition of beryl uses a temperature of 650° - 700°. Preliminary experiments with mixtures of sodium silicofluoride and beryllium oxide at 650° indicated that there was a tendency for the reaction product to show signs of fusion. The temperature finally adopted was 620°. This proved to be most suitable for all the investigations subsequently made.

The reaction mixtures were made by tipping out weighed quantities into an agate morter and mixing intimately for 15 - 20 minutes. This period was considered necessary because of the components being all white in colour. The proportions of the constituents were based on theoretical equations.

The duration of the experiments remained a variable factor throughout the series of investigations. Mixtures were heated for such periods at 620° that either complete reaction resulted or any apparent incompleteness could be interpreted.

Under conditions of sintering, at least two reactions could occur theoretically between sodium silicofluoride and beryllium oxide. Thus

$$2BeO + 2Na_2SiF_6 \rightarrow 2Na_2BeF_4 + SiO_2 + SiF_4 \quad (1)$$

$$2BeO + Na_2SiF_6 \rightarrow 2NaBeF_3 + SiO_2 \quad (2)$$

The reaction product should therefore depend on the proportions of the constituents of the mixture. Two mixtures, corresponding in composition to the proportions given by equations (1) and (2) were therefore subjected to the experimental conditions described previously, for twenty-four hours. X-Radiograms were obtained which were measured. Calculation of the interplanar spacings and subsequent comparison of these values with standard spacings obtained similarly for the individual components showed that no beryllium oxide was present in the reaction mass corresponding to equation (1). That corresponding to equation (2) showed all the spacings of the preceding X-radiogram in addition to all the values and relative intensities associated with beryllium oxide. Both reaction products were in the form of friable white masses.

It was to be inferred, therefore, that the reaction between the two reactants followed a single course which was independent of their relative proportions. This was an essential feature of all reactions subsequently investigated. No evidence for the existence of sodium silicofluoride was found in either reaction product. This implied

complete decomposition of any excess of this substance under the particular experimental conditions. A detailed analysis of the spacings and relative intensities of the individual X-radiograms confirmed the formation of sodium beryllium fluoride (Na_2BeF_4) as the reaction product. The standard data adopted for this substance were calculated from the values given by O'Daniel and Tscheischwili (Z. Krist. 1942, 104, 128). Neither X-radiogram showed any evidence, however, for the existence of silica. This was of interest in that the formation of silica as demanded by the theoretical equations was never established in any reactions described in this section. It is a necessary postulate that it be formed in a reaction between a metal oxide and sodium silicofluoride. Its formation is probably in an amorphous state under the conditions of experiment adopted.

Thermal analysis of the system NaF — BeF_2 has been made by Novoselova and Levina (J. Gen. Chem. U.S.S.R. 1944, 14, 385). The establishment of the existence of two double fluorides of formulae $NaBeF_3$ and Na_2BeF_4 has thereby been made. The compound $NaBeF_3$ is reported to melt at 353° by O'Daniel and Tscheischwili (Neues. Jahrb. Mineral. Geol. Monatsh 1943, 48A, 96). The same authors have assigned a β calcium silicate structure to this compound. The compound Na_2BeF_4 is reported by Novoselova and Levina (loc. cit.) to melt at 615° - 620° which perhaps explains the tendency of the reaction masses to fuse when heated at 630° - 650°.

Novosselova, Vorob'eva and Bagorskaya (J. Gen. Chem. U.S.S.R. 1937, 7, 2789) have reported the formation of sodium beryllium fluoride (Na_2BeF_4) on heating a mixture of beryllium oxide and sodium silicofluoride in the proportions $4BeO:1Na_2SiF_6$ at 700°. The double fluoride Na_3BeF_3 has never been prepared by an analogous reaction. It is evidently only formed by crystallisation from a solution of sodium carbonate and beryllium hydroxide in hydrofluoric acid (O'Daniel and Tschaischwili loc. cit).

Additional evidence of the occurrence of reaction as represented by equation (1) was obtained from the mass variations of the reaction mixture on heating. The percentage loss in weight was in approximate agreement with the theoretical loss caused by the evolution of silicon tetrafluoride as demanded by equation (1). It was to be inferred, therefore, that sodium silicofluoride reacts with beryllium oxide at 620° to produce sodium beryllium fluoride (Na_2BeF_4) and an apparently amorphous form of silica. Silicon tetrafluoride is evolved in the process and the reaction is best represented by the equation

$$2\,BeO + 2Na_2SiF_6 \rightarrow 2Na_2BeF_4 + SiO_2 + SiF_4$$

The reaction is complete in twenty-four hours at this temperature. There were no unexplained lines on the X-radiograms which establish the absence of formation of any oxyfluoride phases such as $2BeO{\cdot}5BeF_2$.

(b) Aluminium oxide.

In view of the fact that no information was available on the possible interaction of sodium silicofluoride and aluminium oxide, the preliminary experiments were performed on the assumption of a complete conversion of the oxide to cryolite (Na_3AlF_6). The reaction mixtures therefore contained proportions of the reactants as given by the equation

$$2Al_2O_3 + 6Na_2SiF_6 \rightarrow 4Na_3AlF_6 + 3SiO_2 + 3SiF_4$$

The same experimental procedure adopted with the experiments on beryllium oxide was used. The temperature was maintained at 620°.

The reaction product of a twenty-four hour run based on the above equation showed slight sintering. X-Ray analysis of this product showed a predominant excess of sodium fluoride, in addition to unreacted alumina and some cryolite. The standard data for sodium fluoride and cryolite were obtained from X-radiograms of the individual compounds. A crystalline specimen of natural cryolite was used. The data for aluminium oxide were obtained from the lists published by Hanawalt, Rinn and Frevel (Ind. Eng. Chem. Anal. Ed. 1938, 10, 457).

The presence of sodium fluoride could only be explained by the decomposition of unreacted sodium silicofluoride. Thus $Na_2SiF_6 \rightarrow 2NaF + SiF_4$

Experiments were therefore performed to verify this assumption. Quantities of sodium silicofluoride were heated in the same apparatus, to constant weight. It was found that constant weight was attained after a minimum period of about four hours. The loss in mass corresponded to a quantitative decomposition into sodium fluoride and silicon tetrafluoride. Sodium fluoride was the only product found on X-ray analysis. Caillat (Ann. Chim. 1943, 20, 367) postulates that in the thermal decomposition of sodium silicofluoride a solid solution of sodium fluoride and silicofluoride is formed after some time which retains the silicon tetrafluoride. An X-radiogram of sodium silicofluoride decomposed to the extent of 60% was therefore obtained. This showed the co-existence of sodium silicofluoride and fluoride with no apparent change in the Bragg angles of the high-angle lines which would have been indicative of mixed crystal formation.

To rule out the possibility of incomplete reaction between the oxide and fluoride, the experiment was repeated with a mixture of the same composition for five days. The X-radiogram of this reaction product was identical with the one obtained previously. It appeared probable, therefore, that this reaction was more complex in its mechanism than the preceding one of beryllium oxide and the same complex fluoride. The presence of unreacted alumina together with sodium fluoride produced by the

decomposition of the silicofluoride showed that the decomposition of the silicofluoride was obviously more rapid than its attack of the oxide. As cryolite had been identified as a reaction product, it was decided to estimate the extent of its formation from the mass of silicon tetrafluoride evolved. A series of six experiments, with separately prepared mixtures of the same composition as previously used, was made. The mixtures were heated individually for twenty-four hours at 620° . Calculation of the conversion of alumina to cryolite showed that the results were distributed between a 25% and 35% conversion.

Conversion of aluminium oxide to cryolite.

Composition of mixtures:- $Al_2O_3 : 3Na_2SiF_6$.

Run No.	% conversion.	Run No.	% conversion.
1	35.1	4	29.0
2	34.1	5	33.2
3	24.8	6	26.7

The variations in results, obviously far exceeded the limits of experimental error and an explanation had to be sought for. It was proposed first to eliminate or confirm the occurrence of reactions in which cryolite and silica were not the only reaction products. There appeared to be a

purely theoretical possibility of the formation of aluminium fluoride as given by the equation

$$2Al_2O_3 + 3Na_2SiF_6 \rightarrow 2Na_3AlF_6 + 3SiO_2 + 2AlF_3$$

The same experimental procedure was adopted with a mixture of this composition. The reaction product obtained by heating such a mixture for twenty-four hours at 620° gave an X-radiogram which was identical with the previous ones obtained. The only detectable difference was in the relative intensities of the sodium fluoride lines. This was in keeping with the relative proportions of the reactants. No additional lines on the X-radiogram which might have indicated the presence of free aluminium fluoride or an oxyfluoride phase of formula $Al_7O_{10}F$ described by Schober and Thilo (Ber. 1940, B, 73, 1219) were found.

The apparent variations in the masses of silicon tetrafluoride evolved may have had a possible explanation in the volatility of sodium fluoride at the temperature of experiment. Pure sodium fluoride was therefore subjected to the same experimental conditions when it was found that the mass variations over twenty-four hour periods were negligible at 620° .

An explanation of the reaction between sodium silicofluoride and aluminium oxide can however be made on the assumption of two distinct phases of reaction.

1. Thermal decomposition of the sodium silicofluoride with subsequent attack of the oxide by the silicon

tetrafluoride. Thus

$$Na_2SiF_6 \longrightarrow 2NaF + SiF_4$$

followed by

$$2Al_2O_3 + 3SiF_4 \longrightarrow 4AlF_3 + 3SiO_2$$

This attack is obviously a comparatively slow process which explains the large proportion of unreacted aluminium oxide in the reaction masses. Such an assumption is not unjustifiable as the reaction is a two phase one between a solid and a gas. Furthermore, the extent of reaction would be determined by the physical conditions operating at the time of reaction. These may be collectively referred to as the "attackability" of the alumina by the silicon tetrafluoride which would explain the mass variations in the tetrafluoride evolved.

2. A direct sintering reaction which results in the production of artificial cryolite. Thus

$$3NaF + AlF_3 \longrightarrow Na_3AlF_6$$

Such a reaction is usually governed by the temperature of experiment. It was found in later syntheses of such fluorides that the reactions were appreciably rapid at a temperature of 600°. The assumption of such a reaction would explain the absence of free aluminium fluoride.

(c) Silica. It was difficult to theorise on a particular course of reaction between sodium silicofluoride

and silica. Equal masses of the reactants were therefore chosen for the preparation of a mixture. The same experimental procedure as detailed previously was employed. The mixture was heated for forty-eight hours at 620°. X-Ray analysis of this reaction product showed the existence of α-quartz and sodium fluoride. No appreciable sintering of the product was visible. The loss in mass corresponded to the complete thermal decomposition of the sodium silicofluoride present. It may therefore be assumed that no reaction occurs between silica and sodium silicofluoride under these experimental conditions.

2. Natural cryolite and beryllium oxide.

It appeared to be of interest to investigate the possibility of any interaction between cryolite and beryllium oxide. The Siemens-Konzern (loc. cit) have recorded that sodium beryllium fluoride (Na_2BeF_4) is preferentially formed when aluminium and beryllium fluorides are reacted together with a quantity of sodium fluoride insufficient to permit the formation of both complex fluorides. The explanation offered is that sodium beryllium fluoride has a greater stability than cryolite. It therefore appeared possible that reaction between beryllium oxide and cryolite might follow the equation

$$2Na_3AlF_6 + 3BeO \longrightarrow 3Na_2BeF_4 + Al_2O_3$$

A mixture of the oxide and fluoride was made in the proportions given by this equation and heated under the experimental conditions used in the preceding reactions for twenty-four hours, at 620°. X-Ray analysis of the reaction product showed the existence of the original components with no evidence whatsoever for the occurrence of any reaction. It was however decided to repeat the experiment under the conditions normally used for the industrial decomposition of beryl. A temperature of 750° was employed. The reaction product from a twenty-four hour run at this temperature showed appreciable sintering and X-ray analysis established the presence of sodium beryllium fluoride, aluminium oxide and sodium fluoride together with the original components of the mixture. The reaction postulated, therefore, does occur. It is difficult, however, to explain the formation of sodium fluoride under these experimental conditions.

3. Sodium silicofluoride and natural beryl.

It was decided to carry out the investigations of the decomposition of natural beryl by sodium silicofluoride at 620°. This was essential for the co-ordination of the results with those of the preceding reactions with the component oxides. A sample of natural beryl supplied by Murex Ltd., and known to approximate closely to the composition $3BeO,Al_2O_3,6SiO_2$ was employed. The specimen was ground to a fine powder in agate and dried for two days at 200°.

The choice of proportions of constituents for reaction mixtures was based on the reactions already known to occur with the individual oxides. It was initially decided to employ sufficient silicofluoride for the complete conversion of the beryllium oxide to sodium beryllium fluoride (Na_2BeF_4) and the alumina to cryolite. Thus

$$2\,BeO + 2Na_2SiF_6 \rightarrow 2\,Na_2BeF_4 + SiO_2 + SiF_4 \quad (1)$$

$$2\,Al_2O_3 + 6Na_2SiF_6 \rightarrow 4\,Na_3AlF_6 + 3SiO_2 + 3SiF_4 \quad (2)$$

Application of equations (1) and (2) to beryl would give

$$3\,BeO,Al_2O_3,6SiO_2 + 6\,Na_2SiF_6 \rightarrow 3\,Na_2BeF_4 + 2\,Na_3AlF_6 + 9\,SiO_2 + 3\,SiF_4$$

A mixture of composition based on this equation was heated for forty four hours at 620°. The reaction product was a friable mass. X-ray analysis of this product established the complete decomposition of beryl. The X-radiogram was not of particularly good quality which was a constant disadvantage in all further work with beryl. The lines were, however, sufficiently distinct to confirm without doubt the presence of sodium berylliumfluoride (Na_2BeF_4), α-quartz, and sodium fluoride as reaction products. No structural evidence for the formation of cryolite was available, though a special search was made for it. Its complete absence could not, however, be definitely maintained as the production of individual spectra by the components of such a complex mixture would be largely

determined by their relative proportions and scattering powers. It has often been found that the resolution of lines of particular constituents of a complex mixture is difficult.

The presence of free sodium fluoride, however, emphasised that excess sodium silicofluoride was being employed. A theoretical equation using less silicofluoride had therefore to be derived. The scheme of decomposition adopted may be formulated by the equations

$$2\,BeO + 2\,Na_2SiF_6 \rightarrow 2\,Na_2BeF_4 + SiO_2 + SiF_4 \quad (1)$$

$$2\,Al_2O_3 + 3\,Na_2SiF_6 \rightarrow 2\,Na_3AlF_6 + 3\,SiO_2 + 2AlF_3 \quad (2)$$

Application of equations (1) and (2) to beryl would give

$$2(3BeO,Al_2O_3,6SiO_2) + 9\,Na_2SiF_6 \rightarrow 6\,Na_2BeF_4 + 2\,Na_3AlF_6 + 18\,SiO_2 + 2\,AlF_3 + 3\,SiF_4.$$

The same experimental conditions of time and temperature were employed with a mixture of composition given by this equation. X-ray analysis of the reaction mass established the presence of the same reaction products as in the preceding investigation.

It was evident that the aluminium oxide was not reacting completely with the silicofluoride under these particular conditions. It was therefore decided to attempt to obtain the minimum quantity of silicofluoride necessary for the complete decomposition of beryl. There was no

reason to question the validity of the equation adopted to represent the reaction of the beryllium oxide as it had been established independently. It was therefore considered best to ignore the possible reaction of aluminium oxide with the silicofluoride and to employ the requisite amount of sodium silicofluoride necessary for the complete conversion of the beryllium oxide to sodium beryllium fluoride (Na_2BeF_4).

It is of interest to note that the adoption of such proportions gives rise to the possibility of two theoretical equations which would represent the decomposition process. Thus

1. $2\,(3\,BeO,Al_2O_3,6SiO_2) + 6\,Na_2SiF_6 \rightarrow 6\,Na_2BeF_4 + 15\,SiO_2 + 2\,Al_2O_3 + 3\,SiF_4$

2. $2\,(3\,BeO,Al_2O_3,6SiO_2) + 6\,Na_2SiF_6 \rightarrow 6\,Na_2BeF_4 + 18\,SiO_2 + 4\,AlF_3$

A mixture of composition given by these equations was heated for twenty four hours at 620°. X-Ray analysis revealed the complete decomposition of the beryl. No evidence for the existance of free sodium fluoride was found in this product. The reaction products established were the same as previously found, namely, sodium beryllium fluoride and α-quartz. No free aluminium oxide or fluoride could be detected. Cryolite was also apparently absent. The loss in mass caused by the evolution of silicon

tetrafluoride approximated to within 10% of the theoretical loss demanded by the first equation which would represent the decomposition under the experimental conditions adopted. It is possible, therefore, that some aluminium fluoride is formed which evades detection by X-ray methods. This may be due to hydrolysis in the subsequent grinding process or the lack of formation in appreciable quantities.

A point of particular interest arose in the investigations of this reaction. The proportion of silicofluoride needed to decompose the mineral was ultimately arrived at by the consideration of the sintering reactions of the component oxides. This was found to be the same as the empirical proportion of one part of sodium silicofluoride to one of beryl which is used industrially.

The chemistry of the silicofluoride process is now placed on a firm theoretical footing. No attempt was made to study the minimum period of time required by the process for completion at 620°. It is possible that the higher temperature of 650° - 700°, used industrially, causes the formation of small quantities of liquid phases which facilitate the decomposition. The formation of cryolite must be regarded as subsidiary to that of sodium beryllium fluoride. It was evidently formed in extremely small quantities, if at all, in the investigations made. Its presence as an industrial reaction product may be attributed to the attack of the aluminium oxide by the silicon

tetrafluoride at the higher temperature employed, followed by conversion of the aluminium fluoride to cryolite by combination with excess sodium fluoride present.

4. Potassium ferric fluoride and

(a) beryllium oxide

The investigations of the reactions between potassium ferric fluoride and the constituent oxides of beryl were conducted on identical lines to those adopted with sodium silicofluoride and the same oxides. The industrial process uses a temperature of 700° and a duration of half an hour. It was, however, decided to maintain the temperature of 620° used in the preceding experiments. The duration of experiment remained a variable factor which depended on the individual reactions investigated.

The success of the ferric fluoride process depends on the fact that sodium ferric fluoride only attacks the beryllium oxide content under the conditions stipulated. It was of interest, therefore, to investigate the reaction with the individual oxide. The reaction which occurs in the industrial process is formulated by the equation,

$$3\ BeO + 2\ Na_3FeF_6 \rightarrow 3\ Na_2BeF_4 + Fe_2O_3$$

The mixtures employed in these investigations were made with proportions based on the analogous equation for the potassium salt. The previously employed procedure of mixing the constituents for 15 - 20 minutes in an agate

mortar was adopted. No attempt at briquetting the mixtures was made; though this is done in the industrial process.

Such a mixture when heated for twenty four hours at 620° sintered to a friable, dark magenta mass. X-Ray analysis revealed the complete absence of beryllium oxide and potassium ferric fluoride. The standard data for these substances were obtained from X-radiograms of the individual compounds. The reaction was therefore complete under these conditions. Potassium beryllium fluoride (K_2BeF_4) and ferric oxide were established as the reaction products. No evidence was present to indicate the formation of any other compound. The standard ferric oxide data were obtained from the lists published by Hanawalt, Rinn and Frevel (Ind. Eng. Chem. Anal. Ed. 1938, 10, 457). Standard interplanar spacings for potassium beryllium fluoride were calculated from the Bragg angles published by O'Daniel and Tscheischwili (Z. Krist. 1942, 104, 348).

The reaction may therefore be represented by the equation

$$3\,BeO + 2\,K_3FeF_6 \rightarrow 3\,K_2BeF_4 + Fe_2O_3.$$

It occurs to completion when a powder mixture is heated for twenty four hours at 620°.

(b) aluminium oxide.

It has been pointed out earlier that the success of

the ferric fluoride process lies in the apparent absence of reaction of the attacking agent and the alumina and silica components of beryl. Experimental verification of this claim was made by heating mixtures of potassium ferric fluoride and aluminium oxide and obtaining X-radiograms of the reaction products.

Mixtures containing equal parts of the components by weight, were used in the absence of a possible theoretical equation. A temperature of 620° was maintained. Such a mixture was heated for 48 hours at this temperature. The reaction product was a friable, deep magenta mass. It was noticed that the product began to deliquesce when ground in an agate mortar. The experiment was therefore repeated and the reaction product crushed on a heated tile as described in the section dealing with experimental techniques. X-Ray analysis of the dry reaction product was thereby made possible. It was found that aluminium oxide, potassium fluoride and ferric oxide constituted the reaction mass.

The absence of any other phases led to the inference that no reaction occurs between potassium ferric fluoride and aluminium oxide under the particular experimental conditions. The conversion of the ferric fluoride to potassium fluoride and ferric oxide was apparently a process of oxidation. The extent of this oxidation was derived from the loss in mass entailed by heating the mixture.

For this purpose, a mixture of the same composition as used in the preceding experiments was subjected to the same experimental conditions. The boat was removed directly from the furnace and allowed to cool in a desiccator over silica gel. Weighings were then made in a dry glass tube provided with a bung. The loss in mass corresponded to a complete conversion of the potassium ferric fluoride to potassium fluoride and ferric oxide. A detailed study of this conversion was made which is described in a later section.

(c) Silica.

Investigations strictly analogous to those made with aluminium oxide were made with silica. A mixture containing equal parts by weight of potassium ferric fluoride and silica was heated for forty-eight hours at 620° . The reaction product was a friable, deep magenta mass which suggested conversion of the potassium ferric fluoride to potassium fluoride and ferric oxide. This assumption was confirmed by the results of X-ray analysis. Quartz, potassium fluoride and ferric oxide were the only detectable reaction products. A check on mass variations indicated that complete conversion of the potassium ferric fluoride to potassium fluoride and ferric oxide had occurred.

It is to be inferred, therefore, that no reaction occurs between potassium ferric fluoride and silica under these experimental conditions.

(d) Natural beryl.

The decomposition of natural beryl by potassium ferric fluoride can be represented by the equation

$$3\,BeO,Al_2O_3,6SiO_2 + 2K_3FeF_6 \rightarrow 3K_2BeF_4 + Al_2O_3 + Fe_2O_3 + 6\,SiO_2$$

The mixtures used in these investigations were therefore based on the proportions given by this equation. A sample of the specimen of beryl employed in the investigations with sodium silicofluoride was used. A mixture was heated for twenty-four hours at 620° and an X-radiogram of the reaction product obtained. Interpretation of this X-radiogram showed the absence of unreacted beryl. Complete reaction under these conditions is therefore to be inferred. Potassium beryllium fluoride, α quartz and ferric oxide were identified as reaction products. No structural evidence for the formation of aluminium oxide was available. It has to be assumed to be present in an amorphous condition; probably due to the low temperature of formation of a refractory oxide. The reaction product was in the form of a brittle, magenta mass.

In view of the fact that the potassium salt was used in this decomposition process, it was decided to determine the minimum period of sintering required to decompose the mineral at 620°. Mixtures, identical in composition to the ones used previously, were heated for various periods of time. The reaction products were subjected to X-ray analysis.

It was found that complete decomposition resulted after a minimum period of about two hours.

The investigations confirm the claim of Kawecki as regards the reaction of an alkali metal ferric fluoride with natural beryl. Potassium ferric fluoride can be used instead of the sodium salt for the decomposition. The process itself may be described as elegant, in that direct decomposition of the ore takes place, in the same manner as that in which the attacking agent reacts with the component oxides, separately.

PART III.

General discussion of results.

General discussion of results:-

The plan of research, adopted in the investigations of the decomposition processes of beryl, was to sinter the oxide constituents of the ore, separately, with the attacking reagents. Correlation of these results with those of experiments conducted with the ore itself was then attempted. This appeared to be the only method of obtaining a better understanding of the apparently complicated chemistry involved in the decomposition of an ore. The results fully justify the plan adopted.

In the silicofluoride process, for instance, reaction between beryllium oxide and sodium silicofluoride was complete under the conditions of experiment. Aluminium oxide, on the other hand, showed a considerably less degree of reactivity. With silica no reaction apparently occurs. A particular complex fluoride has therefore a definite order of reactivity with a series of oxides.

The important feature, however, of the reactions investigated is that the order of reactivity is maintained in the ore. There appears to be the possibility, therefore, of being able to choose suitable attacking agents for the decomposition of ores, from a study of the individual reactions of the constituents oxides. The importance of such a possibility cannot be overestimated in view of the large number of ores which have yet defied satisfactory decomposition. Ilmenite ($Fe\ TiO_3$) is one that may be

mentioned at random. The preferential reactivity of potassium ferric fluoride to the oxide components of beryl has been utilised in the exploitation of ores containing as little as 2% of beryllium oxide by weight. Under particular experimental conditions such attacking reagents, therefore, become highly selective. Valuable information should be derived from the extension of these principles to other ores.

The evolution of silicon tetrafluoride by the thermal decomposition of sodium silicofluoride, apparently, has a role in the decomposition processes utilising sodium silicofluoride. It is evident that in the reaction of sodium silicofluoride with aluminium oxide, the attack of the oxide by this gas is the rate determining process in the conversion of the aluminium oxide to cryolite. Whether the beryllium oxide is similarly first attacked by the silicon tetrafluoride and the beryllium fluoride thereafter converted into sodium beryllium fluoride, is more difficult to decide. The investigation of the sintering process indicated that the conversion follows a stoichiometric equation. The same result can, however, be obtained by a quantitative attack of the beryllium oxide by silicon tetrafluoride. The question as to the actual mechanism will have to remain unanswered until a detailed physico-chemical study of such gas-solid reactions is made.

The possibility of a direct solid reaction appears to be more likely in the case of the ferric fluoride process. The reaction between potassium ferric fluoride and beryllium

oxide is apparently stoichiometric. This is, however, not an absolute criterion. The question may be raised whether any volatile fluoride compound is evolved which attacks the oxides preferentially. The possibility of such a question arises from the fact that potassium ferric fluoride is easily converted into potassium fluoride and ferric oxide by heating in air. It was, however, found that, whatever the gas that is evolved, it is relatively inert. Experimental evidence in support of this statement is detailed in the next section of this thesis.

There is also the possibility that potassium ferric fluoride decomposes at the temperature of reaction, into potassium fluoride and ferric fluoride. This would be followed by attack of the oxides by the ferric fluoride. The assumption of this mechanism is of extreme theoretical interest in that it would imply the preferential reaction of ferric fluorides with oxides in the presence of an alkali metal fluoride. Evidence for this postulate comes from the investigations of the reaction between magnesium fluoride and ferric oxide. These investigations are described in a later section of this thesis. The ferric fluoride evolved in this reaction, combined with silica to produce silicon tetrafluoride. This stands in contrast to the absence of reaction between potassium ferric fluoride and silica. Further treatment of these aspects of the reactions are better reserved for the final discussion in this thesis.

PART IV.

Some experiments on the controlled oxidation of potassium and sodium ferric fluorides.

Some experiments on the controlled oxidation of potassium and sodium ferric fluorides.

(a) Introduction and experimental methods.

Instances of the conversion of fluorides to oxides by ignition in air are common in the literature. Sidgwick (N.V. Sidgwick, The Chemical Elements and their Compounds, Clarendon Press, Oxford, 1950 Vol. 1, page 251) describes barium and strontium fluorides as being converted to the respective oxides by ignition in air above a 1000°. This phenomenon has even been exploited for the analysis of fluorides. Domange (Ann. chim. 1937, I, 225) established the purities of samples of copper, chromium, nickel, cobalt and iron fluorides, prior to the determinations of their heats of formation, by this method. The conversion of potassium ferric fluoride into potassium fluoride and ferric oxide by heating in air was found in the experiments conducted with this complex fluoride and aluminium oxide. The end product recorded a loss in mass which corresponded to a complete conversion into potassium fluoride and ferric oxide. A study of this conversion was attempted in order to obtain some information on the more obvious chemical implications of such a conversion. These may be enumerated as follows.

1. Occurrence or absence of this conversion in an atmosphere of dry oxygen.

2. Possibility of the formation of ferric fluoride by decomposition of potassium ferric fluoride.
3. Chemical nature of the state in which fluorine is lost.
4. Reactivity of the fluorine or fluorine compound evolved.

Experimental procedure.

A sample of potassium ferric fluoride of the specimen detailed in the previous section was used. The apparatus is represented diagrammatically in fig. 1. The fluoride was contained in a platinum boat which was placed on an alundum base. A platinum wire of about four inches length was attached to this base and the other end of the wire joined to a fine nichrome wire that ended in a winch arrangement. The length of the platinum was introduced to prevent the oxidation of the nichrome wire by its presence in the hot region of the furnace tube. The introduction of a winch permitted the drawing of the boat into the hot region, in vacuum. Alternatively, the boat could be cooled within the furnace tube prior to its removal. The arrangement also enabled a desired run to be carried out without variation of the temperature of the furnace. The furnace and temperature measuring arrangements were the same as detailed in the experimental methods of the preceding section. A silica furnace tube was employed which had the advantage of providing conditions for the formation of silicon tetrafluoride in the event of

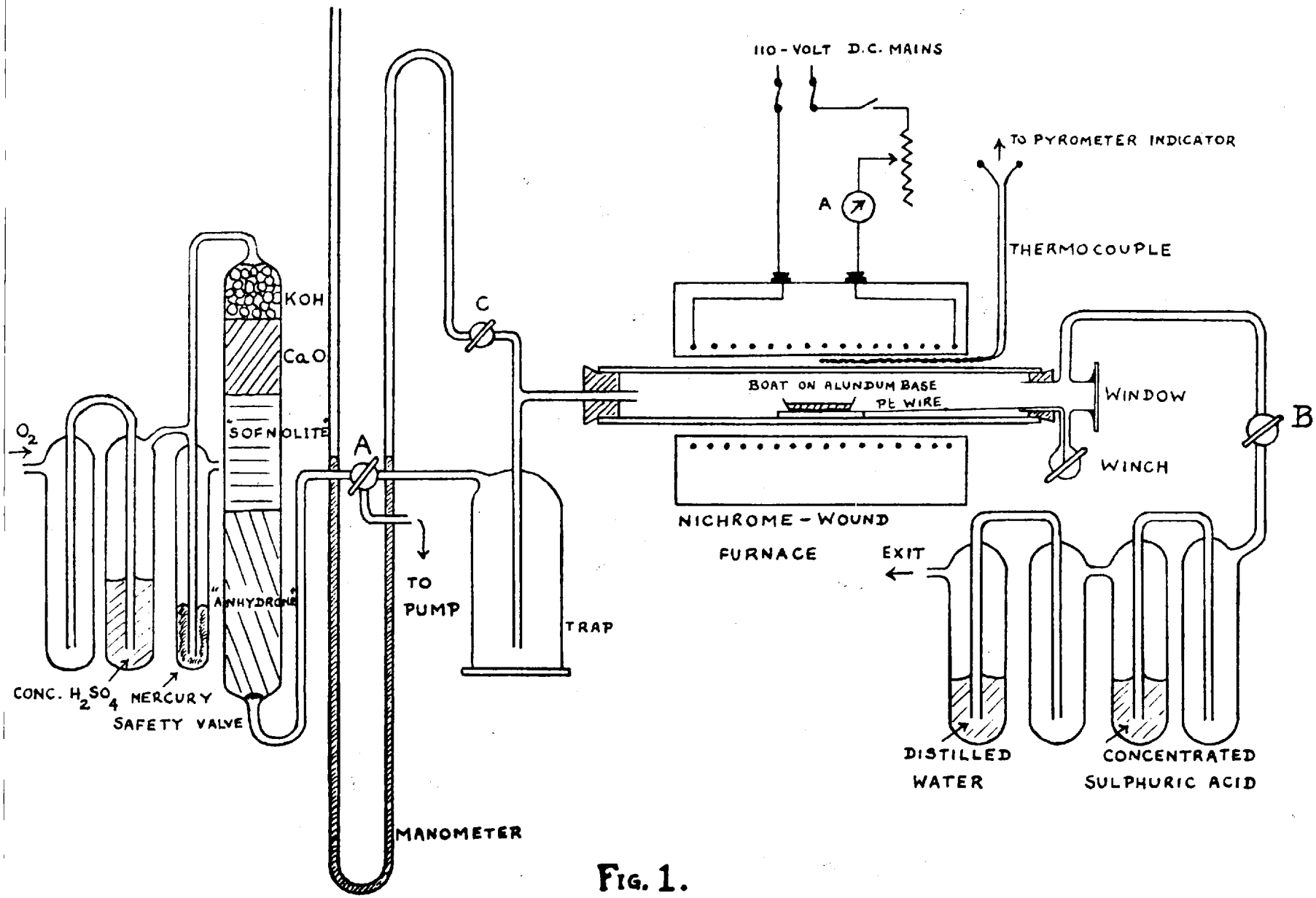

110-VOLT D.C. MAINS
TO PYROMETER INDICATOR
A
THERMOCOUPLE
KOH
CaO
"SOFNOLITE"
C
BOAT ON ALUNDUM BASE
PT WIRE
WINDOW
B
WINCH
O2
A
NICHROME-WOUND
FURNACE
EXIT
TO
PUMP
"ANHYDRONE"
TRAP
CONC. H2SO4
MERCURY
SAFETY VALVE
DISTILLED
WATER
CONCENTRATED
SULPHURIC ACID
MANOMETER

FIG. 1.

any liberation of reactive fluorine compounds. The provision of a window enabled the position of the boat to be seen. This was constructed by grinding an end of a ½" Pyrex tube with carborundum powder and attaching a microscope slide with picein wax. A two-way tap A enabled the furnace tube to be either pumped out by means of a rotary Hyvac pump or filled with oxygen. A manometer and trap were introduced as desirable auxiliaries. Oxygen from a cylinder was introduced through a trap and bubbler arrangement containing "Analar" sulphuric acid. The gas was then passed down a tower containing potassium hydroxide in pellet form, calcium oxide, "Sofnolite" and magnesium perchlorate ("Anhydrone"). This sequence of re-agents ensured that dry acid-free oxygen entered the furnace tube. The removal of possible traces of hydrogen was not considered essential as its occurrence in oxygen prepared from liquid air is only in traces. The exit gases from the furnace tube were bubbled through "Analar" sulphuric acid before being passed into any other liquid. This was considered essential for the maintenance of a perfectly dry atmosphere in the furnace tube. Suitable traps were provided to prevent the possibility of sucking back during pumping operations. A mercury safety valve was incorporated to divert the flow of oxygen in the event of the exit bubbler blocking up.

Experiments were conducted on the following lines. The sample of potassium ferric fluoride was dried for twenty four hours in an oven at 150° and a quantity transferred within the oven to a weighed platinum boat. The mass of the ferric fluoride was then determined by weighing the boat and contents in a glass tube provided with a bung. The tube was previously dried at 150° and the bung at 80°. This procedure was desirable to minimise the time of contact of the potassium ferric fluoride with the atmosphere. The procedure was however essential in the weighing of the end product as deliquescent potassium fluoride was one of the components. The boat was placed in the cooler region of the tube and the system evacuated with tap B closed. Use of the winch arrangement was made to draw the boat into the hot zone in vacuum. The evacuation of the tube was continued for about an hour. Tap A was then turned to cut off the pumping system and permit the entry of oxygen. This gas was admitted at the rate of about a bubble per second so as to ensure the entry of perfectly dry oxygen. Tap C was closed and B opened when the manometer registered atmospheric pressure. The oxygen was then passed at the rate of a bubble about every three seconds. The boat was drawn out of the hot region and allowed to cool in oxygen prior to its removal from the furnace tube.

Results and Discussion.

Potassium ferric fluoride was heated in vacuum for twenty four hours at 600°. No change in mass or colour was noticed. The stability of the compound at this temperature was thereby established. A sample of about five grams of the compound was then heated for twenty four hours in oxygen at 600°. This showed a loss in mass of 8.21%. Incomplete conversion was to be inferred as the theoretical percentage loss for complete conversion is 11.5%. An experiment performed at 650°, however, showed complete conversion in twenty four hours. The formation of potassium fluoride and ferric oxide was confirmed by X-ray analysis. Specimens for obtaining X-radiograms were made by filling and sealing off Lindemann capillaries from a heated plate. This procedure has been described in the previous section.

A series of conversions were then performed to assess the volatility of the potassium fluoride from the end product at 650°. It was found that a loss of 0.5 - 1% of the end product was registered for every further twenty four hours of heating at this temperature. This inability to obtain strictly constant weight, suggested the repetition of the investigations with sodium ferric fluoride.

Attempts to trace the fate of the fluorine lost by the potassium ferric fluoride were less successful. The exit

gases were at first only led through concentrated "Analar" sulphuric acid. The acid from a twenty four hour run at 630° was diluted with about five times its volume of distilled water in a platinum dish. Addition of a 5% solution of ammonium thiocyanate produced no colour. The absence of volatile ferric compounds was thereby established. Such compounds were however scarcely to be expected. Experiments were then performed in which the exit gases were bubbled through distilled water after being passed through sulphuric acid. This was for the detection of the formation of any silicon tetrafluoride. No formation of silica which would be expected by the hydrolysis of silicon tetrafluoride was detected. The liquid, in addition, failed to answer the potassium chloride and alcohol test for hydrofluo-silicic acid. The liquid from one of the experiments was however found to be faintly acidic to litmus. Detection of sulphuric acid spray with barium chloride was not possible. The addition of a solution of calcium chloride however gave a faint turbidity which indicated the presence of hydrofluoric acid. The reproducibility of this result was not possible with further experiments. The exit gases in all experiments possessed no smell.

No further attempts were made to identify the exit gases. It was evident that the loss of fluorine was in a most inactive form. Instead, analogous experiments were

conducted with the sodium ferric fluoride. This compound was found to be stable in vacuum at 600° . Complete conversion to sodium fluoride and ferric oxide resulted on heating in oxygen for twenty-four hours at 650° . Constant weight was attained thereafter, which established the inappreciable volatility of sodium fluoride under these conditions. The iron content of the end product was determined gravimetrically by the method adopted for the analysis of potassium ferric fluoride. These results confirmed the complete conversion of the sodium ferric fluoride to sodium fluoride and ferric oxide.

Analysis of end product.

Weight of product in g.	Fe_2O_3 (obtained)	Fe_2O_3 (theoretical)
0.2882	0.1102	0.1116
0.3098	0.1190	0.1202

The absence of the formation of any volatile iron compounds had therefore to be inferred. No silicon tetrafluoride was evolved at any stage which excluded the possibility of attack of the silica furnace tube. The Pyrex exit tube showed no signs of attack. This was also true of the alundum base which carried the boat. An indication of the formation of hydrofluoric acid when the exit gases

were passed into water was found in one experiment. The phenomenon was however not reproducible. Furthermore, the vigorous drying conditions adopted in the experimental procedure excluded the conversion by hydrolysis with water vapour. The conversion is apparently a slow process in that it was incomplete at 600° after twenty-four hours. The failure of identification of the exit gases cannot be explained by an inadequacy of the quantity of fluorine lost. A five gram sample of potassium ferric fluoride loses about 600 ml. of fluorine which should manifest itself in some form.

The only rational conclusion that could be drawn is that loss of fluorine occurs in the form of a relatively inert oxide of fluorine; probably fluorine monoxide (F_2O). The inert character of this gas has been established (Ruff and Menzel Z. anorg. u. allgem. Chem. 1931, 198, 39) . Its insolubility in water is exploited in its separation from fluorine (H. S. Booth, Inorganic Syntheses, McGraw Hill, New York, 1939, page 110). The kinetics of the decomposition of the gas into fluorine and oxygen at 280° have been studied by Koblitz and Schumacher (Z. physik. Chem. 1934, B 25, 292). The decomposition is apparently an appreciably slow process. It is probable, therefore, that under the conditions of experiment, the fluorine monoxide is swept away from the hot zone by the current of oxygen. Its chemical individ-

unity is thereby maintained. The conversion of potassium ferric fluoride to potassium fluoride and ferric oxide can be explained by this assumption. Though definite proof of the formation of fluorine monoxide is lacking, it appears to be the only explanation that fits the experimental results. Spectroscopic investigations of the exit gases should throw more light on this subject.

S E C T I O N 11

Investigations of the reactions between the alkali metal fluorides and some oxides of group II metals.

PART 1

General Introduction.

General Introduction.

The investigations of reactions between two or more inorganic compounds in the solid state has received considerable attention in the last three decades. The initial impetus for the detailed studies made in this field probably lies in the discovery of a "reaction temperature" by Hedvall and his school (Z. anorg. u. allgem. Chem. 1916, 96, 97 and 1916, 98, 97). Solid reactions were found to proceed at a considerable rate at a particular temperature which was subsequently termed the "reaction temperature". Determinations of the "reaction temperature" for various pairs of compounds led to the generalisation that when a basic oxide was employed as one of the reactants, the reaction temperature (a) remained approximately constant for the same oxide and (b) decreased with increasing basicity of the oxide. The generalisation was based on reactions involving the use of basic oxides such as barium, calcium and strontium oxides and

(a) sulphides, phosphides, carbides and silicides (Hedvall and Norstron. Z. anorg. u. allgem. Chem. 1926, 154, 1).

(b) halogenides (Hedvall, Carping, Lindekrantz and Nelson Z. anorg.u. allgem. Chem. 1931,197,399 .

(c) oxygen containing acid groups such as sulphates phosphates and silicates (Hedvall and Heuberger

(c) Z.anorg u. allgem. Chem. 1922, 122, 18; 1924, 140, 243) and

(d) spinels such as zinc and cobalt aluminates (Hedvall Svensk. Kem. Tid. 1925, 37, 172)

No satisfactory explanation has yet been given to explain these phenomena (Hedvall and Cohn Kolloid-Z. 1939, 88, 224). The "reaction temperature" is not however to be regarded as a fundamental characteristic of a particular oxide. It has been shown in recent years that the textural, energy and lattice states of the reactants play an important role in the ensuing reaction (Cohn Chem. Rev. 1948, 42, 527). Indeed, the reactions are so "structure - sensitive" that no theory has yet been propounded which successfully explains all the phenomena normally associated with solid reactions.

It is surprising that reactions between metal oxides and fluorides have not been investigated from any aspect. Hedvall, Carping, Lindekrants and Nelson (loc. cit) have described the reaction between thallium fluoride and barium oxide as proceeding according to the stoichiometric equation

$$BaO + 2TlF \longrightarrow BaF_2 + Tl_2O$$

Attempts at reaction with lead fluoride and the same oxide resulted in the melting of the mixture because of entectics. Ruff and Busch (Z. anorg. u. allgem. Chem.

1925, 144, 87) attempted to dissolve 0.1 - 0.2% by weight of magnesium oxide in secondary and ternary eutectics of various alkali metal and alkaline earth metal fluoride melts. This was for the purpose of trying to obtain a suitable electrolyte for the electrolytic production of magnesium.

The plan of research proposed, was to sinter suitable mixtures of oxides and fluorides and follow the courses of the reactions by X-ray methods. The alkali metal fluorides appeared to be most suitable for such investigations as their comparatively low melting points justified the probable occurrence of successful reactions in the temperature range 600° - 1000°. Their high degree of crystallinity was also an added advantage. Comparison of some of the structural constants of the alkali metal fluorides with corresponding values for magnesium, calcium, strontium and barium oxides, showed remarkable similarity in some instances. A comparison of some of the data for magnesium oxide and lithium fluoride, and calcium oxide and sodium fluoride, is given in the table following:-

	LiF	MgO	NaF	CaO
ionic radii (r)	Li^{+} 0.60A	Mg^{++} 0.65A	Na^{+} 0.95A	Ca^{++} 0.99A
$r_m^{++} - r_m^{+}$	0.05A		0.04A	
Lattice constants (a)	4.017 k x-units	4.202 k x-units	4.621 k x-units	4.797 k x-units
$a_{oxide} - a_{fluoride}$	0.185 kx-units		0.176 kx-units	
bond distance (M-X)	2.01A	2.10A	2.31A	2.40A
$(M-X)_{oxide} - (M-X)_{fluoride}$	0.09A		0.09A	

The oxides and fluorides, in addition, both possessed the same lattice type (face centred cubic). The experimental methods of investigation were designed to obtain information on the following aspects of the reactions.

1. Occurrence and conditions of occurrence of reactions.
2. Structural states of the reactants and resultants prior to and after completion of reaction.

The thermodynamical criterion governing such reactions is that reactions in systems composed entirely of solids must be exothermic. The occurrence of reaction had however to be first made certain and the identity of the products established before any quantitative interpretations could be made. It was anticipated that double fluorides of the type $A^{+}B^{++}F_3$ would be formed in some of these reactions.

The possible existence of mixed metal-oxygen-fluorine compounds was also not to be overlooked. The crystallographical conditions for the formation of any such compounds were of particular interest as investigations on these lines have not been previously reported. The existence of a few double fluorides has been reported in thermal analyses of alkali metal-alkaline earth metal fluoride systems. No crystallographical data were however available. Of the double fluorides relevant to the reactants chosen, only potassium magnesium fluoride and potassium zinc fluoride have been examined by X-ray methods. Potassium zinc fluoride has been indexed as cubic by Goldschmidt (Geochem. Vert. d. Elem. 1927, VIII). Van. Arkel has indexed potassium magnesium fluoride in a similar fashion (Physica 1925, 5, 167). The compounds have been listed as monoclinic with $a = b = c$ and $\beta = 90^{\circ}$ by Naray-Szabo (Muegyetemi Koslemenyek 1947, No.1, 36). No experimental data for this conclusion are however available.

The investigations of such reactions presented some difficulty in the preparation of suitable mixtures. The extreme deliquescence of potassium, rubidium, and caesium fluorides and the hygroscopic nature of magnesium, calcium, strontium and barium oxides, demanded a technique for preparing the mixtures in a dry state. A rigorous exclusion

of moisture was essential to exclude the possibility of water vapour functioning as an intermediary in the reaction process. The previously discussed phenomenon of the conversion of fluorides to oxides by ignition in air entailed the use of a controlled inert atmosphere in the investigation of these reactions. The various reactants had however to be prepared and subjected to chemical and X-ray analysis prior to the actual investigations of the reactions. The description of these preparations and analyses forms a convenient introduction to the subsequent details of the investigations of the reactions between metal oxides and fluorides.

PART II

Experimental methods.

Experimental methods.

(a) The preparation and chemical and X-ray analysis of reactants.

In view of the fact that the subsequent reactions were to be followed by X-ray methods, the purity and crystallinity of the reactants had to be made certain of, before the preparation of the mixtures. Some of the reactants were available in a pure form. Several had however to be prepared and their purities estimated chemically. Rubidium and caesium were available in the form of the carbonates which were employed for the preparation of the fluorides. The oxides were ignited in air or in a controlled atmosphere, before the preparation of standard mixtures.

The lattice constant values of the reactants had to be known accurately as a check on their values through the various phases of reaction was to be maintained. Reliable and concordant values had been recorded for several of the reactants by different workers. Some of the reactants, on the other hand, had been assigned values which differed from each other more than could be explained by experimental error. This was probably due to the small dimensions of the powder cameras used for the determinations. In such instances, the compounds were re-indexed by precision methods which are described in the next section. The

purity of the specimen employed was assessed chemically before any standard structural data were adopted. The standard interplanar spacings supplied by the A.S.T.M index and by Hanawalt, Rinn and Frevel (Ind. Eng. Chem. Anal. Ed. 1938, 10, 457) were often found to be incomplete. The description of the preparation of the reactants and their chemical and X-ray analyses therefore attempts to co-ordinate the existing crystallographical data and supply any missing information in addition to outlining the practical details involved. The procedure adopted is best detailed under the captions of the individual reactants.

(a) Alkali metal fluorides.

1. Lithium fluoride. Lithium fluoride supplied by British Drug Houses Ltd. was used. The fluoride was dried for six hours in vacuum at 600°. Appreciable sintering occurred at this temperature. The mass was therefore ground in agate and dried for twenty four hours at 150° before the preparation of mixtures. Accurate determination of the lattice constant gave a value of 4.017 ± 0.001 k X-units. This value is compatible with the more recent values reported for lithium fluoride. Values obtained by different workers are listed on the following page

"a" in k X-units	Reference
4.01728	Moeller (Z. Krist. 1937, 97, 170)
4.01807 ± 0.0000 4	Straumanis, Ievinš and Karlsons (Z. physik. Chem. 1939 B42, 143)
4.01736 ± 0.0000 4	Hutchinson and Johnston (J. Am. Chem. Soc. 1940, 62, 1163)

2. Sodium fluoride. Sodium fluoride supplied in the "pure" form by Hopkin and Williams Ltd. was used. The fluoride was ignited in platinum in an electric muffle furnace for six hours to ensure the use of a perfectly dry compound. Appreciable sintering occurred at this temperature. The mass was therefore ground in agate and dried for twenty four hours at 150° before any weighings were performed. Determination of the lattice constant gave a value of 4.621 ± 0.001 k X-units. This value is in keeping with several others obtained by different workers. The more recent values are tabulated below.

"a" in k X-units	Reference
4.620	Davey (Phys. Rev. 1923, 21, 143)
4.619 ± 0.002	Barth and Lund (Centr. Mineral Geol. 1927, A, 57)
4.62345 ± 0.0000 5	Straumanis, Ievinš and Karlsons (Z. physik. Chem. 1939, B42, 143)

3. Potassium fluoride:- Potassium fluoride in the form of an unspecified hydrate supplied by British Drug Houses Ltd., was employed. The fluoride was converted to the anhydrous form by heating in platinum over a steam bath. A crystalline mass resulted which was crushed to a fine powder with a nickel spatula on a porous plate maintained at about 100°. The fluoride was further dried by heating for twenty-four hours at 150°. It was stored in a glass container in an oven at the same temperature. The details for weighing the substance accurately and preparing specimens for X-ray analysis are given in the section on experimental methods. The determination of the lattice constant gave a value of a = 5.332 ± 0.001 k X-units. The compound was completely re-indexed as the confirmation of this value by similar values in the literature was insufficient. The only standard values reported for anhydrous potassium fluoride are listed below

"a" in k X-units	Reference.
5.328 ± 0.006	Davey (Phys. Rev. 1921 16, 102.)
5.332 ± 0.004	Broch, Oftedal and Pabst (Z. physik. Chem. 1929, B3, 209)
5.536 ± 0.010	Finch and Fordham (Proc. (Phys. Soc. 1936. 48, 85)

Broch, Oftedal and Pabst had used a camera of

of 5.189 cm. diameter and Finch and Fordham had employed electron diffraction methods. In view of the fact that small changes of the order of 0.005 k X-units were detected in the lattice constant of potassium fluoride when reacted with oxides, an accurate value for the constant of the pure compound had to be established. The complete crystallographic data for this substance are listed at the end of this section. Confirmation of the purity of the sample employed for obtaining X-radiograms was made by a gravimetric estimation of the potassium content in the form of the anhydrous sulphate. A purity of 99.1% was recorded.

Analysis of potassium fluoride.

Weight of K F in g.	Weight of K_2SO_4	% purity
0.2060	.3062	99.1
0.1890	.2810	99.1

4. Rubidium fluoride. Rubidium carbonate was supplied by Hopkin and Williams Ltd., The method of Eggeling and Meyer (Z. anorg. u. allgem. Chem. 1905, 46, 174) was employed for the preparation of the anhydrous fluoride.

A quantity of the carbonate was tipped into a platinum dish and treated with an excess of 40% hydrofluoric acid of "Analar" grade. The solution was evaporated to dryness on a sand bath and the solid crushed to a fine

powder on a porous tile maintained at about 100°. The fluoride was further dried in vacuum at 200°. This treatment was considered essential for the decomposition of any acid fluorides of the formulae RbF.HF and RbF.2HF which may have been present (Meyer and Taube Z. anorg u. allgem. Chem. 1936, 227, 337). It was found that the fluoride could be best stored in a glass tube in an oven at 150°. The glass showed no signs of being attacked by the fluoride when maintained at this temperature for several months.

The small quantities of the fluoride available did not permit the assessment of its purity by chemical methods. An X-radiogram of a sample of rubidium fluoride permitted the indexing of all the lines on the assumption of a face-centred cubic structure. The only previous determination of the lattice constant value is by Wyckoff and Posnjak (J. Wash. Acad. Sci. 1923, 11, 393) who claim a value of a = 5.63 ± X-units. The determination of all possible powder data was in this case imperative. No standard interplanar spacings of rubidium fluoride are available in the A.S.T.M. index. The complete crystallographical data are listed at the end of this section. A value of a = 5.620 ± 0.001 ± X-units was obtained for the lattice constant.

5. Caesium fluoride. Caesium carbonate supplied by Hopkin and Williams Ltd., was employed for the preparation of the fluoride. The method of preparation

described by Chabrie (Compt. rend. 1901, 132, 680) was adopted. This consisted of dissolving the carbonate in an excess of "Analar" hydrofluoric acid and evaporating the solution to dryness. The fluoride was dried and stored in the manner which has been detailed for rubidium fluoride. An X-radiogram of the compound permitted the indexing of all the lines on the assumption of a face-centred cubic structure. Previous determinations of the lattice constant of this substance left much to be desired by way of accuracy. The results obtained by previous workers are tabulated below.

"a" in k X-units	Reference
6.03	Wyckoff (J. Wash Acad.Sci. 1921, 11, 429)
6.008 ± 0.006	Davey (Phys. Rev. 1923, 21, 143)
6.00	Private communication to Strukturbericht 1913-28,1, 107)

A lattice constant value of $a = 6.002 \pm 0.001$ k X-units was obtained. No standard interplanar spacings are available for this substance in the A.S.T.M. index. The complete crystallographical data are listed at the end of this section.

(b) Group II metal oxides.

1. Magnesium oxide. "Analar" grade magnesium oxide was employed. Samples of the oxide were ignited to constant

weight at 900° in platinum in an electric muffle furnace prior to the making of the mixtures. A lattice constant value of a = 4.202 ± 0.001 k X-units was obtained for this compound. This value is identical with that which is normally attributed to magnesium oxide.

2. Calcium oxide. "Analar" grade calcium carbonate was employed for the preparation of the oxide. The oxide was obtained by calcination of the carbonate at 900° in platinum in an electric muffle furnace. The completion of the process was established on the attainment of constant weight after about six hours under these conditions. A value of a = 4.797 ± 0.001 k X-units was obtained for the lattice constant of the oxide. This is identical to the value normally associated with calcium oxide (Harrington, Am. J. Sci. 1927, 13, 467).

3. Strontium oxide. Strontium carbonate supplied in the form "precipitated with ammonia" by Hopkin and Williams Ltd., was employed for the preparation of the oxide. Use was made of the fact that the dissociation pressure of strontium carbonate reaches one atmosphere at 1155° (Brill Z. anorg. u. allgem. Chem. 1905, 42, 281 and Johnston, J. Am. Chem. Soc. 1908, 30, 1357). The decomposition has however been shown to be rapid only when a temperature of 1295° is reached (Hedvall Z. anorg. u. allgem. Chem.1916, 98, 52).

The procedure adopted for the preparation of the

oxide may be described as follows. A sample of the carbonate was ground in agate and dried for about a day in an oven at 150°. Weighed portions were then transferred to magnesia boats (Triangle M) and then placed in a mullite (Triangle H 5) tube of a platinum-rhodium-wound furnace. The furnace tube was connected through a trap and manometer to a rotary Hyvac pump. The temperature of the furnace was raised to 1100° in about three hours and to 1200° in another hour. Temperature control was by means of a Sunvic control unit and measurements were made by means of a butt-welded platinum and platinum-rhodium alloy thermocouple. A continuous state of evacuation was maintained throughout these heating operations. It was found that at 1200° the manometer showed a pressure of 2 mm. The temperature was raised to 1280° over a period of half an hour. A vigorous evolution of carbon dioxide occurred in this period and the manometer reading showed a pressure of 2 cm. The evolution was complete at the end of about twenty minutes, as shown by the manometer. The temperature of the furnace was however raised to 1300° and maintained in this condition for about half an hour. A temperature of 1400° was then maintained for about two hours. The furnace was cooled in a state of evacuation and the boats removed. It was found that the oxide was present in an easily powdered compact mass. The loss in mass indicated a 98% conversion to the oxide.

Analysis of strontium oxide.

The purity of the strontium oxide was determined by the estimation of the strontium content as anhydrous strontium sulphate, gravimetrically. A sample of the oxide was dried for four hours at 150° and about 0.2 g. tipped into a 600 ml. beaker. Dissolution of the oxide in about 30 ml. of N-HCl solution followed. The procedure adopted for the precipitation and weighing of the strontium as the sulphate was the same as that described by Vogel (A. I. Vogel, Textbook of Quantitative Inorganic Analysis, Longmans, London, 1947, page 364). The oxide was found to be 99.2% pure.

Analysis of strontium oxide.

Weight of SrO in g.	Weight of $SrSO_4$ in g.	% purity.
0.2986	0.5252	99.2
0.2770	0.4870	99.2

Determination of the lattice constant of strontium oxide gave a value of $a = 5.149 \pm 0.001$ k X-units. This value is slightly higher than those previously reported for the same substance. The values available in the literature are tabulated as follows

"a" in k X-units	Reference
5.143	Gerlach (Z. Physik. 1922, 9, 184)
5.146 ± 0.004	Goldschmidt (Geochem. Vert. d. Elem. 1927, VIII)
5.073 ± 0.010	Wilson (Phys. Rev. 1928, 31, 1117)
5.144	Burgess (Z. Physik. 1933, 80, 352)
5.146	R. Glocker, Material-prufung mit Röntgenstrahlen, Berlin 1936, page 160.
5.145	Hubener and Wagener (Z. tech. Physik. 1942, 23, 1)

The high-angle lines of the X-radiogram were extremely sharp and their intensities ideally suited for measurement. Chemical analysis had already established the purity of the compound. There was no reason, therefore, for not adopting the value obtained, as a standard in subsequent X-ray work.

4. Barium oxide. A sample of barium oxide supplied by Hopkin and Williams Ltd. was employed for the preparation of mixtures. No attempt was made to ignite this oxide for obtaining it in a crystalline form on account of the formation of higher oxides. The sample was therefore dried for two hours in an oven at 150° before the preparation of any mixtures. An X-radiogram obtained with a specimen of this oxide was of poorer quality than those obtained with the oxides of magnesium, calcium and strontium. A

determination of the lattice constant gave a value of $a = 5.528 \pm 0.004$ k X-units which is in keeping with the published values tabulated below

"a" in k X-units	Reference
5.531 ± 0.005	Goldschmidt (Geochem. Vert. d. Elem. 1927, VIII)
5.523 ± 0.003	Burgess (Z. Physik. 1933, 80, 352)
5.53	R. Glocker, Material-prufung mit Rontgenstrahlen, Berlin, 1936, page 160.
5.52	Ihbener and Wagener (Z. tech. Physik. 1942, 23, 1)

5. Zinc oxide. "Analar" grade zinc oxide was used in the preparation of suitable mixtures. The oxide was ignited in an alumina (Triangle RR) boat to constant weight at 900° in an electric muffle furnace. A determination of its lattice constant value was not necessary in the circumstances of experiment. A check was maintained on the constancy of the Bragg angle values calculated from X-radiograms of reaction products containing zinc oxide in excess. There were no instances recorded of deviation from values obtained for the pure component which therefore did not justify the re-determination of the lattice constant. In addition, several determinations of the cell constants have been

recently reported e.g. a = 3.24265 ± 0.00001; c = 5.1948 ± 0.00003; c/a = 1.60200 (Burn, Proc. Phys. Soc. 1935, 47, 838).

(c) Group II metal fluorides

1. Magnesium fluoride. A sample of magnesium fluoride supplied by Hopkin and Williams Ltd. was used in a few preliminary experiments. No conclusions were however based on these experiments as a survey of the values published for the cell constants of magnesium fluoride showed that only one attempt at satisfactory indexing of the compound had been made. It was therefore decided to prepare a pure specimen of the compound, assess its purity chemically and attempt to re-index the crystallographic data obtained from an X-radiogram. Samples of the compound which had been investigated on these lines could then be utilised for the stoichiometric synthesis of double fluorides.

Preparation of magnesium fluoride.

Magnesium fluoride was prepared by the method given by Cossa (Gazz. chim. ital. 1877, 7, 212). Magnesium carbonate supplied in the "pure" form by Hopkin and Williams Ltd. was treated with an excess of "Analar" hydrofluoric acid in a platinum dish. The solution was maintained at a temperature of about 80° for an hour on a sand bath and evaporated to dryness by suitably raising the temperature. The fluoride was further dried for twenty four hours in an oven at 150°.

Analysis of magnesium fluoride. The method adopted was to decompose the fluoride by the action of concentrated sulphuric acid and determine the magnesium content, gravimetrically, by conversion of the sulphate to the pyrophosphate. The decomposition was carried out with "Analar" grade concentrated sulphuric acid in platinum. It was found that a considerable excess of sulphuric acid was required for a quantitative decomponition of the fluoride. The acid solution was therefore neutralised with 1:1 ammonia, before the precipitation of the magnesium as magnesium ammonium phosphate was attempted. The procedure given by Vogel (A.I. Vogel, Textbook of Quantitative Inorganic Analysis, Longmans, London, 1947, page 494) was adopted. Electrical stirring was employed during the actual precipitation with the ammonium phosphate solution. Stirring was continued for about an hour after the addition of the reagent. It was found that under these conditions the magnesium ammonium phosphate separated as a fine microcrystalline mass which was ideally suited for subsequent filtration. Analysis by this method gave a purity of 99.8% to the fluoride.

Analysis of magnesium fluoride

Wt. of MgF_2 in g.	Wt. of $Mg_2P_2O_7$ in g.	% purity
0.2480	0.4420	99.8
0.2336	0.4164	99.8

Determination of cell constants.

A tetragonal (rutile) structure has been ascribed to magnesium fluoride by Ferrari (Atti III Congresso naz. chim. pura applicata 1930, 450) with cell constants a = 4.66 and c = 3.08 k X-units. This appears to be the only value available in the literature. The complete indexing of an X-radiogram of a specimen of magnesium fluoride was therefore attempted. The details of the methods employed are described in the section on X-ray techniques. It was found that magnesium fluoride was tetragonal with a = 4.61 ; c = 3.04 k X-units and c/a = 0.660. Inspection of the Miller[1] indices[3] showed that reflections of the types (a) h 0 l with h + l odd (b) 0 k l with k + l odd and (c) 0 0 l with l odd were absent. These absent reflections were characteristic of the space group $P4_2/mnm$ (Internationale Tabellen zur Bestimmung von Kristallstrukturen, Borntraeger, Berlin, 1935) which is that of rutile (TiO_2) as well. The tetragonal (rutile) structure of magnesium fluoride was thereby confirmed and a more accurate determination of the cell constants made possible. The complete crystallographical data are listed at the end of this section.

2. Calcium fluoride. A sample of "pure" calcium fluoride supplied by Hopkin and Williams Ltd. was employed for the preparation of mixtures. The fluoride was ignited for six hours at 900° in platinum in an electric muffle furnace. The product was found to have sintered heavily. The mass

was therefore ground in agate and dried for at least twenty four hours at 150° in an oven, prior to weighing suitable quantities for mixtures.

The crystallographical data obtained from an X-radiogram of calcium fluoride, showed that the substance possessed a cubic structure with a = 5.451 ± 0.001 k X-units. This value is in agreement with numerous similar values published for pure calcium fluoride in the literature. There were no unexplained lines on the X-radiogram which would have indicated the presence of any appreciable amounts of impurities.

3. Strontium fluoride. The method of Berzelius (Pogg. Annalen 1824, 1, 20) was employed for the preparation of a specimen of strontium fluoride. Strontium oxide which had been prepared and analysed as described previously was dissolved in an excess of "Analar" grade hydrofluoric acid contained in a platinum dish. The resulting solution was evaporated to dryness on a sand bath. The anhydrous fluoride was ground in agate and ignited at 700° for thirty minutes in an alumina boat (Triangle RR). This treatment was considered necessary for obtaining the fluoride in a crystalline condition. The ignition in air at 700° excluded the possibility of any conversion to the oxide in view of the work of Duval (Anal. Chim. Acta. 1947, 1, 347) who showed that no detectable conversion occurs at 950°.

Only twelve interplanar spacings for strontium fluoride have been listed by Hanawalt, Rinn and Frevel (loc. cit.). A re-determination of the relevant powder data for this substance was therefore considered essential. For this purpose, establishment of the chemical purity of the sample to be subjected to X-ray diffraction was considered necessary. The strontium fluoride had however to be converted into a soluble form for any gravimetric determination of the strontium content to be attempted. Decomposition with sulphuric acid was not applicable in this instance, because of the insolubility of strontium sulphate. Experiments with other acids eventually showed that complete dissolution is possible by warming with a mixture of equal volumes of concentrated "Analar" nitric acid and distilled water. Determination of the strontium content of such a solution was made in the manner previously detailed for the analysis of strontium oxide. A purity of 99.5% was obtained on the results of this procedure.

Analysis of strontium fluoride.

Wt. of SrF_2 in g.	Wt. of $SrSO_4$ in g.	% purity
0.3410	0.4862	99.5
0.3322	0.4834	99.5

The data obtained from an X-radiogram of strontium fluoride showed that the substance was cubic with a = 5.785 ± 0.001 k X-units. The lattice constant value obtained for this substance is in agreement with values published for strontium fluoride by other workers. The values cited in the literature are tabulated below.

"a" in k X-units	Reference
5.86	van Arkel (Physica 1924, 4, 286)
5.784 ± 0.003	Goldschmidt (Geochem. Vert. d. Elem. 1927 VIII).
5.781	Rumpf (Z. physik.Chem. 1930, B7, 148)
5.782	Ketelaar and Willems (Rec. trav. chim. 1937, 56, 29)

The complete crystallographical data for this substance are tabulated at the end of this section.

4. Barium fluoride. The method of Berzelius (loc. cit.) was adopted in the preparation of a sample of barium fluoride. "Analar" grade barium carbonate was treated with an excess of "Analar" hydrofluoric acid in a platinum dish. The solution of barium fluoride was evaporated to dryness on a sand bath and the anhydrous salt ignited in an alumina (Triangle RR) boat for thirty minutes at 600°. The sample was dried for at least twenty four hours in an oven at 150° before any mixtures were prepared.

The data obtained from an X-radiogram of barium fluoride showed that the substance was cubic with a = 6.183 $\pm$ 0.001 k X-units. This value is in agreement with other values published in the literature, which are listed below.

"a" in k X-units	Reference
6.20	Davey (Phys. Rev. 1922, 19, 248)
6.187 $\pm$ 0.005	Goldschmidt (Geochem. Vert. d. Elem. 1927, VIII)
6.184 $\pm$ 0.003	Brook, Oftedal and Pabst (Z. phys. Chem. 1929, B3, 209)

5. Zinc fluoride. The method of Marignac (Ann. chim. et. phys. 1860, (3), 60, 305) was employed for the preparation of a sample of zinc fluoride. "Analar" grade zinc oxide was treated with an excess of "Analar" hydrofluoric acid in platinum and the solution evaporated to dryness on a sand bath. The anhydrous salt was dried for a further period of twenty four hours in an oven at 150°.

The only attempt to index an X-radiogram of zinc fluoride which is reported in the literature is that of Ferrari (Rend. accad. nazl. Lincei. 1926, 3, 328) who postulates a tetragonal (rutile-type) structure with cell constants a = 4.715 $\pm$ 0.005; c = 3.131 k X-units and c/a = 0.664 $\pm$ 0.01. A possible re-indexing of the

system by the precision methods available was therefore considered desirable. The chemical purity of the specimen of zinc fluoride was estimated prior to obtaining an X-radiogram.

The fluoride was decomposed quantitatively by heating with an excess of "Analar" grade concentrated sulphuric acid in a platinum crucible on a sand bath. The zinc sulphate formed was transferred to a 600 ml. beaker and the zinc content estimated gravimetrically by the pyrophosphate method. The procedure described by Vogel (loc. cit.) was adopted. A purity of 99.2% was established on the results of this analysis.

Analysis of zinc fluoride

Wt. of ZnF_2 in g.	Wt. of $Zn_2P_2O_7$	% purity
0.2072	0.3028	99.2
0.2350	0.3440	99.3

Determination of the cell constants from the data obtained from an X-radiogram of zinc fluoride showed that the substance was tetragonal with $a = 4.69_1$; $c = 3.12_3$ K X-units and $c/a = 0.666$. Characteristic absent reflections of the type described in the X-ray data for magnesium fluoride were found. The rutile-type structure was thereby confirmed.

The complete crystallographic data are listed at the end of this section.

(d) Miscellaneous oxides.

1. Ferric oxide. Ferric oxide was prepared by adding a sample of very pure iron powder (Carbonyl Iron, Grade C, supplied by Mond Nickel Co.) to an excess of hot concentrated "Analar" grade nitric acid and evaporating the solution on a sand bath to dryness. The oxide was obtained by ignition to constant weight in platinum at 900° in an electric muffle furnace. The method of preparation made the presence of any appreciable quantities of impurities most improbable.

2. Zirconium dioxide. A sample of zirconium dioxide supplied by Hopkin and Williams Ltd. was employed. The oxide was ignited in platinum to constant weight at 900° before the preparation of any mixtures.

X-ray data of anhydrous potassium fluoride Copper K_α radiation.

I	θ	$\sin^2\theta$	h k l	Σh^2	increment	a	d
3	14.571	0.06327	111	3	0.02109		3.06
10	16.846	0.08399	200	4	0.02100		2.69
8	24.185	0.16785	220	8	0.02098		1.878
4	28.690	0.23050	311	11	0.02095		1.603
5	30.076	0.25114	222	12	0.02093		1.535
3	35.350	0.33474	400	16	0.02092		1.330
1	39.027	0.39651	331	19	0.02087		1.222
α_1 7	40.233	0.41724	420	20	0.020862	5.3221	1.187
α_2 3	40.323						
α_1 5	45.024	0.50016	422	24	0.020840	5.3249	1.087
α_2 2	45.265						
α_1 2	48.611	0.56284	333 511	27	0.020846	5.3240	1.025
α_2 1	48.746						
α_1 3	54.713	0.66628	440	32	0.020821	5.3273	0.942
α_2 2	54.849						
α_1 3	58.586	0.72839	531	35	0.020811	5.3286	0.901
α_2 2	58.797						
α_1 4	59.927	0.74890	442 600	36	0.020803	5.3296	0.888
α_2 2	60.183						
α_1 4	65.804	0.83203	620	40	0.020801	5.3299	0.843
α_2 2	66.120						

I	θ	$\sin^2\theta$	h k l	Σh^2	increment	a	d
α_1 2	71.017	0.89414	533	43	0.020794	5.3306	0.813
α_2 1	71.379						
α_1 4	73.006	0.91457	622	44	0.020786	5.3316	0.804
α_2 2	73.394						

Extrapolated value a = 5.332 ± 0.001 kX - units.

X-ray data of anhydrous rubidium fluoride Copper K radiation.

I	θ	$\sin^2\theta$	h k l	Σh^2	increment	a	d
7	13.790	0.05687	111	3	0.01896		3.22
10	15.962	0.07561	200	4	0.01890		2.80
8	22.842	0.15070	220	8	0.01884		1.981
8	27.066	0.20695	311	11	0.01881		1.691
6	28.379	0.22596	222	12	0.01883		1.619
6	33.282	0.30120	400	16	0.01882		1.402
4	36.707	0.35724	331	19	0.01881		1.287
7	37.823	0.37600	420	20	0.01880		1.254
α_1 5	42.153	0.45040	422	24	0.018767	5.6114	1.146
α_2 2	42.244						
α_1 3	45.382	0.50675	333 / 511	27	0.018767	5.6114	1.080
α_2 2	45.472						
α_1 2	50.783	0.60034	440	32	0.018761	5.6123	0.992
α_2 1	50.873						
α_1 3	54.232	0.63678	531	35	0.018765	5.6117	0.949
α_2 2	54.253						
α_1 3	55.249	0.67508	442 / 600	36	0.018752	5.6136	0.936
α_2 2	55.701						
α_1 4	59.986	0.74993	620	40	0.018748	5.6141	0.888
α_2 2	60.167						
α_1 2	63.843	0.80572	533	43	0.018738	5.6156	0.856
α_2 1	64.044						

X-ray data of anhydrous rubidium fluoride Copper K radiation.

	I	θ	$\sin^2\theta$	hkl	Σh^2	increment	a	d
α_1	3	65.206	0.82422	622	44	0.018732	5.6165	0.847
α_2	2	65.493						
α_1	2	71.452	0.89885	444	48	0.018726	5.6174	0.811
α_2	1	71.799						
α_1	3	77.709	0.95463	551 711	51	0.018718	5.6186	0.787
α_2	2	78.410						

Extrapolated value a = 5.620 ± 0.001 kX-units.

X-ray data of anhydrous caesium fluoride. Copper K radiation.

I	θ	$\sin^2\theta$	hkl	Σh^2	increment	a	d
8	12.930	0.05018	111	3	0.01670		3.44
10	14.921	0.06628	200	4	0.01657		2.99
9	21.333	0.13238	220	8	0.01655		2.11
8	25.256	0.18202	311	11	0.01655		1.803
6	26.463	0.19853	222	12	0.01654		1.727
3	30.928	0.26423	400	16	0.01651		1.496
5	34.067	0.31370	331	19	0.01650		1.374
6	35.062	0.32997	420	20	0.01650		1.339
6	39.020	0.39632	422	24	0.01651		1.222
6	41.867	0.44534	333 511	27	0.01650		1.153
2	46.574	0.52745	440	32	0.01645		1.059
α_1 3	49.380	0.57622	531	35	0.016463	5.9910	1.013
α_2 2	49.470						
α_1 2	50.330	0.59255	442 600	36	0.016451	5.9931	0.999
α_2 1	50.496						
α_1 3	54.193	0.65769	620	40	0.016445	5.9943	0.948
α_2 2	54.359						
α_1 2	57.240	0.70720	533	43	0.016447	5.9938	0.914
α_2 1	57.391						
α_1 3	58.236	0.72300	622	44	0.016432	5.9967	0.904
α_2 2	58.447						

X-ray data of anhydrous caesium fluoride. Copper K radiation.

I	θ	$\sin^2\theta$	h k l	Σh^2	increment	a	d
α_1 2	62.650	0.78893	444	48	0.016437	5.9959	0.865
α_2 1	62.857						
α_1 4	66.262	0.83732	551 711	51	0.016430	5.9970	0.840
α_2 2	66.564						
α_1 2	67.590	0.85468	640	52	0.016436	5.9959	0.832
α_2 1	67.892						
α_1 2	73.536	0.91966	642	56	0.016423	5.9985	0.802
α_2 1	73.972						
α_1 2	79.735	0.99299	553 731	59	0.016411	6.0005	0.781
α_2 1	80.489						

Extrapolated value a = 6.002 ± 0.001 kX - units.

X-ray data of anhydrous magnesium fluoride. Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
10	13.629	0.0555	0.0556	110	3.26
2	17.609	0.0915	0.0916	101	2.54
10	20.217	0.1194	0.1194	111	2.23
5	21.891	0.1390	0.1390	210	2.06
10	26.776	0.2030	0.2028	211	1.708
5	28.132	0.2223	0.2223	220	1.632
5	30.364	0.2556	0.2552	002	1.522
1	31.856	0.2786	0.2779	310	1.457
7	34.103	0.3143	0.3139	301	1.372
3	35.792	0.3422	0.3417	311	1.315
2	38.912	0.3945	0.3942	212	1.225
2	41.838	0.4450	0.4446	400	1.153
4	43.740	0.4780	0.4775	222	1.113
3	45.063	0.5010	0.5002	330	1.087
2	47.083	0.5363	0.5362	411	1.050
1	48.233	0.5562	0.5558	420	1.032
1	51.953	0.6202	0.6196	421	0.977
1	52.541	0.6301	0.6298	113	0.969
1	56.823	0.7005	0.6998	402	0.919
3	57.652	0.7137	0.7132	213	0.911
1	58.542	0.7276	0.7276	412	0.902

X-ray data of anhydrous magnesium fluoride. Copper K_α radiation.

	I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
	2	60.532	0.7580	0.7585	432 501	0.884
	α_1 2	64.255	0.8113	0.8110	422	0.854
	α_2 1	64.497				
	α_1 4	65.190	0.8240	0.8243	303	0.847
	α_2 2	65.492				
	α_1 5	68.854	0.8698	0.8697	521	0.824
	α_2 3	69.216				
diffuse	α_1 3	81.370	0.9775	0.9777	512	0.778
	α_2 2	82.272				

Lattice constants:- $a = 4.61_1$ kX - units

$c = 3.04_3$ kX - units

$c/a = 0.660$

X-ray data of anhydrous strontium fluoride. Copper K_α radiation.

	I	θ	$\sin^2\theta$	hkl	Σh^2	increment	a	d
	10	13.270	0.05265	111	3	0.01755		3.35
	3	15.368	0.07019	200	4	0.01755		2.84
	10	22.031	0.14073	220	8	0.01759		2.05
	8	26.132	0.19401	311	11	0.01764		1.747
	1	27.415	0.21197	222	12	0.01767		1.671
	4	32.141	0.28305	400	16	0.01769		1.446
	5	35.386	0.33543	331	19	0.01770		1.328
	3	36.473	0.35331	420	20	0.01767		1.294
	6	40.625	0.42393	422	24	0.01767		1.181
	6	43.705	0.47737	511 333	27	0.01768		1.114
	2	48.749	0.56528	440	32	0.01767		1.023
	4	51.842	0.61831	531	35	0.01767		0.978
	2	52.883	0.63598	442 600	36	0.01767		0.965
α_1	3	57.141	0.70560	620	40	0.017640	5.7880	0.915
α_2	2	57.322						
α_1	3	60.613	0.75915	533	43	0.017655	5.7855	0.882
α_2	2	60.794						
α_1	2	61.760	0.77609	622	44	0.017639	5.7881	0.873
α_2	1	61.972						
α_1	2	66.968	0.84687	444	48	0.017643	5.7875	0.835
α_2	1	67.240						

X-ray data of anhydrous strontium fluoride. Cu K$_\alpha$ radiation.

	I	θ	$\sin^2\theta$	h k l	Σh^2	Increment	a	d
α_1	5	71.558	0.89996	{551 / 711	51	0.017646	5.7869	0.810
α_2	3	71.982						
α_1	3	73.339	0.91780	640	52	0.017650	5.7864	0.802
α_2	2	73.762						

Extrapolated value a = 5.786 ± 0.001 kx - units.

X-ray data of anhydrous zinc fluoride. Copper K radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
10	13.383	0.0535	0.0537	110	3.32
8	17.196	0.0874	0.0875	101	2.60
3	19.110	0.1072	0.1074	200	2.35
6	19.743	0.1140	0.1143	111	2.28
3	21.506	0.1344	0.1343	210	2.10
10	26.224	0.1951	0.1949	211	1.742
6	27.625	0.2150	0.2158	220	1.659
4	28.449	0.2418	0.2417	300	1.565
3	31.227	0.2689	0.2685	310	1.484
4	32.950	0.2950	0.2951	112	1.414
8	33.367	0.3025	0.3023	301	1.399
2	37.869	0.3771	0.3767	212	1.253
4	39.618	0.4100	0.4097	321	1.202
2	40.969	0.4299	0.4296	400	1.173
5	42.546	0.4573	0.4572	222	1.138
3	44.060	0.4836	0.4833	330	1.107
4	45.635	0.5112	0.5109	312	1.076
4	46.027	0.5179	0.5171	411	1.071
3	47.152	0.5375	0.5370	420	1.050
2	49.162	0.5723	0.5723	103	1.017
α_1 4	55.509	0.6794	0.6797	213	0.933
α_2 2	55.692				

X-ray data of anhydrous zinc fluoride. Copper K radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
α_1 3	56.697	0.6986	0.6981	510	0.920
α_2 2	56.878				
α_1 4	58.822	0.7319	0.7319	501	0.898
α_2 2	59.063				
α_1 4	61.942	0.7787	0.7787	520	0.871
α_2 2	62.213				
α_1 6	66.358	0.8392	0.8393	521	0.839
α_2 3	66.689				
α_1 2	67.970	0.8592	0.8592	440	0.829
α_2 1	68.302				
α_1 3	70.996	0.8940	0.8945	323	0.813
α_2 2	71.391				
α_1 2	72.808	0.9127	0.9129	530	0.805
α_2 1	73.260				
α_1 6	75.870	0.9404	0.9405	512	0.793
α_2 4	76.480				
α_1 3	79.454	0.9665	0.9666	600	0.782
α_2 2	80.268				

Lattice constants $a = 4.69_1$ kX - units.

$c = 3.12_3$ kX - units

$c/a = 0.666$

(b) Experimental techniques employed in:-

1. Reactions in the temperature range 600° - 1300°.

The plan of research adopted for the investigation of the reactions between metal oxides and fluorides was to subject suitable mixtures of oxides and fluorides to various conditions of time and temperature and follow the course and extent of the individual reactions by X-ray methods. The conditions of temperature required the use of the most appropriate types of furnaces. These were of the type normally employed in high temperature research projects. Other necessities, such as the choice of suitable refractories, were complicated by the inherent properties of fluoride vapours at high temperatures. The conversion of some of the fluorides to oxides in air at these temperatures demanded the use of either a vacuum or a suitable inert atmosphere for the conduction of the experiments. Deliquescence, in the case of potassium, rubidium and caesium fluorides complicated the weighing of the constituents and the subsequent preparation of the mixtures. The same disadvantage was present in obtaining suitable specimens for X-ray diffraction methods. The apparatus and methods eventually employed are best described under appropriate headings.

(a) Apparatus employed.

1. Furnaces and temperature measurements.

Four types of furnaces were employed in the

investigation of the reactions.

1. A Gallenkamp nichrome-wound furnace with a 2' x 1½" "sand finished" silica tube was used for experiments in vacuum. Temperature measurement was by a chromel-alumel thermocouple connected to a Siemens pyrometer indicator. The furnace was run directly off the 110-volt D.C.mains. The current passing through the windings was controlled by a suitable variable resistance. An ammeter and subsidiary fuses were introduced as useful auxiliaries for the maintenance of temperatures in the range 600° - 900°. Variations at a particular temperature in this range were never more than ± 7° over a period of several days.

11. A Towers nichrome wound furnace carrying a 2' x 1" Δ H 5 mullite tube was used in the experiments requiring an atmosphere of nitrogen. The temperature was measured by means of a chromel-alumel thermocouple connected to a Siemens pyrometer indicator. A sensitive 50 ohm variable resistance was used for controlling the temperature of the furnace to ± 5° in the range 600° - 1000°. The furnace was run off the 220-volt D.C. mains through a resistance and ammeter.

111. A Johnson Matthey platinum-rhodium-wound furnace carrying a 2' x 1" Δ H 5 mullite tube was used in the experiments in the temperature range 1000° - 1300°. Temperature control was by means of a "Sunvic" unit. A platinum and platinum-rhodium alloy (13% rhodium) thermocouple

with auto-compensated leads and a Cambridge pyrometer indicator were employed for the measurements of the temperature.

IV. A Johnson Matthey platinum-rhodium-wound furnace carrying a 3' x 1½" ΔR 5 mullite tube was used in the preparation of a specimen of strontium oxide. The details of this furnace arrangement are given in the description of the preparation of a sample of strontium oxide.

2. Refractories. Mullite furnace tubes were found to withstand attack of fluoride vapours very satisfactorily in the temperature range 600° - 1000°. Attack of the tubes was however detected above 1000° when zirconium tetrafluoride and ferric fluoride were evolved as reaction products. Silica tubes showed softening of the inner surface on prolonged contact with alkali metal fluoride vapours in the temperature range 600° - 900°. The consequent tendency of boats to fuse to the tube was avoided by lining the tube with asbestos paper.

Platinum boats were employed wherever the chemical nature of the reactants permitted their safe use. Alumina (ΔRR) boats were however employed in reactions with strontium, barium and zinc fluorides. No attack of the boats was detectable over periods of heating which often extended for several days. Magnesia (ΔM) boats were found most suitable for investigations of the reactions between the alkali metal fluorides and strontium and barium oxides. Their use was found possible as a result of the

comparatively slow reactions which were previously found to occur between magnesium oxide and the same fluorides. Nickel boats were badly attacked by barium oxide at 650°. Silica boats were also found unsuitable as the reaction products tended to fuse to the boats.

(b) Experimental methods. A rigorous exclusion of moisture was maintained in the preparation of the oxide-fluoride mixtures and in their subsequent reactions. This was ensured by either the continuous evacuation of the furnace tube with a rotary Hyvac pump in the manner described in the experiments with potassium ferric fluoride (see also fig. 1.), or by the admission of a carefully dried inert gas like nitrogen. The nitrogen had to be de-oxygenated prior to its admission to avoid the possible conversion of the fluorides to oxides at high temperatures. It was found that no interaction between nitrogen and any of the compounds investigated occurred in the temperature range 600° - 1300°. An appreciable rate of flow of nitrogen through the furnace tube was however not desirable in view of the volatility of potassium, rubidium and caesium fluorides in the temperature range 600° - 700°. It was therefore decided to maintain a pressure of about 10-20 cm. of mercury within the tube, by the introduction of a capillary leak at the exit end of the furnace tube.

The apparatus finally adopted is represented diagrammatically in fig. 2. Nitrogen from a cylinder was

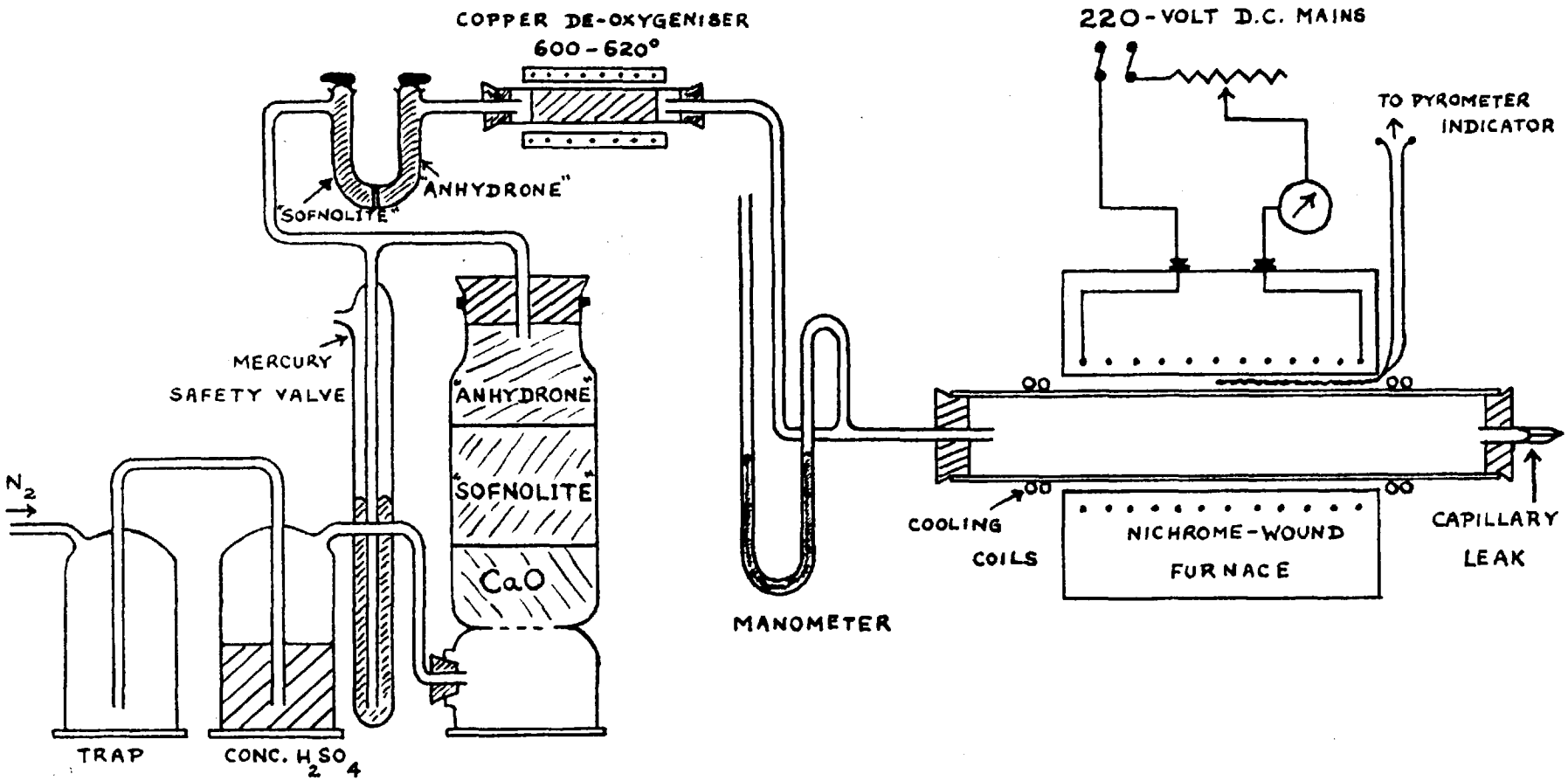

COPPER DE-OXYGENISER
600 - 620°
220 - VOLT D.C. MAINS
TO PYROMETER INDICATOR
"SOFNOLITE"
"ANHYDRONE"
MERCURY SAFETY VALVE
"ANHYDRONE"
"SOFNOLITE"
CaO
N_2
TRAP
CONC. H_2SO_4
MANOMETER
COOLING COILS
NICHROME-WOUND FURNACE
CAPILLARY LEAK

FIG. 2.

bubbled through a trap arrangement containing "Analar" grade concentrated sulphuric acid before being led up a tower containing calcium oxide, "Sofnolite" and magnesium perchlorate("Anhydrone") respectively. A mercury safety valve was introduced to divert the flow of the nitrogen into the atmosphere in the event of the capillary being blocked. The gas was then passed through a U-tube containing "Sofnolite" and "Anhydrone" into a copper de-oxygeniser. This consisted of a length of Pyrex tubing containing a tightly wrapped length of fine copper gauze which was maintained at about 610° by means of a nichrome-wound furnace run directly off the 230-volt A.C. mains. A mercury manometer registered the pressure within the system. The dry oxygen-free nitrogen was introduced into the furnace tube from the de-oxygeniser. The capillary leak consisted of a length of capillary tubing which was fused to a glass tube of wider bore. A filter of glass wool was placed in the glass tube to prevent the capillary from being blocked by the entry of any solid matter. The ends of the furnace tube were cooled by "compo" coils which were connected to the water supply. Radiation stoppers made of Δ F F refractory firebrick were placed at the ends of the furnace tube in experiments employing temperatures in the range 1000° - 1300° .

It was found that with a suitable capillary an excess pressure of 10 - 20 cm. of mercury could be maintained by admitting nitrogen at the rate of a bubble about every

thirty seconds. The ground glass joints of the system were all held in position by copper wire. Inappreciable amounts of oxygen only were present in the nitrogen employed when judged by the fact that copper oxide formation was confined to a few centimetres of the gauze after about six months use. The boats were introduced into and withdrawn from the furnace tube in a rapid stream of nitrogen.

The preparation of standard fluoride-oxide mixtures.

Water was perhaps the least desirable "impurity" in any of the mixtures which were to be subjected to reaction. A procedure was eventually adopted for the preparation of the mixtures which minimised the period of contact of the constituents with the atmosphere.

A 4" x 1" glass specimen tube which had been previously cleaned with dichromate-sulphuric mixture and dried for at least twenty-four hours in an oven at 150° was employed for weighing suitable quantities of lithium and sodium fluorides. The requisite amount of the oxide was then tipped into the same tube and the tube and contents dried at 150° for about four hours. Six steel balls of about 0.5 cm. in diameter and kept permanently in the oven at 150° were introduced into the tube and the tube tightly closed within the oven with a bung which had been dried for several hours at 80°. Sealing of the tube was completed by pouring molten paraffin wax on the bung. The tube and contents were then shaken vigorously for about

twenty minutes and the contents transferred to a weighed boat within the oven at 150°. Weighing of the boat and contents was conducted in a second glass tube provided with a bung. This tube, like the first, was dried for about four hours at 150°. The bung was similarly dried at 80°.

The procedure was modified slightly for use with potassium fluoride. A quantity of the fluoride which was permanently stored in the oven at 150° was transferred to the specimen tube and the bung inserted within the oven. The tube and bung had been previously weighed after cooling in a desiccator over silica gel. The requisite mass of the oxide was weighed in a platinum boat and dried for about four hours at 150°. Quantitative transference of the oxide was invariably found possible within the oven. The mixing was effected by employing steel balls as described above. The criterion adopted for judging the anhydrous state of the mixture was the absence of any tendency for the mixture to "cling" to the sides of the tube at the end of the mixing. Mixtures which showed this tendency were discarded. The procedure was developed into a general routine after a few months' application.

The limited supplies of rubidium and caesium fluorides entailed the application of this method for the preparation of mixtures on a semi-micro scale. The masses of the reactants were chosen in such a manner that not less than 70 mg. of the oxide, which was invariably the smaller

constituent in mass, were weighed. The oxide was contained in a "Vitreosil" boat of about 0.2 g. weight. Transference of the components was always within the oven. Four 1 mm. diameter steel balls were employed for mixing the components. Mixing was effected by smartly tapping the sides of a 2" x 1⅝" specimen tube which was used in these preparations. Samples which showed any signs of adherence to the sides of the tube were discarded. Mixtures of fluorides were prepared in a similar fashion.

The preparation of specimens for X-ray analysis.

The reaction products were crushed with a nickel spatula on a porous plate which was maintained at a temperature of 100° - 150°. Lindemann glass capillaries which had been previously dried for at least four hours at 150° were filled off this plate and immediately sealed by the application of a small flame. Specimens prepared in this manner were stored in previously dried specimen tubes which were sealed with paraffin wax prior to their being subjected to X-ray diffraction.

The efficiency of the method could be judged by the fact that specimens of rubidium fluoride showed no tendency to adhere to the sides of the capillary after being stored for a period of about three months. This fluoride normally turns liquid when exposed to the atmosphere for about two minutes.

Specimens containing caesium compounds were found to

require a much greater exposure time than normally employed, for the production of satisfactory X-radiograms. This is due to the high absorptive power of X-rays by caesium. Attempts were therefore made to dilute the specimens before they were subjected to X-ray diffraction. Gum tragacanth which had been previously dried for at least twenty four hours at 80° was eventually adopted as a diluent.

2. Use of X-ray methods for the analysis of the reaction products, the accurate determination of lattice constants and the crystallographic characterisation of new compounds.

The X-ray methods adopted for the analysis of reaction products have been described in the first section of this thesis. The determination of structural constants and the attempts at assigning discrete compounds to definite crystal classes from data obtained from X-radiograms were of extreme importance in the investigations of the reactions to be described in this section. The theory and procedure involved in such precision work therefore merits some discussion.

The X-ray equipment was the same as outlined previously. Copper targets were employed for obtaining X-radiograms of products from the reactions of the alkali metal fluorides and the oxides of group II metals. A cobalt target was utilised in the examination of the reaction products of

magnesium fluoride and ferric oxide. A 19 cm. diameter camera of the type designed by Bradley, Lipson and Petch (J. Sci. Instruments, 1941, 18, 216) was used for obtaining X-radiograms from which any quantitative interpretations were deduced. An exposure time of about 60 minutes was found necessary for the production of an X-radiogram on Kodak "Industrex" film with a discharge of 15 ma. at 50 k.V. with a copper target. Nickel filters which were employed in some instances for eliminating β radiation required an approximate three-fold increase of the exposure time. Use of a cobalt target entailed exposures of about 100 minutes with a discharge of 10 ma. at 44 k.V. Iron compounds are however self-filtering and the elimination of β radiation was therefore automatic.

The camera had been previously calibrated by measurement of the straight line distances between the high and low angle knife edges and the values checked with pure quartz, as described by Lipson and Wilson (J. Sci. Instruments 1941, 18, 144).

The X-radiograms were measured with a Hilger and Watts measuring device which gave an accuracy of $\pm$ 0.05 mm. The Bragg angles were computed by the method of Bradley and Jay (Proc. Phys. Soc. 1932, 44, 563) which eliminates errors due to film shrinkage in the processing.

The identification of the spectra on a powder photograph.

The crystallinity of the specimens subjected to X-ray diffraction was generally of a high degree. The patterns were therefore well defined and showed good resolution into α_1 and α_2 doublets at the high-angle ends. The elimination of spectra caused by β-radiation was effected by the application of the relationship

$$\frac{\sin^2\theta_\beta}{\sin^2\theta_\alpha} = \frac{\lambda^2_\beta}{\lambda^2_\alpha}$$

The interpretation of the spectra of individual crystal classes is best described separately.

(a) Cubic crystals

The relationship between the unit cell length or lattice constant (a) and the Bragg angles θ is given by the equation

$$a^2 = \left(\frac{\lambda}{2}\right)^2 \cdot \frac{h^2 + k^2 + l^2}{\sin^2\theta}$$

where λ is the wavelength of the radiation producing the spectra and h, k and l are the Miller indices of the crystal plane responsible for the Bragg angle θ (A. Taylor. An introduction to X-ray metallography, Chapman and Hall, London, 1949 page 60). It would be seen, therefore, that for a particular X-radiogram

$$\frac{h^2 + k^2 + l^2}{\sin^2\theta} = \text{a constant}$$

This constant is generally referred to as the increment

and is found by assigning suitable integral values for h, k and l for each value of the Bragg angle.

The failure to obtain a constant value for any particular line on an X-radiogram would signify the presence of some impurity. The establishment of face centred cubic structures was based on the fact that all the Miller indices of such a crystal lattice have $h + k$, $k + l$, and $l + h$ even (C.W. Bunn, Chemical Crystallography, Clarendon Press, Oxford, 1949 page 218).

(b) Tetragonal structures.

The relationship between the cell constants a and c and the Bragg angles for a tetragonal crystal is given by the equation

$$\sin^2\theta = \left(\frac{\lambda}{2}\right)^2 \left\{ \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right\} \quad (1)$$

(Taylor loc. cit. page 72).

Graphical methods for the solution of a and c have been described by Hull and Davey (Phys. Rev. 1921, 17, 549) and Bjurstrom (Z. f. Physik. 1931, 69, 346). Of these, only the logarithmic form of the Bjurstrom method is satisfactory for use over a wide range of axial ratios (Bunn. loc. cit. page 380).

In view of the fact that no crystallographical data were available for most of the tetragonal phases investigated, an alternate method of evaluating a and c

was employed. Equation (1) was transformed into

$$\sin^2\theta = \left(\frac{\lambda}{2}\right)^2 \left(\frac{4}{3}\cdot\frac{h^2 + hk + k^2}{a^2}\right) + \left(\frac{\lambda}{2}\right)^2 \left(\frac{l^2}{c^2}\right)$$

$$= \left\{\frac{4}{3}\left(\frac{\lambda}{2}\right)^2 \cdot \frac{1}{a^2}\right\}(h^2 + hk + k^2) + \left\{\left(\frac{\lambda}{2}\right)^2 \cdot \frac{1}{c^2}\right\}(l)^2$$

$$= k_1 \cdot (h^2 + hk + k^2) + k_2 \cdot (l)^2$$

where k_1 and k_2 are the "a" and "c" increments respectively. Suitable values were assigned to these increments in such a manner that any particular Bragg angle value could be obtained by assuming integral values for h, k and l. The method may be described as a systematic process of trial and error. Several X-radiograms with a large number of lines were however satisfactorily indexed by this method.

(c) Monoclinic structures. The methods adopted for indexing a few monoclinic structures are best described in their actual application to a set of powder data. The description is therefore reserved for the section dealing with the crystallography of the compounds of general formula $A^{+}B^{++}F_3$.

The elimination of systematic errors in lattice parameter determinations.

The systematic errors which have to be corrected for an accurate determination of the lattice parameters may be enumerated as follows.

1. Errors due to film shrinkage.

2. Errors due to eccentricity of the specimen.

3. Errors due to absorption of X-rays by the specimen.

4. Errors due to the refractive indices of crystal fragments.

The procedure adopted for the measurement of the films (Bradley and Jay, Proc. Phys. Soc. 1932, 44, 564) eliminated the errors due to shrinkage on the condition that the shrinkage was uniform. The accuracy of the measurements to $\pm$ 0.05 mm. could not possibly introduce an error of more than $\pm$ 0.0005 k X-units in the lattice constant on the theoretical assumption of the absence of a personal error in the actual process of measurement. Results with an accuracy of greater than $\pm$ 0.001k X-units are however not claimed as the physical significance of values of lattice parameters corrected to four decimal places is difficult to comprehend. To minimise the personal error the same camera was employed for a particular series of reaction products together with practically identical conditions of exposure and processing. Determinations of the lattice constant of an individual compound represented on a series of X-radiograms showed that the maximum deviation in values was 0.002 k X-units when the corrections to be presently described were applied. Variations in parameters of the order of 0.005 k X-units were therefore taken to be of significance in that they at least showed that a change was occurring in a particular direction. It was fortunate that such changes

were only detected in X-radiograms of very good quality.

The errors caused by eccentricity of the specimen and the absorption of X-rays have been shown to result in a proportionate error in spacing which is given by the expression

$$\frac{\Delta d}{d} = \left(\rho \cdot \frac{\cos\varphi}{r} - \frac{r}{2\theta R} - \frac{r}{2\theta \Delta K} \right) \cos^2\theta$$

where $\rho \cdot \cos\varphi$ is the displacement of the axis of rotation in the direction of the X-ray beam, r with the radius of the specimen, R the radius of the film and ΔK the distance from the target of the X-ray tube to the specimen (Bradley and Jay, loc. cit.). The relative error in d is thus very nearly a linear function of $\cos^2\theta$ and must be zero when $\cos^2\theta = 0$. The lattice constant "a" of a cubic crystal was therefore obtained in a corrected form by plotting individual values of the constant, calculated from the Bragg angles of the high-angle lines, against the corresponding $\sin^2\theta$ values and extrapolating to $\sin^2\theta = 1$. The spectra due to α_1 radiation were the only spectra employed for subsequent calculations as the α_2 lines were often too weak to permit of accurate measurement.

Bradley and Jay (loc. cit.) have shown that any correction for errors caused by the refractive indices of crystal fragments is only of the order of 1 in 50,000. Such a correction was therefore of inappreciable magnitude.

Correction for systematic errors by means of graphical

extrapolation was however not satisfactorily possible in the case of tetragonal structures. The method adopted was to obtain appropriate values for the "a" and "c" increments by successive approximation, in such a manner that the calculated $\sin^2\theta$ values for the high-angle lines showed the best approximation to the values obtained from the X-radiograms. It was generally found possible to obtain $\sin^2\theta$ values which differed by not more than one part in a thousand from the experimental values. Such a correspondence would justify the accuracy of the parameters to 0.005 k X-units. The values are however given in a form which indicate that the third place of decimal has some significance e.g. MgF_2, $a = 4.61_1$; $c = 3.04_3$ k X-units.

I Investigations of the Reactions between Magnesium Oxide and the Alkali Metal Fluorides.

1. Investigation of the reaction between magnesium oxide and lithium fluoride.

Introduction:-

The theoretical possibilities of interaction between lithium fluoride and magnesium oxide had to be first considered for the purpose of choosing suitable proportions of oxide to fluoride for the reaction mixtures. The close similarity in the structural constants of magnesium oxide and lithium fluoride has been already pointed out in the general introduction to the investigations of these reactions. Three theoretical courses of reaction could therefore be postulated. They may be represented by the following equations

1. $x\,MgO + y\,LiF \rightarrow x\,MgO.yLiF$

2. $MgO + 2\,LiF \rightarrow MgF_2 + Li_2O$

3. $MgO + 3\,LiF \rightarrow MgLiF_3 + Li_2O$

Equation (1) postulates the formation of a solid solution or mixed metal-oxygen-fluorine compound. No suitable proportions could be chosen on this equation for the reason that the existence of such compounds has not been established. Equation (2) represents a direct double decomposition process which needs one molecular proportion of the oxide to two of the fluoride for complete reaction. The formation of double fluorides of lithium and magnesium has never been reported, and thermal analyses of the system $LiF-MgF_2$ indicate that no such compounds are formed.

It was therefore considered best to adopt the course of double decomposition for the choice of proportions of the reactants relative to one another. The comparatively volatile nature of the alkali metal fluorides at temperatures above 600° had also to be borne in mind. The proportions eventually adopted were 10 mol.% of the oxide to 90 mol.% of the fluoride. These proportions were maintained in most of the reactions investigated. The large excess of fluoride present permitted the course of reaction according to equation (2) or (3). In addition, the oxides produced X-ray spectra in mixtures of these proportions which were comparable in intensity to those of the fluorides. The results of the investigations further justified the choice of such proportions.

The establishment of the existence of a particular component of a reaction product by X-ray methods was based on the matching of the interplanar spacings and relative intensities of the spectra obtained, with standard data for the pure compound. For this purpose the intensities of all the lines of an X-radiogram were estimated visually on the scale of 10 which represented the strongest line to 1 which represented the weakest.

Experimental procedure and results.

A mixture containing 10 mol.% of magnesium oxide was prepared in the manner described previously. A preliminary run with this mixture conducted in a platinum boat in vacuum at 600° for twenty-four hours showed no appreciable

change in the weight of the product. Lithium fluoride was therefore not appreciably volatile under these experimental conditions. An X-radiogram obtained with a specimen of the reaction product showed no extra lines over those of an X-radiogram of the original mixture. The interplanar spacings further established the absence of any reaction. No changes from the values for the pure components were found on the calculation of the lattice constants of magnesium oxide and lithium fluoride. It was evident that reaction does not occur under these experimental conditions. A higher temperature was therefore employed. A mixture of the same composition was accordingly heated in a continuous state of evacuation for thirty-six hours at 720°. The reaction product was found to have sintered heavily. A composition of 13.2 mol.% of the oxide was registered on the basis of the loss of weight of the reaction product. X-Ray diffraction methods indicated the absence of any interaction. Interesting results were however obtained on the calculation of the lattice constants of the individual reactants. The fluoride was found to have a lattice constant of $a = 4.021 \pm 0.001$ kX-units which is an increase of 0.004 kX-units over the value for the pure compound. The magnesium oxide maintained its value of 4.202 ± 0.001 kX-units. To eliminate the possibility of experimental errors in the production of the X-radiogram, the experiment was repeated with a mixture of the same

composition. Identical results were obtained which established the reproducibility of this phenomenon.

It was therefore to be inferred that a small change in the lattice constant of the fluoride does take place under these conditions of experiment. An exact evaluation of the magnitude of this change was difficult to guarantee. The direction of the change, on the other hand, could be taken as a certainty. Comparison of the lattice constant values of magnesium oxide and lithium fluoride showed that the oxide was larger in its unit cell dimensions than those of the fluoride by 0.185 kX-units. A probable explanation of this phenomenon could therefore be made by the assumption of the formation of a mixed crystal phase between the oxide and the fluoride. The direction of change of the lattice constant of the fluoride lends support to this assumption.

In view of the fact that this phenomenon may have had a bearing on the possibility of chemical interaction at a higher temperature, a 10 mol.% oxide mixture was heated for thirty hours at 790°. Volatilization of the fluoride was apparently appreciable at this temperature as the reaction product had a composition approximating to 20 mol.% of the oxide. A crystalline sublimate was found in the furnace tube which was subjected to X-ray diffraction. Pure lithium fluoride having a lattice constant of $a = 4.017 \pm 0.001$ kX-units was established as the composition of the sublimate. It was thereby proved that no volatile compounds of

magnesium oxide and lithium fluoride were evolved from the reaction mass. X-ray examination of the reaction mass obtained by sintering the oxide and fluoride established the presence of magnesium fluoride in addition to that of the original components of the mixture. The standard powder data for magnesium fluoride were obtained from the X-radiogram of the pure compound whose preparation and analysis have been previously described. A few lines which could not be accounted for by the formation of magnesium fluoride were found to agree with the data listed for lithium peroxide (Li_2O_2) by the A.S.T.M. card index. The presence of this compound was however not chemically admissible as Zentnershver and Blumenthal (Bull, intern. acad. polon. sci. Classe. sci. math. nat. 1933, A, 499) have shown that the compound has a dissociation temperature of 195° at one atmosphere pressure. A calculation of the interplanar spacings of lithium oxide (Li_2O) from the powder data supplied for this compound by Zintl, Harder and Deuth (Z. Elektrochem. 1934, 40, 588) showed that one of the unexplained lines of the X-radiogram of the reaction product corresponded in the value of its interplanar spacing with that of the line of strongest intensity of lithium oxide. This was one of the few instances where the definite establishment of the identity of the reaction products was difficult. The various X-ray data are tabulated as follows.

New phases of reaction product			magnesium fluoride		Lithium peroxide		Lithium oxide	
I	θ	d	d	I	d	I/I$_1$	θ	I d
5	13.59	3.27	3.26	10				
3	16.40	2.72			2.73	0.4	16.75	st 2.67
2	17.39	2.57	2.54	2	2.577	1.0		
*7	20.20	2.23	2.23	10	2.23	0.7		
1	24.25	1.873			1.863	0.7		
3	26.38	1.733	1.708	10				
3	28.17	1.630	1.632	5			28.10	st 1.63

* Increase from intensity of 5 in X-radiogram of mixture.

It was to be inferred therefore that the reaction between magnesium oxide and lithium fluoride proceeds according to the equation

$$2LiF + MgO \rightarrow Li_2O + MgF_2.$$

The presence of appreciable quantities of lithium oxide in the reaction product could not be expected as Lemarchands and Jacob (Bull. soc. chim. France 1935, (5), 2, 479) have shown that the oxide is volatile above 600° and very appreciably so at 1000°. The oxide, furthermore, does not give a well defined powder pattern as Zintl, Harder and Dauth (loc. cit.) obtained an X-radiogram of the compound

which only possessed eleven lines of which two were indexed as "strong", two as "medium" and the remaining seven as "weak" in intensity.

The lattice constant of the lithium fluoride present in excess in the reaction product was found to be 4.017 $\pm$ 0.001 kX-units. This was identical with the value associated with the pure compound. The result was however of extreme importance in that it indicated that the lattice constant of the fluoride assumed an enhanced value prior to reaction followed by return to its original value after the reaction had proceeded to some extent. An intermediate stage of absorption of the oxide by the fluoride can therefore be postulated. This can be assumed to be a state of limited mixed crystal formation. The phase is apparently transient in that it breaks down on the occurrence of reaction. This phenomenon, though it is being described for the first time, was found to be in no way exceptional to reactions between metal oxides and fluorides. On the contrary, larger discrepancies in lattice constant values were found in reactions involving the use of potassium fluoride. The directions of change of the lattice constant values were invariably in keeping with the relative dimensions of the oxide and fluoride lattices thereby supporting the assumption of mixed crystal formation.

No change in the lattice constant of the magnesium oxide could be detected from the data obtained from the X-radiogram

of this reaction product. This was found to be true of all the oxides in reactions subsequently investigated.

The reaction was apparently slow when judged by the experimental conditions of time and temperature. An attempt to obtain complete reaction was made by heating a mixture which contained 10 mol.% of the oxide for thirty five days at 750° - 15° in a furnace, with access to the atmosphere. X-ray analysis of the reaction product showed the formation of magnesium fluoride to a greater extent than that found in the product of the run at 790°. Lithium carbonate was found in this reaction product which adds evidence to the formation of lithium oxide in the reaction in vacuum. The reaction was however far from complete as both the original components were represented on the X-radiogram. There were no changes in the lattice constants of either the oxide or the fluoride which is in keeping with the postulate that the enhanced value is of an intermediate state which precedes the occurrence of reaction or is present only at its initial stages.

The maintenance of the lattice constant value for the pure compound by the lithium fluoride in the reaction mass, further indicated that no mixed crystal formation occurs between magnesium fluoride and lithium fluoride. Mixed crystal formation would not normally be expected to occur between these two fluorides because of their dissimilar lattice types. Bergmann and Bergunov (Compt. rend. acad.

sci. U.R.S.S. 1941, (8), 31, 755) have however made a thermal analysis study of the system LiF - MgF_2 in which they claim an unbroken series of mixed crystals for the entire range of compositions at temperatures below 742° at which an eutectic of 33 mol.% of magnesium fluoride occurs. The system has been studied previous to the work of Bergmann and Bergunov by Tacchini (Gazz. chim. ital. 1924, 54, 777) and Ruff and Rusch (Z. anorg. v. allgem. Chem. 1925, 144, 87). Tacchini claims the existence of a minimum at 669° with 45 mol.% magnesium fluoride. Ruff and Rusch, on the other hand, maintain the existence of an eutectic at 725° with 27 mol.% magnesium fluoride. The form of the thermal analysis diagram is evidently still at variance. A series of quenched melts have, in addition, been subjected to X-ray diffraction by Bruni and Levi (Atti. reale. accad. naz. Lincei, 1924, (V), 33, 377). They maintain that a mixture containing 9.4 mol.% of magnesium fluoride showed no X-ray evidence for the presence of magnesium fluoride when quenched from a melt. No change in the lattice constant of lithium fluoride is reported in the interpretation of the same X-radiogram. The results are evidently contradictory to each other as the absorption of magnesium fluoride to the extent of 9.4 mol.% must be manifested in some way in the structure of the lithium fluoride. Zintl and Udgard (Z. anorg. v. allgem. Chem. 1939, 240, 150) quenched mixtures

containing 5, 10 and 15 mol.% of magnesium fluoride at their melting points and subjected specimens of the products to X-ray diffraction. They report the presence of magnesium fluoride in all the specimens investigated, together with no change in the lattice constant of lithium fluoride.

In view of the conflicting evidence for the formation of mixed crystals between magnesium fluoride and lithium fluoride, a mixture of the two florides containing equimolecular proportions by weight was maintained at 790° for twenty four hours in an oxygen-free atmosphere of nitrogen which had an excess pressure of 10 - 15 cm. of mercury. The reaction product was in the form of a heavily sintered mass which showed a 4% loss in weight. Calculation of the lattice constant of lithium fluoride from an X-radiogram of this product showed no deviation from the standard value. No state of mixed crystal formation can therefore be assumed to occur when the fluorides are sintered under these experimental conditions. Lithium fluoride and magnesium fluoride were established as the end products which indicate the absence of formation of any double fluorides when a mixture of the two fluorides is sintered.

The reaction between magnesium oxide and lithium fluoride may therefore be represented by the equation

$$MgO + 2LiF \rightarrow MgF_2 + Li_2O$$

The reaction is apparently slow when judged by the conditions

of time and temperature employed in the investigations. No structural interaction is found between the reactants and resultants. An intermediate state of limited mixed crystal formation between the oxide and fluoride apparently precedes the occurrence of reaction.

2. Investigation of the reaction between magnesium oxide and sodium fluoride.

The investigation of the reaction between magnesium oxide and sodium fluoride was conducted on the lines adopted for that of lithium fluoride and the same oxide which have been described previously. There were no striking similarities in the structural constants of the reactants in contrast to those of the preceding reaction investigated. A double fluoride of the formula $NaMgF_3$ has however been isolated in the thermal analysis of the system $NaF - MgF_2$ by Grube and Stasche (Z. Elektrochem. 1927, 33, 482) and it was of interest to investigate the possibility of the formation of this compound by the interaction of magnesium oxide and sodium fluoride in the manner represented by the equation

$$3NaF + MgO \rightarrow NaMgF_3 + Na_2O. \quad (1)$$

The X-ray methods normally employed in the investigations of these reactions would, in addition, show whether the formation of such a compound involves the intermediate formation of free magnesium fluoride which interacts with the excess of sodium fluoride as given by the equations

$$2NaF + MgO \rightarrow Na_2O + MgF_2$$

followed by $NaF + MgF_2 \rightarrow NaMgF_3$

or whether the course of reaction is given by a direct stoichiometric synthesis represented by equation (1).

Experiments were therefore conducted with mixtures of the oxide and fluoride which contained 10 mol.% of the oxide. The choice of this composition ensured the presence of excess sodium fluoride under all conditions of reaction.

An X-radiogram of a mixture containing 10 mol% of magnesium oxide showed the presence of the spectra of the oxide with intensities comparable to those of sodium fluoride. A sample of this mixture was heated for twenty four hours in platinum at 640° in a continuously evacuated tube. Comparison of the data of an X-radiogram of this end product with the previous one obtained with a specimen of the mixture showed no indication of the formation of new phases. No reaction occurred under these experimental conditions. A mixture of the same composition was therefore heated for seventy two hours at 750° under the experimental conditions employed previously. X-ray analysis of the reaction product revealed the presence of a single extra line over those of the reactants, with interplanar spacing (d) = 1.920 and relative intensity (I) = 2.

Calculation of the lattice constant of the sodium fluoride present in excess gave a value of $a = 4.613 \pm 0.001$ kX-units which is a decrease of 0.003 kX-units from the value obtained for pure sodium fluoride. It was to be inferred, therefore, that mixed crystal formation between the oxide and the fluoride occurred at the initial stages of reaction. The situation could be looked upon as a more

exaggerated version of the phenomenon first detected in the reaction between lithium fluoride and magnesium oxide. No change in the lattice constant of the magnesium oxide present in the reaction product could be detected.

The interplanar spacing of the extra line detected, showed no relationship to the powder data of magnesium fluoride. The experiments were therefore repeated at 700° for forty eight hours with the idea of obtaining more data for the characterization of the new phase. An X-radiogram of the reaction product showed the presence of about ten lines over those of an X-radiogram of the reactants. The data of these lines signified the formation a new phase for which no standard values were available. Calculation of the lattice constant of the sodium fluoride present in excess showed that the compound had a value identical with that of the pure compound. This phenomenon was strictly analogous to that met with in the reaction investigated between magnesium oxide and lithium fluoride.

The establishment of the identity of the new phase was attempted from data obtained from an X-radiogram of sodium magnesium fluoride ($NaMgF_3$). This compound was prepared by sintering a stoichiometric mixture of the constituent fluorides in equimolecular proportions for twenty four hours in platinum at 700° in an atmosphere of dry oxygen-free nitrogen which had an excess pressure of about 15 cm. of

mercury. There were no appreciable changes in weight which guaranteed the composition of the end product. A specimen of this end product, when subjected to X-ray diffraction, showed the formation of a discrete compound. It was therefore possible to synthesize sodium magnesium fluoride by sintering the constituent fluorides under the experimental conditions detailed. This was found to be true of all the double fluorides subsequently investigated.

The data obtained from an X-radiogram of this compound established the formation of sodium magnesium fluoride in the reaction product of the oxide and fluoride at 780°. No structural evidence was however present for the formation of sodium oxide (Na_2O) which would be expected from a reaction represented by the equation

$$3NaF + MgO \rightarrow NaMgF_3 + Na_2O$$

A survey of the thermodynamical data of sodium oxide showed that it is reported to have a theoretical temperature of sublimation of 1275° (Lemarchands and Jacob, Bull. soc. chim. France 1935, (5), 2, 479). The value has not been confirmed experimentally as the oxide decomposes at 400° into the higher oxide; as given by the equation

$$2Na_2O \rightarrow Na_2O_2 + 2Na$$

(Rengade, Ann. Chim. et phys. 1907, (8), 11, 348). The peroxide decomposes on further heating into the oxide and oxygen. Thus

$$2Na_2O_2 \rightarrow 2Na_2O + O_2$$

The peroxide is reported to have a dissociation pressure of one atmosphere at 657° (Isenthersheyer and Blumenthal, Bull. intern. acad. polon. sci. Classe. sci. math. nat. 1933, A, 439). The presence of sodium oxide may therefore be expected in a reaction product at 780°. Its absence may be explained on the grounds of its formation in insufficient quantities to permit of detection by X-ray methods. The absence of any other phase may however be taken as sufficient justification for the representation of the reaction between magnesium oxide and sodium fluoride by the equation

$$3NaF + MgO \rightarrow Na_3MgF_3 + Na_2O.$$

Further evidence for the occurrence of reaction in the manner postulated was obtained from subsequent experiments in which the formation of sodium oxide was established.

A series of experiments was also conducted with mixtures of sodium and magnesium fluorides in view of the reported formation of double fluorides of the general formula $A^{+}_{2}B^{++}F_4$ in some alkali metal-alkaline earth metal fluoride systems. For this purpose mixtures of the compositions $2NaF : MgF_2$ and $NaF : 2MgF_2$ were sintered separately for twenty four hours at 700° in an atmosphere of nitrogen which had an excess pressure of about 15 cm. of mercury. Inappreciable losses in weight guaranteed the compositions of the end products. X-ray investigations with specimens of these products established the formation of sodium

magnesium fluoride ($NaMgF_3$) in each instance together with any excess of the fluoride which was present to a greater extent than 50 mol.% in the original mixture. There were no indications of any changes in the Bragg angle values of the high-angle lines of the X-radiograms which would have suggested the occurrence of appreciable mixed crystal formation between sodium magnesium fluoride and either magnesium or sodium fluoride. This is in agreement with the thermal analysis data of the system $NaF - MgF_2$ reported by Grube and Staache (loc.cit.) and Bergmann and Bergunov (Compt. rend. acad. sci. U.R.S.S. 1941, 31, 753; 1945, 48, 329). The formation of a compound of the formula Na_2MgF_4 by a solid reaction between the constituent fluorides therefore appears most unlikely.

No crystallographical data for the compound sodium magnesium fluoride have been reported. It was found that the unit cell was of the large tetragonal type with a = 7.64 kX-units; c = 7.29 kX-units and c/a = 0.954. The complete data for this compound are listed at the end of the description of this reaction. Sodium magnesium fluoride is decomposed by water. An X-radiogram of the insoluble fraction obtained by leaching with water was found to be the same as one of magnesium fluoride.

The investigation of this reaction was of considerable importance in that it confirmed the occurrence of limited

mixed crystal formation in reactions between oxides and fluorides which was previously found in the investigations with magnesium oxide and lithium fluoride.

X-ray data of the compound sodium magnesium fluoride ($NaMgF_3$). Copper K$_\alpha$ radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (Calculated)	h k l	d
7	11.598	0.0404	0.0404	200	3.83
2	13.006	0.0507	0.0505	210	3.42
8	16.533	0.0810	0.0808	220	2.70
2	18.426	0.0999	0.0999	003	2.43
3	18.684	0.1026	0.1020	301	2.40
8	19.531	0.1117	0.1121	311	2.30
4	20.213	0.1193	0.1201	113	2.23
4	20.634	0.1241	0.1252	222	2.18
4	21.500	0.1353	0.1353	302	2.10
2	21.984	0.1401	0.1403	203	2.05
1	22.226	0.1432	0.1424	321	3.03
10	23.740	0.1621	0.1616	400	1.911
2	24.452	0.1714	0.1717	410	1.858
3	26.420	0.1980	0.1978	114	1.730
3	26.753	0.2026	0.2020	420	1.710
4	27.011	0.2062	0.2060	402	1.694
5	28.371	0.2258	0.2262	332	1.620
6	28.804	0.2321	0.2312	323	1.596
7	29.781	0.2467	0.2464	422	1.549
5	31.205	0.2686	0.2685	304	1.485
1	32.698	0.2919	0.2929	520	1.424
3	34.263	0.3169	0.3179	205	1.367

X-ray data of the compound sodium magnesium fluoride. ($NaMgF_3$) Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
6	34.702	0.3241	0.3232	440	1.352
1	35.292	0.3337	0.3343	441	1.331
1	35.459	0.3365	0.3373	522	1.326
3	36.413	0.3523	0.3524	(503 (433	1.296
2	36.972	0.3617	0.3625	513	1.280
1	37.434	0.3694	0.3684	305	1.265
1	38.760	0.3919	0.3928	523	1.229
5	39.517	0.4049	0.4040	620	1.210
2	41.611	0.4410	0.4401	216	1.158
3	43.787	0.4789	0.4795	425	1.112
3	44.498	0.4913	0.4905	306	1.097
2	45.861	0.5150	0.5140	543	1.072
2	46.451	0.5253	0.5252	640	1.062
2	47.087	0.5364	0.5363	641	1.050
2	47.472	0.5431	0.5439	007	1.044
3	48.556	0.5620	0.5612	406	1.026
4	49.086	0.5711	0.5704	525	1.019
4	49.554	0.5790	0.5797	722	1.011
2	51.103	0.6057	0.6049	(713 (553	0.989
1	52.523	0.6297	0.6302	732	0.970
1	53.496	0.6462	0.6464	800	0.957

X-ray data of the compound sodium magnesium fluoride. ($NaMgF_3$) Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
α_1 2	55.082	0.6723	0.6725	704	0.938
α_2 1	55.132				
α_1 2	58.079	0.7205	0.7205	108	0.906
α_2 1	58.382				
α_1 3	58.833	0.7321	0.7320	635	0.898
α_2 2	59.236				
α_1 2	60.790	0.7618	0.7609	218	0.881
α_2 1	61.092				
α_1 2	61.486	0.7721	0.7716	662	0.875
α_2 1	61.789				
α_1 4	63.711	0.8038	0.8036	626	0.857
α_2 2	64.045				
α_1 2	66.543	0.8415	0.8417	328	0.838
α_2 1	66.876				
α_1 2	69.041	0.8721	0.8726	912	0.823
α_2 1	69.465				
α_1 4	71.542	0.8997	0.8991	009	0.810
α_2 2	71.964				
α_1 3	78.822	0.9624	0.9629	509	0.784
α_2 1	79.609				

Lattice constants $a = 7.64_9$ kX- units

$c = 7.29_6$ kX- units

$c/a = 0.954$

3. Investigation of the reaction between magnesium oxide and potassium fluoride.

A comparison of the structural constants of magnesium oxide with the corresponding values for potassium fluoride showed no obvious similarities. It has however been noticed that mixed crystal formation between magnesium oxide and sodium fluoride does occur, although their lattice constant values differ by as much as 0.419 kX-units. Any reaction between magnesium oxide and potassium fluoride would therefore indicate whether the extension of the phenomena detected in the preceding reactions investigated to larger diversions in the structural values of pairs of oxides and fluorides was possible. The possible formation of potassium magnesium fluoride ($KMgF_3$) was also of interest as some X-ray investigations have been made on the structure of this compound. The existence of a second double fluoride of the formula K_2MgF_4 has, in addition, been postulated in thermal analyses of the system $KF - MgF_2$.

A mixture containing 10.2 mol.% of magnesium oxide was heated for forty hours in a platinum boat at 680° in vacuum. No signs of sintering were visible in the reaction product. A composition of 14 mol.% of the oxide was found for this reaction product on the basis of the loss in weight. An X-radiogram of a sample of this product, however, showed the almost complete absence of the oxide phase, through the proportion of oxide in the product, as shown

by composition, had increased. The possibility of the spectra of magnesium oxide failing to register because of the low concentration of the compound in the product was eliminated by the fact that an X-radiogram of the original mixture showed the presence of both components. Only the two strongest lines of magnesium oxide were present in the X-radiogram of the product at 680°. Calculation of the lattice constant of the potassium fluoride in the reaction product showed that the value was 5.328 ± 0.001 kX-units as against 5.332 kX-units for the pure fluoride. The direction of change of this lattice constant value from that of the pure compound is in keeping with the possibility of mixed crystal formation between magnesium oxide and potassium fluoride. The disappearance of the oxide phase could then be explained on the postulation of the existence of such an intermediate state. No indications of the formation of any new phases were present in the relevant X-radiogram. A mixture containing 10.0 mol.% of the oxide was therefore heated for thirty hours at 750° under the same experimental conditions. Volatilisation of the potassium fluoride was appreciable at this temperature and the reaction product approximated to a 20 mol.% oxide mixture in composition. The reaction product showed signs of appreciable swelling up during the heating operation. X-Ray analysis of this product showed that very little excess potassium fluoride was present. There was, in

addition, a complete disappearance of the oxide phase which indicated complete reaction. A distinct new phase was present which was not magnesium fluoride. The reaction product was therefore leached with water as a possible method of isolating the new phase in a pure state. It was found that the phase was comparatively insoluble. Chemical analysis for the magnesium content by the 8-hydroxyquinoline method described by Miller and McLennan (J. Chem. Soc. 1940, 656) and Chirnside, Pritchard and Rooksby (Analyst 1941, 66, 399) gave a magnesium content which approximated to within 2% of the theoretical value calculated for potassium magnesium fluoride ($KMgF_3$).

It was probable therefore that the reaction between magnesium oxide and potassium fluoride follows the course represented by the equation

$$3KF + MgO \rightarrow KMgF_3 + K_2O$$

Standard X-ray data were however not available for potassium magnesium fluoride. The synthesis of potassium magnesium fluoride was therefore attempted by sintering a mixture of potassium and magnesium fluorides which contained 50 mol.% of each of the constituents, for twenty four hours at 650° in an atmosphere of dry oxygen-free nitrogen having an excess pressure of about 15 cm. of mercury. An X-radiogram of the reaction product showed that complete interaction had occurred. The interplanar spacings of potassium

magnesium fluoride were found to correspond with those of the reaction product of magnesium oxide and potassium fluoride at 750°.

No evidence was found for the existence of potassium oxide in this reaction product. It is probable that the potassium oxide formed is volatile under the conditions of experiment. The theoretical temperature of sublimation of potassium oxide is 883° at one atmosphere pressure (Lamarque and Jacob, Bull. soc. chim. France, 1935, (5), 2, 479) which makes its presence in a reaction product at 750° under continuous evacuation most improbable. The formation of potassium oxide in reactions of this type was however established experimentally in reactions between potassium fluoride and other group II metal oxides which occurred at appreciably lower temperatures than 750°. The course of reaction between magnesium oxide and potassium fluoride may therefore be represented by the equation

$$3KF + MgO \rightarrow KMgF_3 + K_2O$$

The reaction is apparently complete in thirty hours at 750° in vacuum in a mixture containing 10 mol.% of the oxide.

The question remained as to whether the alteration of the conditions of reaction would result in the formation of the double fluoride K_2MgF_4. It was considered advisable to attempt to prepare this compound prior to further experiments with the oxide-fluoride mixtures. The existence

of the compound K_2MgF_4 is claimed on the basis of thermal analysis data by Remy and Seemann (Rec. trav. chim. 1940, 59, 516) and by Bergunov and Bergmann (J. Phys. Chem. U.S.S.R. 1948, 22, 625). Its formation in the three component system LiF - KF - MgF_2 is claimed by Bergmann and Pavlenko (Compt. rend. acad. sci. U.R.S.S. 1941, 30, 818) and in the system KF - NaF - MgF_2 by Bergmann and Bergunov (Compt. rend. acad. sci. U.R.S.S. 1945, 48, 329). Remy and Seemann maintain that K_2MgF_4 separates from a melt containing 78.5 - 87.5 mol.% of potassium fluoride. A mixture of potassium fluoride and magnesium fluoride which contained 83 mol.% of potassium fluoride was therefore heated for twenty four hours at 700° in nitrogen which had an excess pressure of about 15 cm. of mercury. No appreciable loss in weight was recorded. The X-radiogram of the reaction product however showed the existence of potassium magnesium fluoride ($KMgF_3$) and excess potassium fluoride. A quenched melt of the same composition gave identical results. The quenching was performed by dropping a platinum boat which contained the melt into carbon tetrachloride. A slow cooled melt gave the same results as the quenched melt. The only explanation that could be offered to explain these results is that the double fluoride K_2MgF_4 postulated on the thermal analysis evidence is apparently unstable at room temperature and is converted quantitatively into the double fluoride

$KMgF_3$ and potassium fluoride. Experiments conducted in a high temperature camera should throw more light on this problem.

Additional experiments were nevertheless performed with oxide-fluoride mixtures which contained sufficient potassium fluoride for the formation of the double fluoride K_2MgF_4. Potassium magnesium fluoride ($KMgF_3$) and excess potassium fluoride were invariably found as reaction products. The experiments however served the additional purpose of verifying the possibility of mixed crystal formation between potassium magnesium fluoride ($KMgF_3$) and potassium fluoride. No indication of such an occurrence was observed. In addition, the potassium fluoride which was present in excess on the completion of reaction had a lattice constant value identical with that of the pure compound. This lends further support to the postulate that mixed crystal formation between an oxide and a fluoride is only of a transitory character and breaks down with progress of the reaction.

Potassium magnesium fluoride ($KMgF_3$) was first prepared by Dubois (Compt. rend. 1893, 120, 678) by adding magnesium oxide to molten potassium fluoride. Van Arkel (Physica 1925, 5, 167) showed that it possessed a "perovskite" type of structure with a cubic unit cell of approximately 4.00A. Van Arkel's work has apparently been accepted without question when judged by the fact that practically all text-

books on crystallography allude to the cubic structure of this compound. Naray-Szabo (Magyar Kemiai Folyoirat, 1947, No.1, 36) listed potassium magnesium fluoride as monoclinic with $a = b = c = 8.00$A and $\beta = 90^{\circ}$. No data is however given for this postulate. It has been found possible to verify this monoclinic structure postulated by Naray-Szabo from the data obtained from an X-radiogram of the compound. The unit cell may be described as being monoclinic with $a = b = c = 8.00$ kX-units and $\beta = 91^{\circ}\,18'$. The complete X-ray powder data are listed in the section dealing with monoclinic structures. Potassium magnesium fluoride was found in addition to be insoluble in and undecomposed by water.

4. Investigation of the reaction between magnesium oxide and rubidium fluoride.

The investigations of the reactions between magnesium oxide and lithium, sodium and potassium fluorides have shown that intermediate mixed crystal formation could be detected in each of the individual reactions. Experiments with rubidium fluoride and the same oxide were therefore of interest. The complete interaction of magnesium oxide and potassium fluoride at 750° when compared to the extremely slow reactions of lithium and sodium fluorides at the same temperature, with magnesium oxide, showed that a given oxide had apparently a definite order of reactivity with a series of fluorides. Any reaction between rubidium fluoride and magnesium oxide was therefore of interest for the purpose of adding further information to the apparent generalities which were manifested by the preceding reactions.

A mixture of rubidium fluoride and magnesium oxide which contained 10.0 mol.% of the oxide failed to register its oxide content on an X-radiogram. This is to be expected on considerations of the diffracting powers and concentrations of the individual atomic species. Mixtures containing 20.0 mol.% of the oxide were therefore employed in these investigations. Such a mixture showed only the four strongest lines of the oxide on an X-radiogram. A further increase in the oxide content was however not practicable

for the reason that a reaction of the type represented by the equation

$$3RbF + MgO \rightarrow RbMgF_3 + Rb_2O$$

would require a 75 mol.% fluoride content in the mixture for complete reaction. An excess of rubidium fluoride at every stage of reaction was desirable as changes in the lattice constant of the fluoride had been noticed in the preceding experiments.

A mixture containing 20 mol.% of the oxide was heated for four hours at 725° in platinum in an atmosphere of dry oxygen-free nitrogen which had an excess pressure of about 15 cm. of mercury. Fusion of the reaction mixture was not anticipated as the recorded melting point of rubidium fluoride is 780° (Dergunov and Bergmann, J. Phys. Chem. U.S.S.R. 1948, 22, 625). The mixture was however found to have melted at 725° which necessitated working at a lower temperature. A similar run which was conducted for twenty four hours at 700° proved that the fluoride was completely volatile under these conditions of experiment. Investigations were therefore made at 650°. A mixture containing 20 mol.% of the oxide when heated for twenty four hours at this temperature showed a composition of 23 mol.% of the oxide. An X-radiogram of this reaction product showed the presence of two lines of "d" = 2.90 and 2.20 and "I" = 2 and 1 respectively. Magnesium oxide was established in this product by the fact that its two strongest lines were present. The rubidium

fluoride present in excess showed no change in lattice constant from that of the pure compound. Incomplete reaction was to be inferred from the data of this X-radiogram. It was also evident that no intermediate mixed crystal formation between magnesium oxide and rubidium fluoride was present at the initial stages of reaction. The lines indicative of the new phase showed no correspondence in their interplanar spacings to the strongest lines of magnesium fluoride. The possibility of double decomposition had therefore to be ruled out. This was confirmed by the fact that an X-radiogram of the reaction product of a mixture containing 20.2 mol.% of the oxide heated for seventy two hours under the same experimental conditions as employed in the preceding investigation showed the appearance of a new phase which was not magnesium fluoride. Magnesium oxide was present in this reaction product as well. No change in the lattice constant of the rubidium fluoride present in excess could be detected. It appeared very probable that the new phase was rubidium magnesium fluoride ($RbMgF_3$) which has been shown to exist by the thermal analysis[2] of the system RbF - MgF_2 by Remy and Seemann (Rec. trav. chim. 1940 59, 516). It was found possible to synthesize this compound in the manner described for the preparation of potassium magnesium fluoride. Considerable expansion of the powder mixture was found to occur on sintering the

mixture of the constituent fluorides. The reaction product was in the form of a comparatively voluminous mass. It is of interest to note that the same phenomenon was observed in the synthesis of potassium magnesium fluoride and found to be true of all subsequent investigations which involved the preparation of double fluorides by this method. The standard data obtained from an X-radiogram of rubidium magnesium fluoride confirmed the formation of this compound in the reaction product of the oxide and fluoride. Evidence was also obtained for the formation of rubidium oxide (Rb_2O) which justifies the representation of the reaction between magnesium oxide and rubidium fluoride by the equation

$$3RbF + MgO \rightarrow RbMgF_3 + Rb_2O$$

The reaction is apparently a slow process in that it is incomplete after seventy two hours at 650° in a mixture containing 20.2 mol.% of magnesium oxide.

Remy and Seemann (loc. cit.) claim the existence of the double fluorides Rb_2MgF_4 in addition to that of the compound $RbMgF_3$. It was found that the isolation of such a compound, by strictly analogous methods to those employed for the investigations on the potassium compound K_2MgF_4, was not possible. The same arguments which were applied to the potassium compound may therefore be held to be valid in this instance as well.

No X-ray data for the compound $RbMgF_3$ have been published.

It was fortunate that standard data are given for rubidium oxide by the A.S.T.M. card index (first supplementary set of cards). The diffraction pattern of rubidium magnesium fluoride is extremely complex as shown by the fact that it possesses about seventy lines. Careful study of the data, however, made it possible for the compound to be indexed as monoclinic with $a = b = c = 8.17$ kX-units and $\beta = 88^{\circ}\,30'$. The complete crystallographical data for this compound are discussed and listed in the section dealing with monoclinic structures. It was also found that rubidium magnesium fluoride was insoluble in and undecomposed by water. The compound was found to be undecomposed after being heated for seventy two hours in a continuous state of evacuation at 700°.

5. Investigation of the reaction between magnesium oxide and caesium fluoride.

The investigation of the reaction between magnesium oxide and caesium fluoride represented that of the pair of reactants which showed the greatest disparity in the values of the structural constants of an alkali metal fluoride and an oxide of a group II metal. The possibility of the formation of a double fluoride of the formula $CsMgF_3$ was also of added interest for the reason that the existence of such a compound has not been previously reported.

Mixtures which contained approximately 20 mol.% of the oxide were employed in these investigations for reasons enumerated in the description of the reaction between rubidium fluoride and the same oxide. An X-radiogram of a specimen of a mixture of this composition was found to possess only the three strongest lines of magnesium oxide. Gum tragacanth had to be employed as a diluent in the preparation of specimens for X-ray diffraction methods because of the high absorptive power of X-rays of caesium compounds. A preliminary run with a mixture containing 20.2 mol.% of magnesium oxide showed that fusion occurred at 630° . Subsequent reactions were therefore investigated in the temperature range 600° - 625° . The reaction product of a mixture which contained 20.0 mol.% of the oxide and was heated for four and a half hours at 625° in platinum in an atmosphere

of dry oxygen-free nitrogen having an excess pressure of about 15 cm. of mercury, showed signs of heavy sintering. No appreciable loss in weight was detected. The interpretation of an X-radiogram of this reaction product showed the presence of the reactants in addition to that of a new phase. This new phase was not of magnesium fluoride which eliminated the possibility of double decomposition.

An attempt at synthesizing the possible double fluoride $CaMgF_4$ by sintering a stoichiometric mixture of the constituent fluorides at 650° in a controlled atmosphere of nitrogen was found to be successful. Standard data which were obtained from an X-radiogram of a specimen of this compound allowed the identification of this phase in the reaction product of magnesium oxide and caesium fluoride. There was no structural evidence for the presence of caesium oxide in this reaction product. The caesium fluoride which was present in excess, moreover, showed no discrepancy in the value of its lattice constant and that previously obtained for the pure compound. Intermediate mixed-crystal formation could not therefore be inferred to be present at the initial stages of reaction.

Subsequent experiments with a mixture containing 20.0 mol.% of magnesium oxide showed that the reaction was complete at 625° in forty-eight hours under the same experimental conditions. X-Ray analysis confirmed the formation of this compound. The course of reaction between caesium fluoride and magnesium oxide may therefore be represented

by the equation

$$3\,CsF + MgO \rightarrow CsMgF_3 + Cs_2O.$$

No thermal analysis of the system CsF-MgF_2 has been reported. Experiments which were conducted to detect the possible formation of the double fluoride $CsMgF_4$ showed that the compound, if it does exist, cannot be prepared by sintering a mixture containing the constituent fluorides in stoichiometric proportions, for twenty-four hours at 650° in nitrogen. The possibility of the existence of solid solutions between caesium magnesium fluoride and caesium or magnesium fluoride was investigated by sintering mixtures of the relevant fluorides and subjecting the products to X-ray diffraction. No indication of such occurrences were found in the range of composition of 33 - 66 mol.% of magnesium fluoride in mixtures of magnesium fluoride and caesium fluoride.

Caesium magnesium fluoride was found to have a large tetragonal unit cell with a = 9.37 kX-units; c = 8.70 kX-units and c/a = 0.929. The complete X-ray data of this compound are listed at the end of this description. It was found that the compound was insoluble and undecomposed by water. Quantitative decomposition into caesium and magnesium fluorides however takes place when a sample is heated for twenty-four hours at 650° in a vacuum. The employment of the nitrogen entrainment technique in the investigations of the reaction between the oxide and the fluoride was

therefore most fortunate as the decomposition of caesium magnesium fluoride in vacuum may otherwise have led to difficulty in the correct interpretation of the course of the reaction and the possible failure of the isolation of the new compound caesium magnesium fluoride.

X-ray data of caesium magnesium fluoride (Cs_3MgF_5)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
3	10.165	0.0312	0.0312	002	4.36
4	11.113	0.0372	0.0379	102	3.99
8	12.099	0.0439	0.0446	112	3.67
10	13.426	0.0539	0.0538	220	3.31
2	13.935	0.0586	0.0581	202	3.19
8	14.497	0.0627	0.0616	221	3.07
7	15.340	0.0700	0.0702	003	2.91
2	15.836	0.0745	0.0751	311	2.82
5	16.228	0.0781	0.0789	103	2.75
1	17.253	0.0879	0.0875	320	2.59
2	18.053	0.0960	0.0953	321	2.48
4	18.882	0.1047	0.1039	213	2.38
6	19.218	0.1084	0.1077	400	2.34
8	19.806	0.1148	0.1144	410	2.27
7	20.722	0.1251	0.1248	004	2.17
3	21.703	0.1367	0.1375	313	2.08
1	23.000	0.1527	0.1523	332	1.968
7	24.070	0.1663	0.1658	422	1.887
6	24.719	0.1749	0.1756	510	1.840
6	25.083	0.1796	0.1786	224	1.815
5	25.870	0.1904	0.1913	333	1.763
3	26.314	0.1964	0.1952	520	1.736
4	26.876	0.2043	0.2048	423	1.702

X-ray data of caesium magnesium fluoride ($CsMgF_3$)
Copper K$_\alpha$ radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
6	27.705	0.2162	0.2154	440	1.654
6	28.263	0.2242	0.2232	441	1.625
2	28.661	0.2300	0.2288	530	1.605
3	29.756	0.2464	0.2459	334	1.550
3	30.312	0.2547	0.2556	305	1.525
3	31.204	0.2684	0.2692	620	1.485
3	32.048	0.2816	0.2808	006	1.450
3	32.742	0.2925	0.2930	504	1.422
4	33.436	0.3036	0.3029	630	1.396
3	33.904	0.3111	0.3107	631	1.380
2	34.551	0.3216	0.3200	524	1.356
4	35.232	0.3328	0.3341	632	1.333
2	35.925	0.3443	0.3443	711 551	1.311
2	36.161	0.3485	0.3481	316	1.303
1	36.784	0.3585	0.3578	641	1.285
1	37.282	0.3669	0.3671	604	1.270
3	38.044	0.3797	0.3812	642	1.249
5	38.971	0.3955	0.3957	117	1.223
3	39.423	0.4032	0.4019	336	1.212
1	39.876	0.4112	0.4105	650	1.200
2	40.283	0.4180	0.4183	651	1.190
5	41.233	0.4344	0.4360	227	1.167
4	42.031	0.4482	0.4495	317	1.149

X-ray data of caesium magnesium fluoride ($CsMgF_3$)

Copper K_α radiation.

	I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
	2	42.621	0.4585	0.4576	820	1.136
	2	43.224	0.4689	0.4692	008	1.124
	3	43.822	0.4794	0.4807	653	1.111
	5	45.033	0.5005	0.5009	803	1.087
	4	45.633	0.5108	0.5096	536	1.076
	1	46.391	0.5242	0.5247	705	1.062
	3	46.979	0.5346	0.5353	654	1.052
	4	47.643	0.5460	0.5462	841	1.041
	5	48.563	0.5620	0.5622	(814 (744	1.027
	4	50.961	0.6033	0.6038	428	0.991
	2	51.851	0.6185	0.6185	109	0.978
	4	52.482	0.6291	0.6302	652	0.970
	2	53.103	0.6395	0.6387	209	0.962
	2	53.510	0.6464	0.6455	219	0.957
	2	53.901	0.6528	0.6528	940	0.951
	4	54.535	0.6635	0.6644	528	0.945
	2	55.108	0.6728	0.6730	1000	0.938
α_1	4	58.080	0.7205	0.7212	951	0.906
α_2	2	58.260				
α_1	2	59.162	0.7372	0.7384	826	0.895
α_2	1	59.347				
α_1	2	60.749	0.7613	0.7605	870	0.881
α_2	1	61.020				

X-ray data of caesium magnesium fluoride ($CsMgF_3$)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
α_1 2	63.087	0.7952	0.7952	961	0.862
α_2 1	63.448				
α_1 3	65.605	0.8294	0.8289	1111	0.844
α_2 2	65.937				
α_1 2	67.264	0.8506	0.8509	1043	0.833
α_2 1	67.672				
α_1 3	69.004	0.8716	0.8725	(1122 (1052	0.823
α_2 2	69.333				
α_1 3	71.739	0.9020	0.9011	3110	0.809
α_2 2	72.073				
α_1 2	72.414	0.9136	0.9146	4210	0.804
α_2 1	73.049				

Lattice constants $a = 9.37_0$ kX - units

$c = 8.70_4$ kX - units

$c/a = 0.929.$

II Investigations of the Reactions between Calcium Oxide and the Alkali Metal Fluorides.

1. Investigation of the reaction between calcium oxide and lithium fluoride.

The investigations of the reactions between magnesium oxide and the alkali metal fluorides have been described in some detail for the purpose of drawing attention to the plan of research adopted in the investigations of these oxide-fluoride reactions. It would be seen that information was best collected on the lines which may be enumerated as follows.

(a) The occurrence of reaction and the conditions governing such an occurrence.

(b) The determination of the lattice constants of all the existing phases in the various intermediate stages of reaction.

(c) The synthesis and crystallography of the double fluorides formed as reaction products.

(d) The possibility of structural interaction between the reactants and resultants.

(e) The co-ordination of thermal analysis data with the observations made on the reactions.

The descriptions of the investigations of the reactions between calcium oxide and the alkali metal fluorides may therefore be given in such a way as to avoid unnecessary repetition of experimental methods and have a more direct bearing on the general problems which confronted the investigations of reactions between metal oxides

and fluorides.

A mixture of calcium oxide and lithium fluoride which contained 10.8 mol.% of the oxide was heated for twenty-four hours at 700° in platinum, with continuous evacuation. The composition of the reaction product approximated to a 12 mol.% oxide content. X-Ray analysis revealed that the pattern of the oxide were scarcely registered on the X-radiogram. This indicated an absorption of the oxide by the fluoride for the reason that an X-radiogram of the original mixture showed the presence of both components with lines of comparable intensities. An increase in the lattice constant of the lithium fluoride by 0.004 kX-units from the value for the pure compound was, in addition, recorded. The direction of change of the lattice constant and the absence of the characteristic pattern of the oxide suggested the formation of a mixed crystal phase between the oxide and the fluoride. The situation was comparable to those met with in the preceding reactions of magnesium oxide and the alkali metal fluorides. It was moreover found that the phenomenon was reproducible. In view of the fact that no new phases were detected by X-ray methods, it was proposed to heat the same reaction product for a further forty-eight hours at 800° under the same experimental conditions. X-Ray diffraction methods showed that complete conversion to calcium fluoride had occurred. Two additional interplanar spacings which corresponded to the spacings of the strongest lines of lithium

oxide gave some support for the assumption of the formation of this compound. The reaction between calcium oxide and lithium fluoride may therefore be represented by the equation

$$CaO + 2LiF \rightarrow CaF_2 + Li_2O$$

The reaction is appreciably rapid when compared to that of magnesium oxide and the same fluoride. No changes in the lattice constant values of calcium and lithium fluorides from the standard values for the pure substances could be detected in the data obtained from the X-radiogram of this reaction product. The absence of mixed crystal formation between calcium fluoride and lithium fluoride in the composition range 13 - 65 mol.% was, in addition, established separately. No thermal analysis data for the system LiF-CaF_2 have been reported. Investigations conducted on the possible formation of double fluorides by sintering stoichiometric mixtures of the constituent fluorides established the absence of such compounds.

2. Investigation of the reaction between calcium oxide and sodium fluoride.

The similarities in the relative structural constants of calcium oxide and sodium fluoride have been enumerated in the general introduction to the descriptions of these reactions. A parallelism could therefore be drawn between this pair of reactants and magnesium oxide and lithium fluoride. Any reaction was therefore of interest as the apparent generalities which were manifested in the preceding reaction between magnesium oxide and lithium fluoride could be either extended or shown to be only particular for the reaction in question.

A mixture containing 10.1 mol.% of calcium oxide was heated for twenty-four hours at 650° in platinum in a vacuum. The product was in the form of a friable mass. An X-radiogram obtained with a specimen of this reaction product showed incomplete reaction to calcium fluoride and sodium oxide. No changes in the lattice constants of the calcium and sodium fluorides present in the reaction product, from the standard values obtained for the pure compounds could be detected. The constant of the oxide remained unchanged as well. It appeared possible that the extent of reaction had reached such a stage that any intermediate mixed crystal phase formed by the oxide and the fluoride was no longer present. A stage of reaction which was considered initial by the fact that an X-radiogram of the product showed only the three strongest lines of calcium fluoride was obtained by heating a mixture

containing 10.2 mol.% of the oxide for twenty-four hours at 600° in vacuum. No changes in the lattice constant of the sodium fluoride could be detected from the data obtained from this X-radiogram. It was to be inferred that no intermediate mixed-crystal phase could be isolated in this reaction. This was confirmed by the failure to detect such a stage in several reaction products which showed either the absence of reaction or its initial stages. A possible explanation, apart from the actual denial of the existence of such a state in this reaction, is that the intermediate phase is of insufficient stability for it to be isolated at room temperature. The problem is dealt with in greater detail in the discussion of these reactions. Attempts to obtain complete reaction between the oxide and fluoride showed that the reaction was slow. A mixture containing 10.0 mol.% of the oxide was heated for five days at 600° under the same experimental conditions. X-Ray analysis showed incomplete reaction under these conditions. The lattice constants of the resulting calcium fluoride and the calcium oxide and sodium fluoride present in excess showed no changes from the values of the pure compounds at any of the stages of reaction that were investigated.

The absence of mixed crystal formation between calcium fluoride and sodium fluoride was established for the range 33 - 66 mol.% by sintering appropriate mixtures of the two fluorides for twenty-four hours at 650° in nitrogen. This

is in agreement with the thermal analysis data of the system NaF - CaF_2 reported by Fedotieff and Iljinski (Z. anorg. u. allgem. Chem. 1923, 129, 151). Absence of double fluorides of calcium and sodium was also established on the results of these experiments.

The reaction between calcium oxide and sodium fluoride could be represented by the equation

$$CaO + 2NaF \rightarrow CaF_2 + Na_2O$$

The complete list of data which were obtained from the X-radiogram of the reaction product of the oxide and fluoride at 650° is tabulated below as representative of the method by which conclusions were normally drawn in the X-ray investigations of these reactions.

Identification of new phases at 650°. Copper K_α radiation.

	New phases			Calcium fluoride		Sodium oxide	
	I	θ	d	d	I/I_1	d	I/I_1
	6	14.111	3.16	3.16	0.67	3.20	0.7
	3	23.109	1.96			1.962	1.0
	6	23.532	1.93	1.93	1.00		
	2	33.560	1.39			1.39	0.7
	3	34.398	1.36	1.370	0.23		
	3	38.004	1.230	1.256	0.23		
	2	38.650	1.232			1.252	0.6
	3	43.767	1.112	1.117	0.30		
	1	47.231	1.048	1.050	0.10		
α_1	2	52.980	0.963	0.968	0.05		
α_2	1	53.104					
α_1	2	56.409	0.924	0.925	0.07	0.926	0.5
α_2	1	56.582					
α_1	2	63.181	0.862	0.866	0.05		
α_2	1	63.40					
α_1	2	67.722	0.831	0.835	0.02	0.836	0.5
α_2	1	68.029					

3. Investigation of the reaction between calcium oxide and potassium fluoride.

The investigation of the reaction between calcium oxide and potassium fluoride was of interest in the possible formation of the compound potassium calcium fluoride ($KCaF_3$). The existence of this double fluoride has been established[3] by Krause and Bergmann (Compt. rend. acad. sci. U.R.S.S. 1942, 35, 20). No crystallographic data have however been reported for the compound which may otherwise have shown what relationships exist between this compound and the corresponding magnesium compound ($KMgF_3$).

A mixture containing 10.4 mol.% of the oxide was heated for twenty four hours at 750° in platinum in a vacuum. Considerable sintering was found to occur. An X-radiogram of this reaction product showed the presence of the original components together with two extra lines of "d" = 2.18 and 1.780 and "I" = 2 and 1, respectively. These values were not indicative of the formation of calcium fluoride, which eliminated the possibility of the occurrence of a double decomposition reaction. Calculation of the lattice constants of the reactants present in excess showed that while no change was discernible in the value of the oxide, that of the fluoride showed a decrease of 0.003 kX-units from the standard value obtained for the pure substance. The phenomenon was apparently another instance of the

occurrence of mixed crystal formation between an oxide and a fluoride at the initial stages of interaction.

It was found possible to synthesise potassium calcium fluoride by sintering a mixture which contained the stoichiometric proportions of the constituent fluorides for twenty four hours at 700° in nitrogen. Standard data obtained from an X-radiogram of this compound suggested its formation in the reaction between calcium oxide and potassium fluoride.

The definite formation of potassium calcium fluoride was established from the data obtained from an X-radiogram of the product of a run with a mixture containing 10.3 mol.% of the oxide, at 780° for twenty four hours. Attempts at complete reaction were impracticable because of the relatively high volatility of potassium fluoride at this temperature.

No thermal analysis of the system $KF - CaF_2$ has been reported. The possibility of mixed crystal formation between potassium fluoride and potassium calcium fluoride was however eliminated by X-ray studies of sintered products of the constituent fluorides at 700° in the range 33 - 66 mol.%. Potassium calcium fluoride was the only product formed in these investigations, which, in addition, shows that a compound of the formula K_2CaF_4 cannot be obtained by these methods.

It was found possible to assign a monoclinic structure

to potassium calcium fluoride with $a = b = c = 8.30$ kX-units and $\beta = 92^{\circ}36'$. Details of the methods employed and the complete data for the compound are described in the section on monoclinic structures.

The potassium fluoride present in the reaction products of oxide-fluoride mixtures heated for twenty four hours at 760° showed no variation in its lattice constant value from that of the pure compound. The reaction is therefore analogous to those previously described which showed intermediate mixed crystal formation. The presence of potassium oxide in the reaction product at 760° could not be established. The absence of any other phases is however sufficient justification for the assumption that the reaction between calcium oxide and potassium fluoride could be represented by the equation

$$3KF + CaO \rightarrow KCaF_3 + K_2O$$

4. Investigation of the reaction between calcium oxide and rubidium fluoride.

The existence of the compound rubidium magnesium fluoride and its formation as a reaction product by interaction of magnesium oxide and rubidium fluoride suggested the possibility of the formation of an analogous compound in the reaction of calcium oxide with the same fluoride. The existence of a double fluoride of the formula $RbCaF_3$ has not been previously reported, a fact which attached some importance to the investigation of the reaction to be described.

Mixtures containing approximately 20 mol.% of the oxide were employed in these investigations. The reasons for adopting these proportions have been discussed in the description of the reaction between magnesium oxide and the same fluoride. An X-radiogram of a mixture containing 20.2 mol.% of the oxide showed only the three strongest lines of the oxide phase. A sample of this mixture was heated for twenty four hours at 650° in platinum in an atmosphere of nitrogen having an excess pressure of about 15 cm. of mercury. The product showed heavy sintering and a loss in weight of approximately 2% of that of the original mixture. An X-radiogram of this product showed that complete interaction had occurred. Calcium fluoride could not be detected as a constituent of the reaction

product which signified the possible formation of a double fluoride of calcium and rubidium.

It was found possible to prepare the compound rubidium calcium fluoride ($RbCaF_3$) by sintering a stoichiometric mixture of the constituent fluorides at 650° in nitrogen. Standard data obtained from an X-radiogram of this compound proved that it was formed in the reaction between calcium oxide and rubidium fluoride. Rubidium oxide was, in addition, detected in the reaction product, which made possible the representation of the reaction by the equation

$$3RbF + CaO \rightarrow RbCaF_3 + Rb_2O$$

No change in the lattice constant value of the rubidium fluoride present in excess, in the reaction product, from the standard value for the pure compound could be detected. A similar experiment conducted with a mixture containing 20.0 mol.% of the oxide for four hours gave a reaction product which on X-ray analysis was found to contain only a small proportion of rubidium calcium fluoride. This assumption was based on the fact that only the three strongest lines of rubidium calcium fluoride were registered on an X-radiogram of a specimen of this product. The determination of the lattice constant of the rubidium fluoride present in this reaction product gave a value of $a = 5.620 \pm 0.001$ kX-units which is identical with the value previously determined for the pure compound. Similar results obtained with reaction products showing only the

initial stages of reaction indicated that a mixed crystal phase between the oxide and the fluoride could not be isolated.

No thermal analysis data of the system $RbF - CaF_2$ are available. There were however no indications of mixed crystal formation between these two fluorides in the range 33 - 66 mol.% when suitable mixtures were sintered for twenty four hours at 625° in nitrogen. Rubidium calcium fluoride ($RbCaF_3$) was invariably the reaction product in these investigations. The results also suggest that a possible second double fluoride of the formula Rb_2CaF_4 cannot be prepared by these methods.

Rubidium calcium fluoride was found to be decomposed by water into calcium fluoride and rubidium fluoride. A similar decomposition occurs when the compound is heated in a vacuum at 700°. The compound was found to be cubic with $a = 4.443 \pm 0.001$ kX-units. The complete X-ray data of this compound are listed below.

X-ray data of rubidium calcium fluoride ($RbCaF_3$).

Copper K_α radiation.

I		θ	$\sin^2\theta$	hkl	Σh^2	Increment	a	d
1		9.975	0.03003	100	1	0.03003		4.44
10		14.177	0.05999	110	2	0.03000		3.14
7		17.456	0.08995	111	3	0.02999		2.57
8		20.283	0.12015	200	4	0.03004		2.22
8		25.134	0.18044	211	6	0.03007		1.811
7		29.366	0.24038	220	8	0.03005		1.569
6		33.250	0.30061	310	10	0.03006		1.405
4		35.094	0.33047	311	11	0.03004		1.338
5		36.893	0.36032	222	12	0.03003		1.282
α_1	6	40.309	0.42007	321	14	0.030005	4.4378	1.186
α_2	2	40.504						
α_1	2	45.875	0.48040	400	16	0.030003	4.4379	1.109
α_2	1	45.981						
α_1	6	47.291	0.54001	330 411	18	0.030001	4.4381	0.999
α_2	2	47.412						
α_1	6	50.767	0.59965	420	20	0.029993	4.4386	0.993
α_2	2	50.888						
α_1	4	54.319	0.65974	332	22	0.029989	4.4388	0.947
α_2	1	54.485						

X-ray data of rubidium calcium fluoride ($Rb\ CaF_3$).

Copper K_α radiation (contd.)

I		θ	$\sin^2\theta$	hkl	Σh^2	increment	a	d
5	α_1	58.022	0.71952	422	24	0.029980	4.4395	0.906
2	α_2	58.218						
8	α_1	61.982	0.77942	431 510	26	0.029978	4.4396	0.871
3	α_2	62.230						
7	α_1	71.443	0.89868	521	30	0.029956	4.4413	0.811
3	α_2	71.696						
4	α_1	78.244	0.95826	440	32	0.029946	4.4421	0.785
2	α_2	78.965						

Extrapolated value a = 4.443 ± 0.001 kX-units.

5. Investigation of the reaction between calcium oxide and caesium fluoride.

The investigations of the reaction between magnesium oxide and caesium fluoride resulted in the discovery of the new compound caesium magnesium fluoride. It was therefore of interest to investigate the possibility of reaction between calcium oxide and caesium fluoride to detect the possible formation of an analogous calcium compound.

An X-radiogram of a mixture of calcium oxide and caesium fluoride which contained 20.0 mol.% of the oxide showed that all the oxide lines with Bragg angles less than 45° were recorded. The presence of calcium oxide could therefore be established with a degree of certainty in these mixtures, though a determination of its lattice constant was not possible. The first attempt at reaction was by heating a mixture containing 20.2 mol.% of the oxide for four hours in a platinum boat at 600° in an atmosphere of nitrogen which had an excess pressure of 10 - 15 cm. of mercury. An X-radiogram of this reaction product showed the existence of both the reactants together with at least one new phase which did not contain calcium fluoride. There was no change in the value of the lattice constant of the caesium fluoride in this reaction product from that of the pure compound. The existence of intermediate structural states of the nature of mixed crystals was therefore deemed most unlikely.

Attempts at the synthesis of a double fluoride of calcium and caesium resulted in the isolation of a new compound, caesium calcium fluoride ($CsCaF_3$). The synthesis was effected by sintering a stoichiometric mixture of the constituent fluorides for twenty-four hours at 600° in nitrogen. Conversion to the double fluoride was attended by considerable expansion of the reaction mass, a phenomenon which was common to all the syntheses of the double fluorides investigated. Standard X-ray data obtained for this compound permitted the confirmation of its formation in the reaction between calcium oxide and caesium fluoride.

Complete reaction between calcium oxide and caesium fluoride was obtained by heating a mixture which contained 20.0 mol.% of the oxide for twenty-four hours at 650° with the usual inert gas technique. The caesium fluoride present in excess was found to have a lattice constant value identical with that of the pure compound. It was to be inferred therefore that no mixed crystal formation occurs between caesium fluoride and caesium calcium fluoride. This was found to be true of calcium fluoride and caesium calcium fluoride as well. Experimental evidence for this statement was obtained from the lattice constants of the compounds concerned in products obtained by sintering mixtures of calcium fluoride and caesium fluoride containing 33 mol.% and 66 mol.% of caesium fluoride for twenty-

four hours respectively, caesium calcium fluoride ($CsCaF_3$) was invariably the reaction product, which also points to the absence of the formation of a double fluoride of the formula Cs_2CaF_4.

Caesium calcium fluoride was found to be decomposed by water into calcium fluoride and caesium fluoride. Decomposition on the same lines occurred when the compound was heated for twenty-four hours at 700° in a vacuum. It was also noticed that the compound assumed a dark buff coloration when exposed to X-rays. The colour gradually faded when the specimen was removed from the source. It is possible that the compound has interesting luminescent properties. Caesium calcium fluoride was found to have a simple cubic structure with $a = 4.514 \pm 0.001$ kX-units. The complete X-ray data for this compound are listed at the end of this description.

A complete X-ray analysis of the reaction product obtained by sintering a mixture of calcium oxide and caesium fluoride at 650° showed conversion of the reactants to caesium calcium fluoride and caesium oxide. The course of the reaction may therefore be represented by the equation

$$3\,CsF + CaO \rightarrow CsCaF_3 + Cs_2O$$

X-ray data of the compound caesium calcium fluoride ($CsCaF_3$)
Copper radiation.

I	θ	$\sin^2\theta$	h k l	Σh^2	increment	a	d
4	9.919	0.02965	100	1	0.02965		4.47
10	14.206	0.05874	110	2	0.02937		3.17
8	17.242	0.08787	111	3	0.02929		2.60
10	20.004	0.11702	200	4	0.02926		2.25
3	22.496	0.14639	210	5	0.02928		2.01
10	24.775	0.17561	211	6	0.02927		1.835
8	28.912	0.23372	220	8	0.02922		1.591
4	30.830	0.26271	221 300	9	0.02919		1.501
8	32.717	0.29209	310	10	0.02921		1.424
6	34.498	0.32074	311	11	0.02916		1.358
5	36.280	0.35019	222	12	0.02919		1.300
2	38.031	0.37951	320	13	0.02920		1.249
α_1 10	39.677	0.40765	321	14	0.029118	4.5048	1.204
α_2 4	39.767						
α_1 2	43.044	0.46589	400	16	0.029118	4.5048	1.126
α_2 1	43.234						
α_1 3	44.689	0.49467	322 410	17	0.029100	4.5063	1.093
α_2 2	44.795						
α_1 8	46.350	0.52355	330 411	18	0.029086	4.5075	1.062
α_2 3	46.471						
α_1 2	48.041	0.55239	331	19	0.029073	4.5085	1.034
α_2 1	48.162						
α_1 8	49.702	0.58173	420	20	0.029087	4.5074	1.008
α_2 3	49.853						

X-ray data of the compound caesium calcium fluoride ($CsCaF_3$)
Copper K radiation.

I	θ	$\sin^2\theta$	hkl	Σh^2	increament	a	d
α_1 2	51.383	0.61052	421	21	0.029073	4.5085	0.984
α_2 1	51.533						
α_1 7	53.114	0.63967	332	22	0.029076	4.5082	0.961
α_2 2	53.265						
α_1 8	56.601	0.69701	422	24	0.029042	4.5108	0.921
α_2 3	56.828						
α_1 2	58.439	0.72610	430 500	25	0.029044	4.5097	0.902
α_2 1	58.610						
α_1 2	60.330	0.75502	431 510	26	0.029039	4.5111	0.885
α_2 1	60.587						
α_1 4	62.323	0.78426	333 511	27	0.029047	4.5105	0.868
α_2 2	62.565						
α_1 5	66.566	0.84183	432 520	29	0.029029	4.5118	0.838
α_2 2	66.883						
α_1 8	68.921	0.87058	521	30	0.029019	4.5126	0.824
α_2 3	69.283						
α_1 6	74.507	0.92866	440	32	0.029021	4.5125	0.798
α_2 3	74.990						
α_1 5	78.055	0.95717	441 522	33	0.029005	4.5137	0.786
α_2 2	78.765						
α_1 8	83.219	0.98601	433 530	34	0.029000	4.5140	0.774
α_2 3	84.532						

Extrapolated value a = 4.514 ± 0.001 kX-units.

III Investigations of the Reactions between Strontium Oxide and the Alkali Metal Fluorides.

1. Investigation of the reaction between strontium oxide and lithium fluoride.

The investigations between strontium oxide and the alkali metal fluorides were adopted as a sequence to the investigations with magnesium and calcium oxides and the same fluorides. The plan of research was therefore to determine, if possible, the conditions of reaction between strontium oxide and the respective fluorides by the application of X-ray methods to products obtained by sintering mixtures of the oxide and the fluorides under various experimental conditions.

An X-radiogram of a mixture of strontium oxide and lithium fluoride which contained 10.0 mol.% of the oxide showed all the characteristic lines of the individual components. A check on the lattice constants of the reactants was thereby possible in products obtained in the various phases of reaction. A sample of this mixture was heated for twenty-four hours at 650° in a vacuum. The product showed heavy sintering and X-ray analysis of this product showed complete conversion of the strontium oxide to strontium fluoride. Lithium oxide was, in addition, established as a reaction product. The course of the reaction is apparently one of double decomposition which may be represented by the equation

$$SrO + 2\,LiF \rightarrow SrF_2 + Li_2O$$

There were no changes in the lattice constant values of the lithium fluoride and the strontium fluoride present in the reaction mass, from those of the individual compounds. Absence of mixed crystal formation between these two fluorides was therefore to be inferred under these experimental conditions. Verification of this statement was obtained by sintering three mixtures of strontium fluoride and lithium fluoride which contained 33, 50 and 66 mol.% of one of the components, for twenty-four hours at 650° in nitrogen, and subjecting the products to X-ray diffraction. The absence of the formation of double fluorides of strontium and lithium was also to be inferred on the results of these experiments. No thermal analysis data for the system SrF_2-LiF are however available for further evidence of the absence of mixed crystal formation and double fluorides in this particular system.

A mixture of the oxide and fluoride which contained 10.1 mol.% of strontium oxide was then heated for twenty-four hours at 550° in a vacuum. X-Ray analysis of this product indicated that interaction of the components was only in its initial stages. There were no changes in the lattice constants of the individual reactants from those of the pure compounds, which suggested that an intermediate mixed crystal formed between the oxide and the fluoride could not be isolated. This assumption was found to be correct on the basis of the results of a second experiment repeated on identical lines.

2. Investigation of the reaction between strontium oxide and sodium fluoride.

Mixtures which contained approximately 10 mol.% of strontium oxide and 90 mol.% of sodium fluoride were employed in these investigations. A preliminary experiment was performed by heating a mixture which contained 10.0 mol.% of the oxide for twenty-four hours at 650° in a vacuum. X-ray analysis of the reaction product showed that complete interaction had occurred with the formation of strontium fluoride and sodium oxide. No change in the lattice constants of the strontium fluoride and the excess sodium fluoride present in the reaction product, from those of the pure compounds, could be detected. It was to be inferred that double decomposition occurs between strontium oxide and sodium fluoride as given by the equation

$$SrO + 2\,NaF \rightarrow SrF_2 + Na_2O$$

The absence of structural interaction between the products of reaction and the sodium fluoride present in excess was also to be inferred from the results of this experiment. Mixed crystal formation between strontium fluoride and sodium fluoride in the composition range 33 - 66 mol.% was, in addition, shown not to occur, by the usual method of sintering mixtures of the two fluorides for twenty-four hours at 650° in nitrogen and subjecting specimens of the reaction products to X-ray diffraction.

An initial stage of reaction, which was obtained by

heating a mixture containing 10.2 mol% of the oxide for twenty hours at 530° under the same experimental conditions, showed no variation in the lattice constant value of the sodium fluoride from that of the pure substance. The possible existence of an intermediate mixed crystal between the oxide and the fluoride could not, therefore, be established.

The reaction between strontium oxide and sodium fluoride is apparently one of double decomposition in which no intermediate structural states can be isolated. The experiments with mixtures of strontium fluoride and sodium fluoride further indicate the absence of mixed crystal formation between these two compounds in the solid state and the absence of the formation of any double fluorides of strontium and sodium.

3. Investigation of the reaction between strontium oxide and potassium fluoride.

A comparison of the lattice constant value of strontium oxide with that of potassium fluoride showed that a similarity existed between these two constants. Potassium fluoride is face-centred cubic with a = 5.332 kX-units while strontium oxide is of the same lattice type with a = 5.149 kX-units. The reaction between strontium oxide and potassium fluoride was therefore of interest in the possible isolation of an intermediate state of mixed crystal formation between the oxide and the fluoride.

A mixture which contained 10.0 mol.% of the oxide was subjected to X-ray diffraction. The X-radiogram obtained with this specimen showed the characteristic lines of both the components which enabled a check on their lattice constant values to be maintained in the subsequent product of interaction. The first attempt at reaction was made by heating a sample of this mixture for thirty hours at 680° in a vacuum. The reaction product showed no signs of sintering. It was furthermore found that the volatility of potassium fluoride under these experimental conditions was inappreciable. X-Ray analysis of this product established the occurrence of complete reaction with the formation of strontium fluoride and potassium oxide. This was the first instance where structural evidence was available for the formation of potassium oxide; its formation in previous experiments had to be assumed on the absence of any other possible reaction

product. The course of the reaction may therefore be represented by the equation

$$SrO + 2KF \rightarrow SrF_2 + K_2O$$

No changes in the lattice constant values of the potassium fluoride and strontium fluoride in the reaction produced from those of the pure compounds could be detected. It was to be inferred therefore that no structural interaction occurs between the products of reaction and the excess potassium fluoride. Separate experiments were also performed with mixtures of potassium fluoride and strontium fluoride in the composition range 33 - 66 mol.%. Mixtures of the stoichiometric compositions $2SrF_2 : KF$, $SrF_2 : KF$ and $SrF_2 : 2KF$ were heated individually for twenty-four hours at 650° in nitrogen. No changes in the lattice constants of the components of these mixtures could be detected from the data obtained from the X-radiograms of these products. The absence of the formation of double fluorides of strontium and potassium under these experimental conditions was in addition to be inferred from the results of these investigations. No thermal analysis data of the system $KF - SrF_2$ are, however, available for additional evidence of the absence of mixed crystal or compound formation between these two fluorides.

An initial stage of reaction between strontium oxide and potassium fluoride was obtained by heating a mixture which contained 10.0 mol.% of the oxide for twenty-four hours

at 550°. The lattice constant of the potassium fluoride present in this reaction product showed a diminished value of a = 5.328 kX-units in comparison to the value of a = 5.332 kX-units for the pure compound. An initial stage of mixed crystal formation between the oxide and the fluoride can therefore be isolated in this reaction. Similar results were obtained with a run carried out with a mixture containing 10.2 mol.% of the oxide for twenty hours at 600°. No change in the lattice constant value of the oxide phase from that of the pure compound could be detected from the data obtained from the X-radiograms of both these reaction products.

4. Investigation of the reaction between strontium oxide and rubidium fluoride.

Mixtures of strontium oxide and rubidium fluoride which contained approximately 20mol.% of the oxide were employed in these investigations. An X-radiogram of a mixture containing 20.1 mol.% of the oxide showed the presence of all the strontium oxide lines with Bragg angles below about 55°. The establishment of the existence of strontium oxide in reaction products obtained by heating mixtures of this composition therefore appeared possible. A sample of this mixture was heated for three hours at 600° in an atmosphere of nitrogen which had an excess pressure of about 15 cm. of mercury. X-ray analysis of the product indicated an initial stage of reaction because of the appearance of three extra lines over those of the reactants. The data were, however, sufficient to establish the formation of strontium fluoride. No change in the lattice constant of the excess rubidium fluoride from that of the pure compound could be detected. It was therefore to be inferred that no mixed crystal phase between the oxide and the fluoride could be isolated at the initial stages of reaction. Complete interaction between the oxide and fluoride was later found to be possible by heating a mixture containing 20.0 mol.% of the oxide for twenty four hours under the same experimental conditions. Strontium

fluoride and rubidium oxide were established as the reaction products, which justify the representation of the reaction by the equation

$$SrO + 2RbF \rightarrow SrF_2 + Rb_2O$$

A determination of the lattice constant of the strontium fluoride formed gave a value of $a = 5.786 \pm 0.001$ kX-units which is identical with that of the pure compound. Similar observations were made on the lattice constant of the rubidium fluoride present in excess. There was apparently no mixed crystal formation between the products of reaction and the rubidium fluoride, which was in excess of that required for complete interaction with the oxide.

Additional experiments were performed with mixtures of strontium fluoride and rubidium fluoride with an idea of detecting any mixed crystal formation between the two fluorides in the solid state. Three mixtures of the stoichiometric compositions $2SrF_2 : RbF$, $SrF_2 : RbF$ and $SrF_2 : 2RbF$ were heated separately for twenty four hours at 600° in nitrogen. No interaction between the fluorides was found to occur under these experimental conditions. It was therefore evident that no double fluorides of strontium and rubidium could be prepared by this method. There were no changes in the lattice constant values from those of the pure compound. The possibility of mixed crystal formation between these two fluorides in the range 33 - 66 mol.% was thereby

eliminated. No thermal analysis data for the system NaF - BrF_2 are available for additional verification for these conclusions.

5. Investigation of the reaction between strontium oxide and caesium fluoride.

The investigations of the reaction between strontium oxide and caesium fluoride were carried out with mixtures of the oxide and fluoride which contained approximately 20 mol.% of the oxide. An X-radiogram of a mixture containing 19.8 mol.% of the oxide showed all the characteristic lines of strontium oxide with Bragg angle values less than about 55°. A sample of this mixture when heated for two hours at 600° in nitrogen having an excess pressure of about 15 cm. of mercury gave a heavily sintered friable mass. X-ray analysis of this reaction product showed that strontium fluoride was present in small quantities in view of the fact that only the three strongest lines of this compound were registered. No change in the lattice constant of the caesium fluoride from that of the pure compound could be detected. It appeared improbable that the isolation of a mixed crystal between the oxide and the fluoride could be effected under these experimental conditions. Complete conversion of the oxide to strontium fluoride was found possible by heating a mixture containing 20.0 mol.% of the oxide for twenty four hours at 600° in nitrogen.

Caesium oxide was established as an additional reaction product. The reaction between strontium oxide and caesium fluoride may therefore be represented by the

equation

$$SrO + 2CsF \rightarrow SrF_2 + Cs_2O$$

The lattice constant of the caesium fluoride in excess in this reaction product showed no change in its value from that of the pure compound. No structural interaction between the products of reaction and this fluoride may therefore be assumed to occur.

Mixtures of strontium fluoride and caesium fluoride were also heated for twenty four hours at 600° in nitrogen and the products subjected to X-ray diffraction. It was found that no mixed crystal formation occurred in the range 33 - 66 mol.% between strontium fluoride and caesium fluoride under these experimental conditions. In addition, no interaction between the fluorides was found to take place, which shows that stable double fluorides of strontium and caesium cannot be prepared by these methods.

IV Investigations of the Reactions between Barium Oxide and the Alkali Metal Fluorides.

1. Investigation of the reaction between barium oxide and lithium fluoride.

The choice of barium oxide and lithium fluoride as a pair of reactants in the investigations of reactions between metal oxides and fluorides represented that of the fluoride of the smallest with the oxide of the largest lattice dimensions, in the series of reactants investigated. Further interest in the reactions involving the use of barium oxide was stimulated by the fact that some reactions of this oxide with a few halides have been investigated by Hedvall. These previous investigations have been referred to in some detail in the general introduction to the description of these reactions.

Mixtures of barium oxide and lithium fluoride which contained approximately 10 mol.% of the oxide were used in these investigations. An X-radiogram of a mixture containing 10.2 mol.% of the oxide showed the characteristic spectra of both components with comparable intensities. The resolution of the high-angle lines of barium oxide was not particularly sharp, which was a constant disadvantage in this series of experiments.

A sample of this mixture was heated for twenty four hours at 690° in a vacuum. No appreciable loss in weight was recorded. An X-radiogram of a specimen of the reaction product appeared to be of considerable interest as complete

reaction of the oxide had apparently occurred with the production of a new phase which had a simple cubic structure. There was, in addition, no change in the lattice constant of the lithium fluoride present in excess from that of the pure compound. The possibility of mixed crystal formation between the products of reaction and the lithium fluoride present in excess was thereby eliminated. The new phase was obviously not of barium fluoride as shown by the general nature of the diffraction pattern. The possibility of the existence of a double fluoride of barium and lithium was at this stage considered most improbable in view of structural considerations which are detailed in the description of the crystallography of the compound, barium lithium fluoride which was eventually isolated. The synthesis of this compound was effected by heating a mixture of barium fluoride and lithium fluoride for twenty four hours at 630° in nitrogen. Standard data obtained from an X-radiogram of this compound showed that it was formed in the reaction between barium oxide and lithium fluoride. Lithium oxide (Li_2O) was also established as a constituent of the reaction product of the oxide and the fluoride. The reaction between barium oxide and lithium fluoride may therefore be represented by the equation

$$BaO + 3LiF \rightarrow BaLiF_3 + Li_2O$$

An initial stage of reaction was obtained by heating

a mixture containing 10.0 mol.% of the oxide for two hours at 600°. The data obtained from an X-radiogram of this product showed that no change in the lattice constant of the lithium fluoride or the barium oxide from the standard values of the pure compounds occurs at the initial stages of the reaction. The isolation of a mixed crystal phase between the oxide and the fluoride was therefore considered impossible under these experimental conditions.

Mixtures of barium fluoride and lithium fluoride of the stoichiometric compositions $2BaF_2 : LiF$ and $BaF_2 : 2LiF$ were, in addition, heated for twenty four hours at 630° in nitrogen. X-ray analysis of the reaction products showed that barium lithium fluoride ($BaLiF_3$) was the only compound formed in both instances. The possible existence of a double fluoride of the formula Li_2BaF_4 could not therefore be established by these methods. No changes in the lattice constants of any of the phases present in these reaction products from those of the corresponding pure compounds could be detected. It is to be inferred therefore, that no mixed crystal formation occurs between barium lithium fluoride ($BaLiF_3$) and either lithium fluoride or barium fluoride, in the composition ranges investigated.

No thermal analysis data for the system $LiF - BaF_2$ have been reported. The lowest melting points of the systems $MgF_2 - BaF_2 - LiF$ and $MgF_2 - BaF_2 - CaF_2$ LiF have however been studied by Konishi (J. Soc. Chem. Ind. Japan 1936,

38, 209) though no reference to the existence of the discrete compound, barium lithium fluoride, has been given. It was found that this double fluoride was insoluble in and undecomposed by water. The structure of the compound was found to be simple cubic with $a = 3.986 \pm 0.001$ kX-units. The complete crystallographical data for this compound are listed below.

X-ray data of the compound barium lithium fluoride ($BaLiF_3$)
Copper K_α radiation.

I	θ	$\sin^2\theta$	h k l	Σh^2	increment	a	d
10	11.189	0.03765	100	1	0.03765		3.96
10	15.886	0.07499	110	2	0.03750		2.81
10	19.570	0.11216	111	3	0.03739		2.30
8	22.741	0.14945	200	4	0.03736		1.990
8	25.625	0.18705	210	5	0.03741		1.779
10	28.238	0.22389	211	6	0.03732		1.626
8	33.100	0.29822	220	8	0.03728		1.409
6	35.410	0.33571	221 300	9	0.03730		1.328
8	37.645	0.37302	310	10	0.03730		1.260
10	39.820	0.41002	311	11	0.03728		1.202
7	41.994	0.44773	222	12	0.03731		1.150
7	44.138	0.48502	320	13	0.03731		1.105
α_1 10	46.207	0.52113	321	14	0.037224	3.9845	1.065
α_2 4	46.343						
α_1 4	50.526	0.59591	400	16	0.037244	3.9834	0.997
α_2 1	50.647						
α_1 10	52.700	0.63279	322 410	17	0.037223	3.9845	0.966
α_2 4	52.882						
α_1 10	54.920	0.66963	330 411	18	0.037202	3.9855	0.939
α_2 4	55.101						
α_1 10	57.230	0.70706	331	19	0.037214	3.9849	0.914
α_2 4	57.457						

X-ray data of the compound barium lithium fluoride ($BaLiF_3$)
Copper radiation.

I	θ	$\sin^2\theta$	hkl	Σh^2	increment	a	d
α_1 10	59.616	0.74416	420	20	0.037208	3.9853	0.891
α_2 4	59.828						
α_1 10	62.106	0.78125	421	21	0.037202	3.9855	0.870
α_2 4	62.380						
α_1 10	64.811	0.81884	322	22	0.037220	3.9846	0.849
α_2 4	65.083						
α_1 10	70.861	0.89279	422	24	0.037200	3.9856	0.813
α_2 4	71.274						
α_1 10	74.626	0.92974	430 500	25	0.037190	3.9863	0.797
α_2 4	75.139						
α_1 10	79.428	0.96640	431 510	26	0.037171	3.9873	0.782
α_2 4	80.259						

Extrapolated value a = 3.988 ± 0.001 kX - units.

2. Investigation of the reaction between barium oxide and sodium fluoride.

Mixtures of barium oxide and sodium fluoride which contained approximately 10 mol.% of the oxide were employed in the investigations of the reaction between barium oxide and sodium fluoride. The first attempt at reaction was by heating a mixture containing 10.2 mol.% of the oxide for twenty four hours at 650° in a vacuum. The sodium fluoride present in the mixture was found to be inappreciably volatile under these conditions of experiment. The reaction product was a friable mass. X-ray analysis revealed that complete conversion to barium fluoride and sodium oxide had occurred. The reaction between barium oxide and sodium fluoride may therefore be represented by the equation

$$BaO + 2NaF \rightarrow BaF_2 + Na_2O$$

The lattice constant of the sodium fluoride present in excess in the reaction mass showed no change from that of the pure compound. It was to be inferred therefore that no structural interaction occurs between this fluoride and the products of reaction.

The possibility of mixed crystal formation between barium fluoride and sodium fluoride was also investigated by sintering mixtures of suitable composition of the two fluorides for twenty four hours at 650° in nitrogen. Stoichiometric mixtures of the compositions $2BaF_2 : NaF$,

BaF_2 : NaF and BaF_2 : 2NaF were employed. It was found that no interaction between the two fluorides occurred under these experimental conditions. Any double fluorides of barium and sodium cannot therefore be assumed to form under these experimental conditions. There were no changes in the lattice constant values of the barium fluoride and the sodium fluoride in any of these reaction products. It can be inferred that no mixed crystal formation occurs between these two fluorides under the conditions of experiment.

An initial stage of reaction was obtained by heating a mixture containing 10.1 mol.% of barium oxide for five hours at 600° in a vacuum. No change in the lattice constant of the sodium fluoride present in this reaction product from that of the pure compound could be detected. No intermediate mixed crystal formation between the oxide and the fluoride therefore occurs.

3. Investigation of the reaction between barium oxide and potassium fluoride.

The reaction between barium oxide and potassium fluoride was of some interest because of the similarity of the ionic radii of potassium and barium (K^+ = 1.33 A ; Ba^{++} = 1.35 A). The investigations were carried out with mixtures of the oxide and fluoride which contained approximately 10 mol.% of the oxide. The first attempt at reaction was by heating a mixture containing 10.0 mol.% of the oxide for five hours at 600° in a vacuum. The product was a friable mass which showed no loss in weight. X-ray analysis of this product showed partial conversion to barium fluoride. No structural evidence for the existence of potassium oxide (K_2O) was found in the data obtained from this X-radiogram. The reaction was apparently in its initial stages, as shown by the existence of only the four strongest lines of barium fluoride. No change in the lattice constant value of the potassium fluoride present in this reaction product from that of the pure compound could be detected. The assumption of the absence of any stable mixed crystals between the oxide and the fluoride at the initial stages of reaction was therefore justifiable.

Complete reaction was found to occur when a mixture of barium oxide and potassium fluoride containing 10.2 mol% of the oxide was heated for twenty four hours at 650° under the same experimental conditions as described previously.

Barium fluoride and potassium oxide were established as the constituents of the reaction product. The reaction between the oxide and the fluoride may therefore be represented by the equation

$$BaO + 2KF \rightarrow BaF_2 + K_2O$$

There was no change in the lattice constant of the potassium fluoride present in excess in this reaction mass. The same was true of that of the barium fluoride formed as a reaction product. It is to be inferred, therefore, that no mixed crystal formation occurs between these two fluorides under the experimental conditions employed. The thermal analysis of the system KF - BaF_2 has been carried out by Tushin and Bankow (Z. anorg. u. allgem. Chem. 1913, 81, 360) who have shown that only a eutectic is present. Additional experimental verification of the absence of mixed crystal formation between barium fluoride and potassium fluoride was obtained by sintering suitable mixtures of the two fluorides for twenty four hours at 650° in an atmosphere of dry oxygen-free nitrogen having an excess pressure of about 15 cm. of mercury. Three mixtures which corresponded to the stoichiometric proportions $2BaF_2$: KF ; BaF_2 : KF and BaF_2 : 2KF were employed in these investigations. It was found that no interaction occurred between barium fluoride and potassium fluoride which eliminates the possibility of the formation of any double fluorides of potassium and barium under these experimental conditions. In addition,

there were no changes in the lattice constant values of the individual fluorides from those of the pure compounds which showed that no stable mixed crystal formation was possible by sintering mixtures in the composition range 33 - 66 mol.% at 650°.

4. Investigation of the reaction between barium oxide and rubidium fluoride.

A comparison of the values of the structural constants of barium oxide with the corresponding values of rubidium fluoride showed that these two potential reactants had comparable lattice constants (a_{BaO} = 5.520 kX-units; a_{RbF} = 5.620 kX-units). Any reaction between barium oxide and rubidium fluoride was therefore of interest for the possible occurrence of mixed crystal formationbetween the oxide and fluoride.

An X-radiogram of a mixture of barium oxide and rubidium fluoride which contained 20.0 mol.% of the oxide showed only the three strongest lines of barium oxide. The establishment of the existence of this compound in a reaction product of the oxide and fluoride was therefore difficult. Any evaluation of its lattice constant in such instances was, in addition, impossible. A sample of the mixture which contained 20.0 mol.% of the oxide was heated for three hours at a temperature of 600° in an atmosphere of dry oxygen-free nitrogen which had an excess pressure of about 15 cm. of mercury. The product was a heavily sintered mass which showed no appreciable loss in weight. X-Ray analysis revealed that the reaction was in its initial stages as shown by the fact that only the three strongest lines of barium fluoride were present on the X-radiogram. There was no change in the lattice constant of the rubidium

fluoride present in excess, from that of the compound. It therefore appeared improbable that intermediate mixed crystal formation between the oxide and the fluoride occurred at the initial stages of reaction. This assumption was confirmed by the results of a second run carried out under the same conditions of experiment. A similar experiment performed with a mixture containing 20.0 mol.% of the oxide at 550° for three hours showed that no interaction between the oxide and the fluoride occurs under these conditions. The existence of a stable intermediate structural state prior to the occurrence of reaction may therefore be ruled out.

Complete reaction was found to occur when a mixture containing 20.0 mol.% of the oxide was heated for twenty hours at 600° under the same experimental conditions as used in the previous experiments. Barium fluoride and rubidium oxide were established as constituents of the reaction product. The reaction between barium oxide and rubidium fluoride may therefore be represented by the equation

$$BaO + 2\ RbF \rightarrow BaF_2 + Rb_2O$$

There was, in addition, no indication of changes in the lattice constant values of the barium fluoride formed, and the rubidium fluoride present in excess, in the reaction product, from those of the pure compounds. No structural interaction between the products of reaction and the rubidium fluoride present in excess may therefore be assumed to

occur under the particular experimental conditions. Three mixtures of the stoichiometric compositions $2BaF_2 : RbF : RbF$ and $BaF_2 : 2\ RbF$ were however sintered separately for twenty-four hours at 650° in nitrogen. X-Ray methods, when applied to the reaction products, showed that no interaction between barium fluoride and rubidium fluoride occurs under these experimental conditions. The possibility of the formation of any double fluorides of barium and rubidium was thereby eliminated. There were no changes in the lattice constant values of the barium fluoride and the rubidium fluoride present in any of these products, from those of the pure compounds, which made the existence of stable mixed crystal phases between these two fluorides at the temperature employed for the investigations, most improbable. No thermal analysis data for the system BaF_2 - RbF are available for additional confirmation of this assumption.

5. Investigation of the reaction between barium oxide and caesium fluoride.

The reaction between barium oxide and caesium fluoride represented that of the oxide and the fluoride with the largest lattice dimensions in the series of reactants adopted in this research. Mixtures of the oxide and fluoride which contained approximately 20 mol.% of the oxide were employed in the investigations of this reaction. An X-radiogram of a mixture containing 20.1 mol.% of the oxide showed only the three strongest characteristic lines of barium oxide, which made the definite establishment of the presence of this compound in subsequent reaction products, difficult. A sample of the mixture which contained 20.1 mol % of the oxide was heated for three hours at 600° in an atmosphere of nitrogen having an excess pressure of about 15 cm. of mercury. The reaction product was a friable mass which showed no appreciable loss in weight. X-Ray analysis of this reaction product showed that complete interaction with the formation of barium fluoride and caesium oxide had occurred. The reaction may therefore be represented by the equation

$$BaO + 2\,CsF \rightarrow BaF_2 + Cs_2O$$

There was no change in the lattice constant of the caesium fluoride present in excess, which indicated absence of structural interaction between the products of reaction and this fluoride. The barium fluoride was found to have a

lattice constant of 6.183 $\pm$ 0.001 kX-units, which is identical with that of the pure compound.

No thermal analysis data for the system BaF_2 - CaF_2 are available. The possible formation of mixed crystals between caesium fluoride and barium fluoride was therefore investigated by sintering suitable mixtures of the two fluorides for twenty-four hours at 630° in an atmosphere of nitrogen. Mixtures corresponding to the stoichiometric proportions of 2 BaF_2 : CsF ; BaF_2 : CsF and BaF_2 : 2 CsF were employed. The application of X-ray diffraction methods to the end products of these experiments showed that no formation of any double fluorides of barium and caesium could be detected under these experimental conditions. The lattice constant values of the barium fluoride and the caesium fluoride present in these products showed no changes from the values of the pure compounds. No structural interaction can therefore be assumed to occur under these conditions of experiment. An initial stage of reaction between the oxide and the fluoride was obtained by heating a mixture which contained 20.1 mol.% of barium oxide for an hour at 500° under the conditions used in the previous experiments. No change in the lattice constant value of the caesium fluoride present in the reaction product from that of the pure compound could be detected. It appeared most improbable therefore, that a stable mixed crystal between the oxide and the fluoride could be isolated by these experimental methods.

V Investigations of the Reactions between Zinc Oxide and the Alkali Metal Fluorides.

1. Investigation of the reaction between zinc oxide and lithium fluoride.

The results of the investigations of the reactions between the alkali metal fluorides and magnesium, calcium, strontium and barium oxides, show that some gradation of the reactivity of a particular oxide with the series of fluorides was manifested. This aspect of reactions between metal oxides and fluorides will be treated at greater length in the discussion of the general nature of oxide-fluoride reactions. It appeared advisable, however, that the additional investigations of the reactions of an oxide such as zinc oxide with the individual alkali metal fluorides would be of considerable importance in the confirmation of any generalities which could be drawn from the results of the previous investigations. A distinction of fundamental character between zinc oxide and the other oxides employed in these investigations is that this oxide is tetragonal in its structure as opposed to the face-centred cubic lattices of the others. Experiments involving the use of zinc oxide were performed on similar lines to those followed in the previous reactions investigated. Attempts were made to study the courses of the individual reactions by the application of X-ray methods. Mixtures of zinc oxide and lithium fluoride which contained approximately 10 mol.% of zinc oxide were employed in these investigations. An X-radiogram of a mixture containing 20.0 mol.% of the oxide showed the characteristic lines of both components

with comparable intensities. Attempts at reaction were made by heating samples of this mixture for seventy-two hours at 650° , 750° and 800° in an atmosphere of dry oxygen-free nitrogen which had an excess pressure of about 15 cm. of mercury. X-ray analysis of the reaction products showed that no interaction between the oxide and the fluoride occurs under any of these conditions. There were no changes in the lattice constant of the lithium fluoride and the Bragg angle values of the high-angle lines of zinc oxide, from the corresponding data of the pure compounds. The possibility of mixed crystal formation between the oxide and the fluoride was therefore eliminated. The formation of zinc fluoride was however established in the reaction product of a mixture containing 20.0 mol.% of the oxide which was heated for six days at 825° under the same experimental conditions as employed previously. There was no structural evidence for the formation of lithium oxide, which is to be expected from the results of the investigations of the reactions of other oxides with lithium fluoride. No change in the lattice constant of the lithium fluoride present in the reaction product from that of the pure compound could be detected. The reaction between zinc oxide and lithium fluoride is obviously extremely slow. It may be assumed however to be one of double decomposition which can be represented by the equation

$$ZnO + 2\,LiF \rightarrow ZnF_2 + Li_2O$$

2. Investigation of the reaction between zinc oxide and sodium fluoride.

Mixtures of zinc oxide and sodium fluoride which contained approximately 10 mol.% of zinc oxide were employed in these investigations. The reaction was found to be comparable with that of lithium fluoride and the same oxide in that samples of a mixture containing 10.0 mol.% of the oxide showed no interaction when heated for seventy-two hours at each of the temperatures of 650°, 750°, and 800° in nitrogen. It was however found that the compound sodium zinc fluoride ($NaZnF_3$) could be prepared by heating a stoichiometric mixture of the component fluorides for twenty-four hours at 650° in nitrogen. The existence of this compound has been shown by Wagner (Ber. 1886, 19, 897). Sodium zinc fluoride was found to be tetragonal with a = 7.74 kX-units, c = 8.13 kX-units and c/a = 1.050. The crystallographical data[5] for this compound are listed[0] at the end of this description. Some formation of this double fluoride was detected in the reaction product of a mixture containing 10.2 mol.% of the oxide which had been heated for six days at 825°. The reaction is apparently extremely slow and may be assumed to occur as represented by the equation

$$ZnO + 3\,NaF \longrightarrow NaZnF_3 + Na_2O$$

There were no indications of the formation of a mixed crystal phase between the oxide and the fluoride in any of the X-radiograms of the reaction products.

X-ray data of sodium zinc fluoride ($NaZnF_3$)
Copper K radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
10	11.459	0.0394	0.0394	200	3.87
5	12.803	0.0491	0.0493	210	3.47
8	16.306	0.0789	0.0788	220	2.74
6	17.166	0.0871	0.0877	221	2.61
3	19.704	0.1136	0.1146	222	2.23
2	21.031	0.1288	0.1281	320	2.14
1	21.680	0.1365	0.1370	321	2.08
10	23.432	0.1581	0.1576	400	1.934
3	23.854	0.1634	(0.1639 (0.1627	(322 (114	1.903
2	24.801	0.1759	0.1764	411	1.834
2	26.074	0.1931	0.1934	402	1.751
4	26.406	0.1978	0.1970	420	1.730
2	26.753	0.2026	0.2033	412	1.709
7	28.912	0.2337	0.2334	105	1.591
7	29.456	0.2419	0.2415	314	1.564
8	31.539	0.2736	0.2728	215	1.471
6	32.943	0.2956	0.2946	521	1.415
2	34.679	0.3238	0.3241	441	1.352
2	35.298	0.3339	0.3349	530	1.331
1	35.910	0.3440	0.3438	531	1.312
5	38.967	0.3955	0.3957	443	1.223
2	40.870	0.4282	0.4287	924	1.175
1	43.995	0.4826	0.4827	700	1.108

X-ray data of sodium zinc fluoride ($NaZnF_3$)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	h k l	d
5	44.961	0.4993	0.4991	336	1.088
2	46.501	0.5272	0.5268	307	1.059
4	47.704	0.5485	0.5480	642	1.039
1	48.388	0.5590	0.5584	335	1.029
1	48.886	0.5677	0.5681	436 806	1.021
1	50.109	0.5887	0.5880	615	1.003
1	51.448	0.6117	0.6116	208	0.984
3	56.813	0.7004	0.7003	328	0.919
α_1 3	58.322	0.7242	0.7241	009	0.903
α_2 2	58.456				
α_1 2	60.995	0.7650	0.7651	636	0.879
α_2 1	61.221				
α_1 2	63.984	0.8075	0.8077	910	0.855
α_2 1	64.301				
α_1 2	64.754	0.8181	0.8185	508	0.850
α_2 1	65.071				
α_1 3	67.310	0.8512	0.8520	664	0.833
α_2 2	67.637				
α_1 2	69.419	0.8764	0.8767	850	0.821
α_2 1	69.842				
α_1 2	74.175	0.9257	0.9263	608	0.799
α_2 1	74.560				

X-ray data of sodium zinc fluoride ($NaZnF_3$)
Copper K radiation.

I	θ	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	hkl	d
α_1 3	77.708	0.9547	0.9555	940	0.787
α_2 2	78.342				
α_1 2	80.894	0.9749	0.9742	771	0.779
α_2 1	81.769				

Lattice constants $a = 7.74_5$ kX- units

$c = 8.13_0$ kX- units

$c/a = 1.050$

3. Investigation of the reaction between zinc oxide and potassium fluoride.

It has been shown that the reactions between zinc oxide and lithium and sodium fluorides are extremely slow. Investigations of the reaction between potassium fluoride and the same oxide indicated that the same property was attached to this reaction as well. Mixtures of zinc oxide and potassium fluoride which contained approximately 10 mol.% of the oxide were employed in these investigations. It was found that no interaction occurred in samples of a mixture containing 10.0 mol.% of the oxide which were heated separately for seventy two hours at 650° and 750° in an atmosphere of nitrogen. Results obtained from X-radiograms of these products showed the absence of any mixed crystal formation between the oxide and the fluoride. The double fluoride of formula $KZnF_3$ was synthesized by heating a stoichiometric mixture of the component fluorides for twenty four hours at 650° in nitrogen. The existence of this compound has been previously reported by Wagner (Ber. 1886, 19, 877). The compound has been indexed as cubic by Goldschmidt (Geochem. Vert. d. Elem. 1927, VIII) with $a = 4.050 \pm 0.005$ kX-units. Naray-Szabo (Muegyetemi Kozlemenyek 1947, No.1, 36) however lists this compound as monoclinic with $a = b = c = 8.10$ kX-units and $\beta \simeq 90°$. It was found that the X-ray data for this compound could be explained on the assumption of a tetragonal unit cell

with a = 6.49 kX-units; c = 6.08 kX-units and c/a = 0.932. The complete data for this compound are listed at the end of this description. Potassium zinc fluoride was established as a reaction product in the mass obtained by heating a mixture containing 10.0 mol.% of the oxide for six days at 600° in nitrogen. There was no evidence for the formation of potassium oxide which is in keeping with similar observations made previously on reactions involving the formation of potassium oxide at 300°. The reaction may therefore be assumed to occur as given by the equation

$$ZnO + 3KF \rightarrow KZnF_3 + K_2O$$

X-ray data of potassium zinc fluoride ($KZnF_3$)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
8	11.000	0.0364	0.0361	002	4.03
4	14.903	0.0661	0.0655	220	2.99
10	15.686	0.0731	0.0737	300	2.84
5	16.843	0.0839	0.0827	301	2.66
5	19.443	0.1107	0.1098	302	2.31
3	21.295	0.1320	0.1310	400	2.12
9	22.392	0.1451	0.1445	004	2.02
4	24.546	0.1727	0.1728	421	1.852
3	25.299	0.1826	0.1835	332	1.800
2	26.505	0.1992	0.1999	422	1.724
5	27.831	0.2179	0.2182	304	1.648
2	29.862	0.2479	0.2490	512	1.545
2	30.513	0.2578	0.2586	205	1.515
5	32.593	0.2901	0.2913	225	1.428
5	32.924	0.2953	0.2948	600	1.416
1	34.070	0.3138	0.3146	532	1.373
1	34.431	0.3197	0.3188	523	1.361
5	37.031	0.3627	0.3637	622	1.277
4	41.257	0.4349	0.4349	641	1.166
1	43.879	0.4805	0.4803	544	1.110
5	45.416	0.5073	0.5072	643	1.080
2	49.512	0.5784	0.5776 (724) 0.5779 (008)		1.012

X-ray data of potassium zinc fluoride ($KZnF_3$) using copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
2	50.148	0.5894	0.5897	660	1.002
1	52.223	0.6249	0.6238	662	0.973
4	53.839	0.6519	0.6516	308	0.953
2	56.763	0.6995	0.6995	902	0.920
α_1 5	58.320	0.7242	0.7233	(655 (336	0.903
α_2 3	58.475				
α_1 2	60.605	0.7592	0.7582	726	0.882
α_2 1	60.846				
α_1 2	64.327	0.8123	0.8126	771	0.853
α_2 1	64.583				
α_1 5	68.621	0.8674	0.8681	950	0.825
α_2 3	69.028				
α_1 6	75.703	0.9390	0.9389	944	0.793
α_2 3	76.246				

Lattice constants $a = 8.49_4$ kX-units

$c = 8.08_9$ kX-units

$c/a = 0.952.$

4. Investigation of the reaction between zinc oxide and rubidium fluoride.

Mixtures of zinc oxide and rubidium fluoride which contained about 20 mol.% of the oxide were employed in these investigations. The choice of these proportions was based on their use in the reactions involving rubidium fluoride and other group II metal oxides. It was found that all the characteristic spectra of the components were registered on an X-radiogram of a specimen of a mixture containing 20.0 mol.% of the oxide. A double fluoride of the formula $RbZnF_3$ was synthesized by heating a stoichiometric mixture of the constituent fluorides for twenty four hours at 630° in nitrogen. It was found that this compound had a tetragonal unit cell with a = 8.69 kX-units; c = 8.00 kX-units and c/a = 0.921. The X-ray data of this compound are listed at the end of this description. Samples of a mixture containing 20.0 mol.% of the oxide were heated for twenty four hours at 600° and 650° in an atmosphere of nitrogen. X-ray analysis of the reaction products showed that no interaction had occurred. There were in addition no indications of mixed crystal formation between the oxide and fluoride. Rubidium zinc fluoride was however identified in the reaction product of a mixture containing 20.2 mol.% of zinc oxide which was heated for four days at 650° in nitrogen. There was no evidence for the presence of rubidium oxide in this product, which may be explained as

being due to the relative complexity of the particular X-radiogram. The reaction may however be assumed to occur as represented by the equation

$$ZnO + 3RbF \rightarrow Rb_3ZnF_3 + Rb_2O.$$

X-ray data of rubidium zinc fluoride ($RbZnF_3$)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
3	14.425	0.0621	0.0626	220	3.09
10	15.901	0.0751	0.0760	212	2.81
5	17.154	0.0870	0.0874	311	2.61
10	18.222	0.0978	0.0986	113	2.46
4	19.430	0.1106	0.1109	321	2.31
2	20.666	0.1246	0.1251	400	2.18
1	22.580	0.1475	0.1475	004	2.00
6	23.816	0.1631	0.1631	114	1.905
5	24.420	0.1710	0.1698	412	1.861
2	25.610	0.1868	0.1866	214	1.780
1	27.238	0.2095	0.2101	224	1.681
7	28.354	0.2255	0.2257	314	1.620
1	29.899	0.2483	0.2492	324	1.544
2	30.551	0.2584	0.2594	441	1.514
7	31.489	0.2728	0.2726	404	1.473
5	32.842	0.2940	0.2931	225	1.419
2	33.822	0.3098	0.3098	523	1.382
7	34.021	0.3130	0.3128	620	1.372
5	34.609	0.3226	0.3220	621	1.354
3	35.242	0.3330	0.3332	443	1.333
1	36.418	0.3524	0.3519	630	1.296
2	38.559	0.3885	0.3888	632	1.234

X-ray data of rubidium zinc fluoride (Rb_2ZnF_3)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hk l	d
1	39.614	0.4065	0.4066	640	1.207
1	40.820	0.4273	0.4279	712 552	1.177
1	42.342	0.4536	0.4536	730	1.142
1	43.864	0.4801	0.4807	445	1.110
5	44.905	0.4983	0.4994	634	1.090
5	47.654	0.5462	0.5452	812 742	1.041
3	50.191	0.5902	0.5901	008	1.001
3	51.597	0.6142	0.6137	705	0.982
2	53.824	0.6515	0.6525	546	0.953
4	55.368	0.6771	0.6781	912	0.935
α_1,3	60.853	0.7628	0.7624	825	0.880
α_2,2	61.048				
α_2,2	64.335	0.8125	0.8122	764	0.853
α_1,1	64.576				
α_1,5	67.093	0.8485	0.8485	329	0.834
α_2,3	67.395				
α_1,3	71.740	0.9018	0.9025	836	0.809
α_2,2	72.162				
α_1,2	74.585	0.9294	0.9288	657	0.797
α_2,1	75.097				
α_1,2	76.303	0.9439	0.9440	1042	0.791
α_2,1	76.876				

Lattice constants $a = 8.69_3$ kX-units

$c = 8.00_6$ kX-units

$c/a = 0.921.$

5. Investigation of the reaction between zinc oxide and caesium fluoride.

Mixtures of zinc oxide and caesium fluoride which contained approximately 20 mol.% of the oxide were employed in these investigations. Preliminary runs carried out with samples of a mixture containing 20.1 mol.% of the oxide showed that no interaction between the oxide and the fluoride occurred when the mixtures were heated for twenty four hours at 600° and 650° in nitrogen. There were, in addition, no indications of the existence of a mixed crystal phase between the oxide and the fluoride in any of these reaction products.

It was however found possible to prepare the compound caesium zinc fluoride ($CsZnF_3$) by heating a stoichiometric mixture of the constituent fluorides for twenty four hours at 650° in nitrogen. The compound was found to be tetragonal with $a = 9.87_5$ kX-units; $c = 9.02_8$ kX-units and $c/a = 0.914$. The complete X-ray data of this compound are listed at the end of this description. Caesium zinc fluoride was identified in the reaction product of an oxide-fluoride mixture containing 20.0 mol.% of the oxide, which was heated for four days at 650° in nitrogen. No evidence for the existence of caesium oxide was present, which may be explained by the relative complexity of the particular X-radiogram. The reaction between zinc oxide and caesium

fluoride may therefore be assumed to occur in the manner represented by the equation

$$ZnO + 3CsF \rightarrow Cs_3ZnF_3 + Cs_2O$$

X-ray data of caesium zinc fluoride (Cs_3ZnF_5)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
2	11.061	0.0368	0.0376	211	4.02
6	12.794	0.0490	0.0485	220	3.87
7	13.759	0.0566	0.0558	221	3.23
2	14.226	0.0605	0.0606	310	3.13
2	16.004	0.0760	0.0773	113	2.79
10	17.029	0.0858	0.0861	321	2.63
2	19.922	0.1161	0.1160	004	2.26
1	20.374	0.1212	0.1212	420	2.21
2	22.575	0.1475	0.1463	214	2.01
1	23.554	0.1596	0.1588	(431 (502	1.926
5	24.461	0.1715	0.1709	304	1.858
2	25.397	0.1813	0.1813	005	1.807
6	28.316	0.2251	0.2251	334	1.622
5	28.859	0.2330	0.2315	611	1.598
3	30.442	0.2567	0.2550	541	1.522
6	32.949	0.2958	0.2969	700	1.415
4	34.043	0.3134	0.3134	543	1.374
2	34.583	0.3221	0.3226	316	1.356
4	35.248	0.3131	0.3338	505	1.333
1	37.087	0.3637	0.3640	416	1.278
1	38.458	0.3863	0.3873	535	1.237
2	40.659	0.4245	0.4237	625	1.181

X-ray data of cesium zinc fluoride ($CsZnF_3$)
Copper K_α radiation.

I	θ	$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	hkl	d
3	41.623	0.4411	0.4411	822	1.158
2	42.256	0.4522	0.4523	407	1.144
2	43.823	0.4794	0.4792	606	1.111
2	44.853	0.4970	0.4969	910	1.091
2	46.491	0.5260	0.5259	912	1.061
2	47.787	0.5486	0.5492	447	1.036
α_1 2	49.339	0.5755	0.5761	646	1.013
α_2 1	49.493				
α_1 2	49.987	0.5866	0.5872	609	1.004
α_2 1	50.167				
α_1 2	52.127	0.6232	0.6237	835	0.974
α_2 1	52.277				
α_1 2	56.537	0.6960	0.6963	339	0.921
α_2 1	56.823				
α_1 2	58.133	0.7217	0.7220	1004 864	0.905
α_2 1	58.400				
α_1 3	60.792	0.7618	0.7623	1102	0.881
α_2 2	61.003				
α_1 2	62.493	0.7860	0.7896	3120	0.867
α_2 1	62.736				
α_1 2	66.986	0.8472	0.8462	907	0.835
α_2 1	67.377				

X-ray data of caesium zinc fluoride ($CsZnF_3$)
Copper K_α radiation.

	I	θ	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	hkl	d
α_1	3	71.521	0.8935	0.9003	668	0.811
α_2	2	71.923				

Lattice constants $a = 9.87_5$ kX - units

$c = 9.02_8$ kX - units

$c/a = 0.914.$

VI Investigation of the reaction between ferric oxide and magnesium fluoride.

The investigation of reactions between metal oxides and fluorides of types different from those of the alkali metal fluorides and group II metal oxides was considered desirable for the study of these reactions from a wider aspect. Ferric oxide was chosen as a potential reactant in view of the fact that it could be prepared in a pure state from carbonyl iron. A survey of the literature showed that this oxide had not been previously reported to react with a metal fluoride. An attempt at reaction between sodium fluoride and ferric oxide by sintering a mixture containing equimolecular proportions of the constituents for twenty four hours at 750° in nitrogen was unsuccessful. It appeared probable, therefore, that for any attempt at successful reaction a fluoride of higher melting point which permitted a higher temperature of experiment should be employed. Magnesium fluoride was eventually chosen, as a quantity of this substance had been previously prepared in a pure state.

The first attempt at promoting reaction between ferric oxide and magnesium fluoride was by heating a mixture containing equimolecular proportions of the reactants for six hours at 1200° in a furnace with access to the atmosphere. An alumina (Triangle RR) boat was employed,

and showed no signs of being attacked under these experimental conditions. The proportions of the reactants relative to each other were based on the theoretical possibility of a mixed metal-oxygen-fluorine compound being formed as given by the equation

$$MgF_2 + Fe_2O_3 \rightarrow MgFe_2F_2O_3$$

This reaction is analogous to the formation of magnesium ferric oxide which can be represented by the equation

$$MgO + Fe_2O_3 \rightarrow MgFe_2O_4$$

A loss in weight of the reaction product produced of about 4% of that of the original mixture was recorded. The product was a dark brown friable mass which showed heavy sintering. X-ray analysis of this product showed the formation of magnesium ferric oxide ($MgFe_2O_4$). Standard X-ray data for this compound were obtained from the lists published by Hanawalt, Rinn and Frevel (Ind. Eng. Chem. Anal. Ed. 1938, 10, 457). The reaction was incomplete as shown by the presence of both the original components of the mixture. There were no indications of any changes in the lattice constants of the reactants, the Bragg angle values of the high-angle lines of the X-radiogram being identical with those for X-radiograms of the pure components. The apparent absence of a reaction product containing fluorine necessitated an explanation as to how the elimination of fluorine from the products of reaction

was effected. The situation was comparable to those previously met with, in the conversion of fluorides to oxides by ignition in air. Two explanations may be put forward to explain the presence of magnesium ferric oxide in this reaction product: (a) heating with access to air permitted the replacement of fluorine by oxygen in a mixed metal-oxygen-fluorine compound (b) the magnesium ferric oxide was formed by a reaction represented by the equation

$$3MgF_2 + 4Fe_2O_3 \rightarrow 3MgFe_2O_4 + 2FeF_3$$

The loss in weight of the reaction product could then be explained on the basis of the replacement of fluorine by oxygen on the assumption of the first explanation and by the volatilization of the ferric fluoride formed on the assumption of the second. Ferric fluoride has been shown to volatilise above 1000° without melting (Poulenc Ann. chim. et phys. 1894, (7), 2, 5).

Further experiments were therefore performed in a dry oxygen-free atmosphere of nitrogen which eliminated the possibility of the replacement of fluorine by oxygen. Magnesium ferric oxide was formed as a reaction product which indicated the occurrence of reaction of the type postulated by equation (b) above. There was however no evidence for the formation of ferric fluoride in the X-radiograms of the reaction products. It was found that the gases leaving the furnace had an irritating odour

reminiscent of silicon tetrafluoride. Moist litmus paper was turned red by these gases. Experiments with mixtures of the reactants were therefore repeated and the exit nitrogen passed through concentrated sulphuric acid and distilled water respectively. A gelatinous suspension which tended to block the delivery tube was formed in the bubbler containing distilled water, after the mixture had been heated for two hours at 1200°. Further experiments were therefore carried out with the delivery tube dipping below a mercury surface. An attempt to isolate the suspension by filtering the contents of the bubbler through a No.42 filter paper showed that the precipitate was dispersed on washing. Hydrofluosilic acid was however established as a constituent of the filtrate by the potassium chloride and alcohol test.

It was to be inferred therefore that ferric fluoride was evolved from the reaction mass and attacked the mullite furnace tube with the formation of silicon tetrafluoride. Thus

$$4FeF_3 + 3SiO_2 \rightarrow 3SiF_4 + 2Fe_2O_3$$

Definite confirmation of the formation of ferric fluoride was however desirable. The experiments were therefore repeated and a rapid stream of nitrogen passed through the system. It was hoped that the ferric fluoride evolved would be carried away in this stream and condense in the cooler regions of the furnace tube prior to inter-

action with the mullite. A feathery deposit was found in the region of the furnace tube immediately outside the luminous part, after five hours at 1200°. X-ray analysis of a specimen of this deposit showed that it was of ferric fluoride. The standard X-ray data of anhydrous ferric fluoride were obtained from the A.S.T.M. card index (first supplementary set). The reaction between ferric oxide and magnesium fluoride may therefore be represented by the equation

$$3MgF_2 + 4Fe_2O_3 \rightarrow 3MgFe_2O_4 + 2FeF_3$$

It was decided to attempt to obtain complete interaction between these two compounds by heating a mixture of composition given by the above equation at 1200° in an atmosphere of nitrogen. The extent of reaction was assumed to be given by the loss in weight entailed by the liberation of ferric fluoride. The course of the reaction was also followed by obtaining X-radiograms of specimens of the reaction products. It was found that the extent of reaction fell rapidly with time and that the reaction had to be promoted at intervals by grinding the products in agate before being subjected to a further period of heating. Complete reaction was attained after a period of fourteen days at 1200°. The mass variations over this period are tabulated on the following page.

Evolution of ferric fluoride from reaction mass.

Days	% loss in weight	Days	% loss in weight
1	8.07	8	1.74
2	4.13	9	1.28
3	1.74	10	0.97
4	1.45	11	0.21
5	4.23	12	0.00
6	2.11	13	0.00
7	1.55	14	0.00

regrounded

regrounded

The variations are also represented graphically in fig. 3. There were no indications of changes in the lattice constants of the magnesium ferric oxide, magnesium fluoride and ferric oxide in the course of the reaction. The magnesium ferric oxide eventually produced was found to have a cubic structure with a lattice constant of "a" = 8.390 $\pm$ 0.001 kX-units. The value of the constant for a sample fired at 1200° by Clark, Alley and Badger (Am. J. Sci. 1931, 22, 539) is "a" = 8.366 $\pm$ 0.001 kX-units. The complete crystallographical data of this compound are listed at the end of this description.

X-ray data of magnesium ferric oxide.

Cobalt K_α radiation.

I		θ	$\sin^2\theta$	hkl	Σh^2	increment	a	d
4		10.671	0.03427	111	3	0.01142		4.83
7		17.603	0.09145	220	8	0.01144		2.96
10		20.778	0.12530	311	11	0.01140		2.52
6		25.342	0.18322	400	16	0.01145		2.09
6		31.581	0.27433	422	24	0.01143		1.706
6		33.801	0.30949	333 511	27	0.01146		1.606
7		37.256	0.36647	440	32	0.01145		1.476
2		42.613	0.45834	620	40	0.01146		1.320
4		44.556	0.49224	533	43	0.01145		1.274
1		47.857	0.54980	444	48	0.01144		1.205
α_1	2	53.182	0.64088	642	56	0.011443	8.3446	1.115
α_2	1	53.364						
α_1	3	55.223	0.67462	553 731	59	0.011434	8.3481	1.087
α_2	2	55.377						
α_1	2	58.815	0.73185	800	64	0.011435	8.3477	1.044
α_2	1	58.989						
α_1	2	65.141	0.82330	660 822	72	0.011435	8.3477	0.984
α_2	1	65.320						
α_1	4	67.813	0.85740	555 751	75	0.011432	8.3486	0.964
α_2	3	68.111						
α_1	3	73.808	0.91462	840	80	0.011433	8.3484	0.933
α_2	2	73.365						

Extrapolated value $a = 8.350 \pm 0.001$ kX-units.

XXI Investigation of the reaction between zirconium dioxide and calcium fluoride.

The investigation of the reaction between zirconium dioxide and calcium fluoride was adopted as a sequel to the reaction between ferric oxide and magnesium fluoride. The point of interest lay in the probable evolution of zirconium tetrafluoride (ZrF_4) from the reaction mass and its subsequent behaviour to the mullite furnace tube.

Mixtures of zirconium dioxide and calcium fluoride were prepared with the proportions of the constituents given by the theoretical equation

$$2CaF_2 + 3ZrO_2 \rightarrow 2CaZrO_3 + ZrF_4$$

The first attempt at reaction was by heating a mixture of the reactants for six hours at 1200° in an atmosphere of dry oxygen-free nitrogen. The exit gases were led through a bubbler containing concentrated sulphuric acid of "Analar" grade, followed by one containing distilled water with a layer of mercury at the bottom. The reaction product was a very heavily sintered mass which had to be subsequently broken up in a percussion mortar. A weight loss of 2.5% of the original mixture was recorded. Specks of a gelatinous material were found in the distilled water at the end of this run. The solution was found to answer the potassium chloride and alcohol test for hydrofluosilic acid which proved that silicon tetrafluoride was present

in the exit gases. The situation was similar to that encountered in the reaction between magnesium fluoride and ferric oxide. X-ray analysis of the reaction product showed that the three strongest lines of calcium zirconium oxide ($CaZrO_3$) were present on the X-radiogram of a specimen of the product. There was no evidence for the formation of zirconium tetrafluoride. The assumption of the reaction between zirconium dioxide and calcium fluoride occurring on the lines given by the equation

$$2CaF_2 + 3ZrO_2 \rightarrow 2CaZrO_3 + ZrF_4$$

was however justifiable, for the reason that the formation of calcium zirconium oxide could not be explained by any other mechanism. Zirconium tetrafluoride has been shown to sublime at temperatures below 1200° by Hott (Trans. Electrochem. Soc. 1917, 31, 374). This property is incidentally a well known practical difficulty in the removal of silica from zirconium compounds with hydrofluoric acid. Experiments were repeated for twenty four hours under the experimental conditions used previously. The evolution of silicon tetrafluoride was confirmed. X-ray analysis of the reaction products showed the definite formation of calcium zirconium oxide. No indications of changes in the lattice constants of the calcium fluoride could be detected in any of these X-radiograms which makes the presence of stable

intermediate mixed crystal formation between the oxide and the fluoride most improbable. Calcium zirconium oxide has been investigated crystallographically by Hagaw (Proc. Phys. Soc. 1946, 58, 114). Monoclinic symmetry has been postulated for this compound but complete crystallographical data are not available. It was however found possible to prepare a sample of calcium zirconium oxide by firing a stoichiometric mixture of the constituent oxides for six hours at 1500°. The data obtained from an X-radiogram of a specimen of this sample were used for the identification of this compound in the reaction products of the oxide and fluoride. Attempts at isolating the zirconium tetrafluoride by passing in a rapid stream of nitrogen were unsuccessful. Subsequent experiments, which were performed to obtain some idea of the rate of reaction; showed that the reaction was extremely slow. The isolation of detectable quantities of zirconium tetrafluoride under these experimental conditions is therefore difficult. A series of experiments were performed to obtain some idea of the loss in weight of a mixture of zirconium dioxide and calcium fluoride when sintered at 1200°. It was found that the loss was inappreciable after about three days under these experimental conditions. Attempts to promote the reaction by grinding the products at twenty four hour intervals appeared to have no appreciable influence on the rate of the

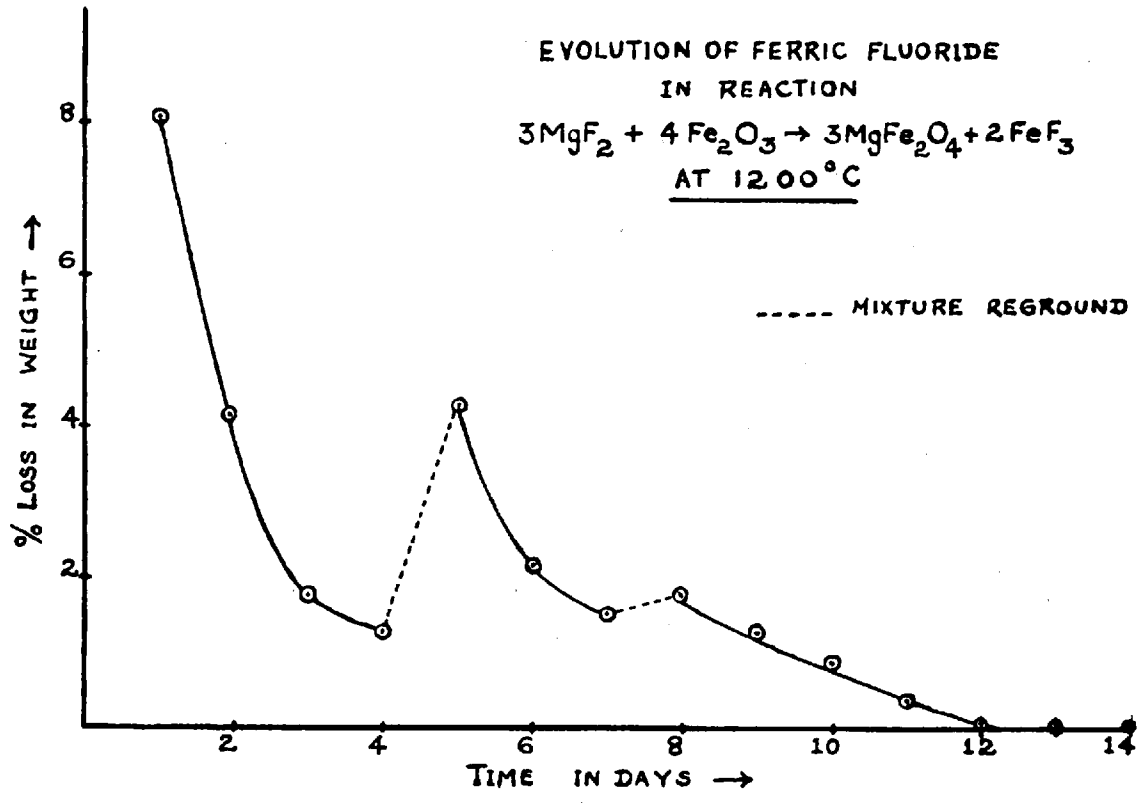
reaction. The weight losses over a period of six days are listed below.

Evolution of zirconium tetrafluoride at 1200°.

Days	% loss in weight
1	4.19
2	2.90
3	0.85
4	0.40
5	0.33
6	0.26

weight of mixture = 7.414 g.
total % loss in weight = 9.03
theoretical % loss for complete reaction = 31.6

These values are also represented graphically in fig. 3. The reaction between zirconium dioxide and calcium fluoride at 1200° is therefore a slow process which is accompanied by the evolution of zirconium tetrafluoride. Interaction of this fluoride with the mullite furnace tube results in the presence of silicon tetrafluoride in the exit gases. The alumina (Triangle RR) boats employed in these experiments showed no signs of being attacked which restricts the formation of silicon tetrafluoride to interaction between the zirconium tetrafluoride and the material of the furnace tube.


EVOLUTION OF FERRIC FLUORIDE
IN REACTION
$3MgF_2 + 4Fe_2O_3 \rightarrow 3MgFe_2O_4 + 2FeF_3$
AT 1200°C
----- MIXTURE REGROUND
% LOSS IN WEIGHT →
TIME IN DAYS →
2
4
6
8
10
12
14

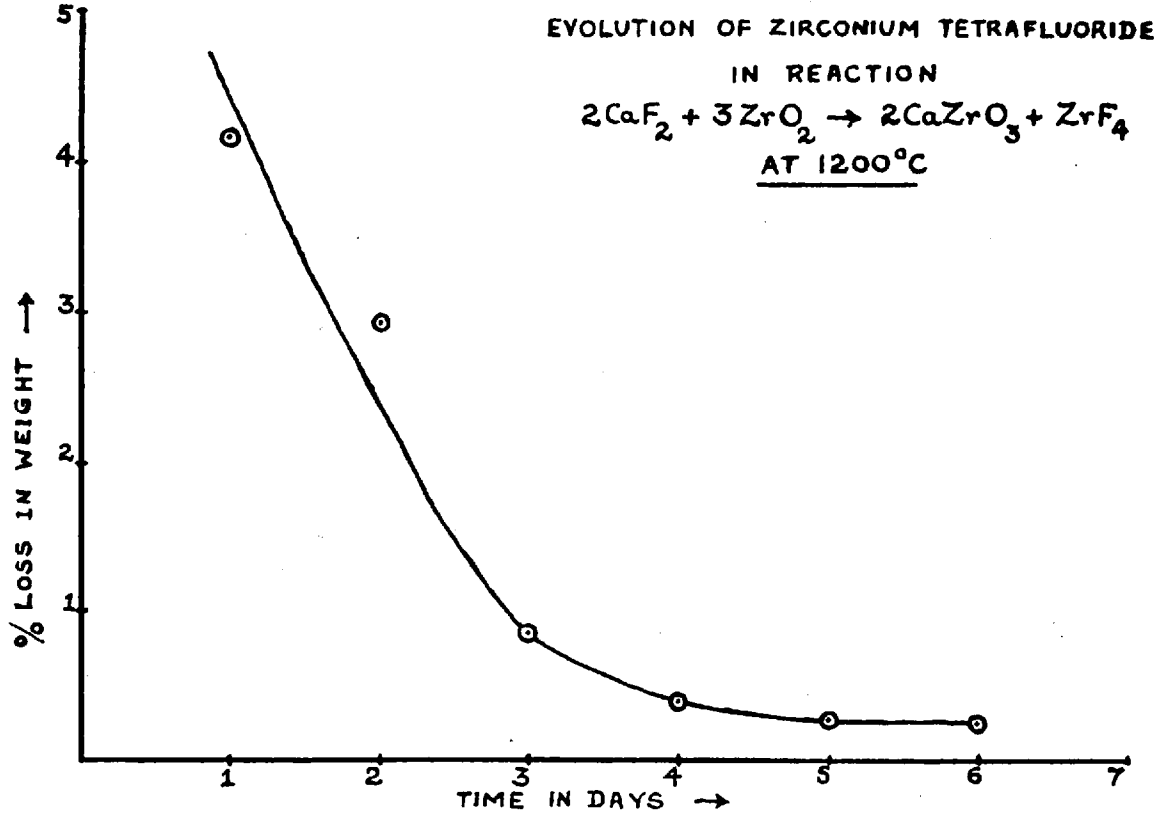

EVOLUTION OF ZIRCONIUM TETRAFLUORIDE
IN REACTION
$2CaF_2 + 3ZrO_2 \rightarrow 2CaZrO_3 + ZrF_4$
AT 1200°C
% LOSS IN WEIGHT →
TIME IN DAYS →
1
2
3
4
5
6
7

FIG. 3.

Part III. Discussion of the reactions between the alkali metal fluorides and magnesium, calcium, strontium, barium and zinc oxides.

Part III Discussion of the reactions between the alkali metal fluorides and magnesium, calcium, strontium, barium and zinc oxides.

The investigations of the reactions between the alkali metal fluorides and the oxides of magnesium, calcium, strontium, barium and zinc have been made by sintering mixtures containing suitable proportions of the reactants under different experimental conditions and subjecting specimens of the products to X-ray diffraction. It was found that under conditions of sintering the reactions were slow. The majority of the reactions needed sintering of mixtures containing approximately 10 mol.% of the oxide for about thirty hours in the temperature range 650° - 750° for complete reaction to occur. A few reactions such as that of magnesium oxide and lithium fluoride were incomplete even after a period of thirty five days under these conditions. The other extreme in these reactions was manifested by barium oxide and caesium fluoride between which reaction was complete in three hours at 600°. Attention has already been drawn, in the introduction to the present research, to the occurrence of a definite "reaction temperature" in the reactions between two inorganic compounds in the solid state. The comprehension of the exact physical significance of this temperature is difficult for the reason that most solid reactions are

"structure sensitive" and the particular reaction temperature would therefore depend on several factors besides the actual "history" of the substances used as reactants. The thermodynamic criterion of the occurrence of reaction in systems composed entirely of solids, as in other systems is that the free-energy change associated with the reaction must be negative.

The co-existence of liquid phases is not unlikely in the reactions investigated. The alkali metal oxides formed as reaction products have, in general, lower melting points than the temperatures reported to for successful reaction. This phenomenon, though postulated probably to occur in these reactions, is one of the chief obstacles to the elucidation of the kinetics of reactions involving two apparently solid phases. The existence of equilibrium states in the reactions investigated is in addition impossible because of the rigorous conditions needed for the occurrence of such a state (Hammann Z. anorg. u. allgem. Chem. 1935, 142, 21).

The procedure adopted in these investigations was to determine the minimum conditions necessary for the onset of a particular reaction. The X-ray criterion of the presence of only a very few characteristic spectra of the reaction products on an X-radiogram was employed for defining such a state. The reaction of the same oxide with the fluoride of the metal homologous to the one employed

previously was then attempted under the same experimental conditions. By this means some idea of the "reactivity" of a particular oxide with the individual alkali metal fluorides was established. The ultimate picture is obviously only qualitative but such a representation of the general characters of these reactions was considered necessary prior to the elucidation of the detailed mechanism of these processes. The adoption of these criteria for the recognition of what may be termed the "reactivity" of a particular oxide with a series of fluorides shows that barium oxide, for instance, manifests this property to about the same degree, in its reactions with each of the alkali metal fluorides. The data listed in the table following show that mixtures of barium oxide and alkali metal fluorides require heating for 2 - 3 hours at 600° for the production of a specimen in which the resultants could be detected by X-ray methods. Caesium fluoride is apparently exceptional in that it requires what may be termed less drastic conditions for the occurrence of reaction with the same oxide. This phenomenon is peculiar to all reactions involving the use of caesium fluoride which may be attributed to the low melting point of the fluorides. Strontium oxide behaves in a fashion similar to that of barium oxide as would be seen from the table following.

Minimum experimental conditions for the occurrence of reaction

	Barium oxide		Strontium oxide	
	period of heating in hours	temperature in °C.	period of heating in hours	temperature in °C.
Lithium fluoride	2	600	24	550
Sodium fluoride	5	600	24	550
Potassium fluoride	5	600	20	625
Rubidium fluoride	3	600	3	600
Caesium fluoride	1	500	2	600

The reaction of potassium fluoride and strontium oxide is an apparent exception in this instance. The constancy of the conditions required for reaction of a particular oxide with a series of fluorides is comparable to the constant "reaction temperatures" of barium, strontium and calcium oxides with sulphides, phosphides, halides and spinels found by Hedvall and his school. Reference has already been made to this phenomenon in the general introduction to the research on these reactions. The generality however breaks down completely in the reactions of magnesium oxide with the alkali metal fluorides. Mixtures of magnesium oxide and sodium fluoride, for instance, needed seventy-two hours at 750° for reaction to be detected; rubidium fluoride and the same oxide on the other hand required only twenty-four hours at 650° . Calcium oxide behaves in a fashion similar

to that of magnesium oxide as would be seen from the table below.

Minimum experimental conditions for the occurrence of reaction.

	Magnesium oxide		Calcium oxide	
	period of heating in hours.	temperature in °C.	period of heating in hours.	temperature in °C.
Lithium fluoride	36	720	24	700
Sodium fluoride	72	750	24	600
Potassium fluoride	40	680	24	750
Rubidium fluoride	24	650	4	650
Caesium fluoride	4½	625	4	600

It has been pointed out by Hedvall and Cohn (Kolloid-Z 1939, 88, 224) that an explanation of the constancy of the reaction temperature of a particular oxide with different classes of compounds is difficult. The same is apparently true of the "reactivities" of a particular oxide with a series of fluorides.

The same data may, however, be employed for discussing the reactions of a particular fluoride with a series of oxides. The results in these instances are more striking when compared to those obtained with the oxides, for the reason that each particular fluoride shows without exception an increasing order of "reactivity" with the oxides of magnesium, calcium, strontium and barium respectively. The results are given in a tabulated form on pages 249 & 250.

It has been pointed out previously that one of the characteristics of reactions between oxides and other classes of inorganic compounds was the decrease of the "reaction temperature" with increase in the basic properties of the oxide. This generality is apparently manifested in the increasing "Reactivity" of a particular fluoride with oxides of increasing basic properties. The comparatively slow rates of reaction of the alkali metal fluorides with zinc oxide add confirmation to this generalization. It is difficult to explain how the basic character of an oxide which is normally the attribute of a solution plays a part in reactions which are essentially solid in their state of occurrence. The explanation probably lies in the fact that the periodicity of properties manifested in the association of solids with liquids has its analogues in the solid state. It is felt that the problem is more fundamental than it appears to be and may be dismissed with these remarks.

Though the similarity in structural constants between particular pairs of oxides and fluorides provided the main impetus for this research, it would be seen that similarity in ion sizes and unit cell dimensions apparently play no obvious part in the actual kinetics of the reactions. The small departures in the lattice constants of some of the fluorides from the values normally associated with the pure compounds are of particular significance in that they imply that absorption of the oxide by the fluoride occurs.

The majority of the instances of this phenomenon failed to show a diminishing of the oxide content by X-ray methods. A few reactions, however, such as that of lithium fluoride with calcium oxide showed appreciable absorption of the oxide prior to reaction. The directions of change in the lattice constants were in all instances in keeping with the postulate of limited mixed crystal formation. The fluorides were in addition heated individually under the same experimental conditions for verification of possible variations in the individual lattice constant values on different heat treatments. It has been shown earlier that the maximum limits of variation detected in such instances were of the order of 0.002 kX-units. The X-ray methods adopted further guaranteed the validity of the results. Typical changes in the lattice constants of potassium fluoride are shown in fig. 4. The reactions involving the use of rubidium fluoride and caesium fluoride were characterised by the absence of instances of intermediate mixed crystal formation. The relatively large ionic radii of rubidium and caesium and the comparative rapidity of the reactions may provide an explanation for the failure to isolate mixed crystals. It was however found that intermediate mixed crystals could be isolated in most of the reactions in which a similarity in the structural constants of the reactants was manifested. The reaction between sodium fluoride and caesium oxide provided an apparent exception in that isolation of mixed crystals was not possible. There

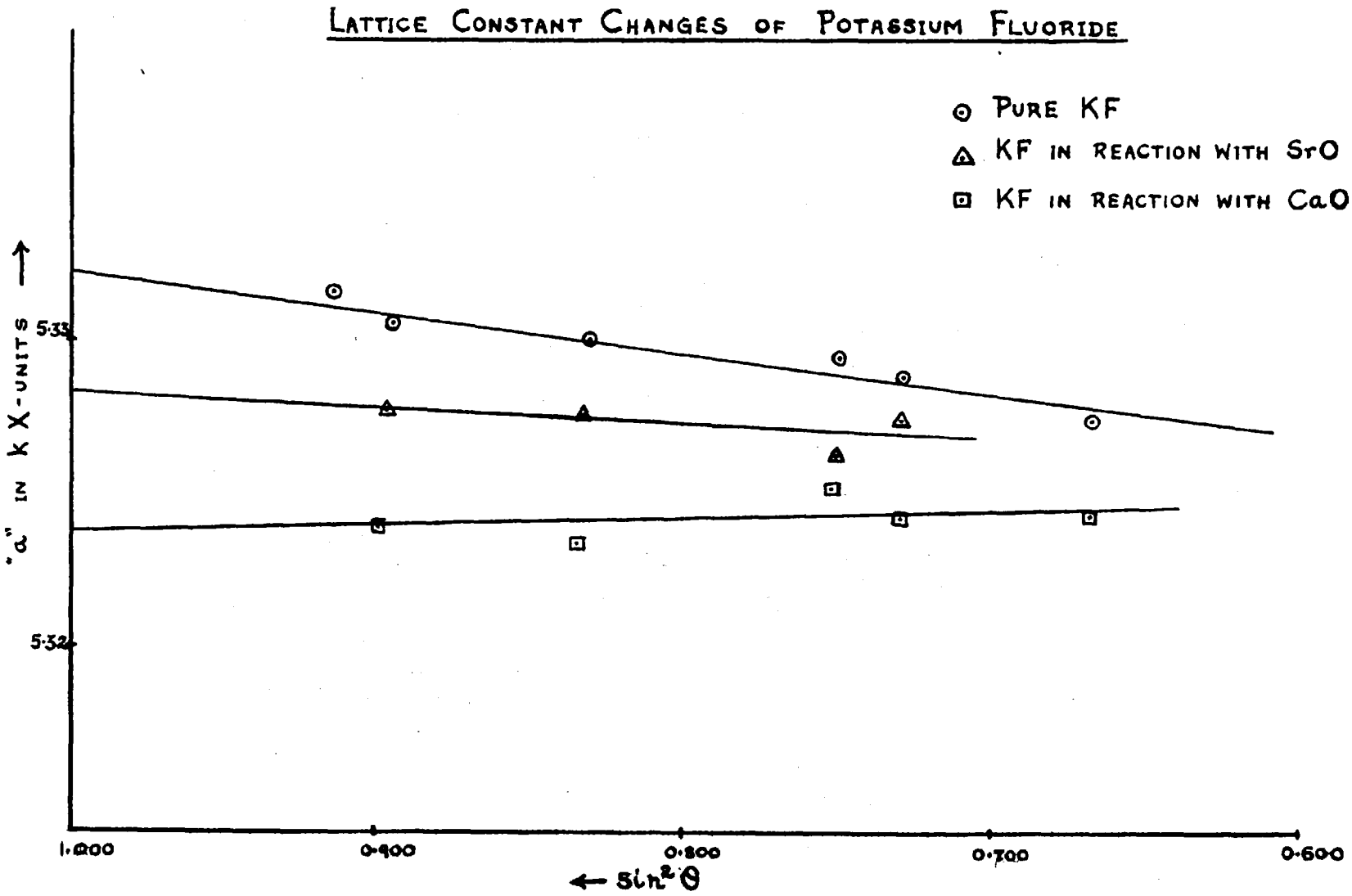

LATTICE CONSTANT CHANGES OF POTASSIUM FLUORIDE
PURE KF
KF IN REACTION WITH SrO
KF IN REACTION WITH CaO
"a" IN kX-UNITS
5·33
5·32
1·000
0·900
0·800
0·700
0·600
← sin²θ

FIG. 4.

is no reason to believe why such a state should not exist. It is probable that such states are found at high temperatures and decompose on cooling to room temperature. Further work with high temperature cameras should give more information on these aspects of mixed crystal formation. The reactions with zinc oxide, on the other hand, though extremely slow, failed to show any intermediate structural states. The dissimilarity in the lattice types of zinc oxide and the alkali metal fluorides, however, make the existence of such states most improbable.

The occurrence of mixed crystal formation between oxides and fluorides of the same lattice type is of considerable theoretical significance in that it shows that fluorine and oxygen ions which have comparable ionic radii ($a_{F^-} = 1.36A$; $a_{O^{--}} = 1.40A$) cannot easily co-exist in the same crystal lattice. It is probable that a mixed oxygen-fluorine lattice is unstable because of the different valencies and polarizabilities of the individual ionic species.

The reaction products were in all instances found to have no structural interaction with the excess of the alkali metal fluorides present. It was unfortunate that the oxides of all the alkali metals were present in such small quantities in the reaction products as to prevent any evaluation of their structural constants.

The reactions themselves could be classified into two groups.

(a) Reactions involving double decomposition e.g.

$$2\,LiF + CaO \rightarrow Li_2O + CaF_2$$

(b) Reactions involving the formation of double fluorides, e.g.

$$3\,KF + MgO \rightarrow KMgF_3 + K_2O$$

There are no outstanding features peculiar to either course of reaction other than the chemical identities of the reactants. There was, in addition, no experimental evidence in reactions which resulted in the formation of double fluorides for a sequence of stages as given by the equations

$$2\,KF + MgO \rightarrow K_2O + MgF_2$$

followed by

$$MgF_2 + KF \rightarrow KMgF_3$$

It is however difficult to maintain, on the results of these investigations, that such an intermediate stage is definitely absent, for the reason that the ability to isolate any intermediate stage would depend on the relative rates of reaction of the individual processes.

The production of double fluorides in the oxide-fluoride reactions necessitated the synthesis of these compounds and their crystallographic examination. Correlation of these results with the thermal analysis data for the relevant binary systems of fluorides, when available, throws more light on the structural interaction of the alkali metal fluorides and those of group II. metals. The absence of mixed crystal formation between magnesium fluoride and

lithium fluoride, contrary to the reports of some workers, shows that further investigations on these systems are necessary. The thermal analyses of the possible binary systems of alkali metal and group II metal fluorides reported in the literature are far from complete. The isolation of the possible double fluorides is however of some help in predicting the general character of the equilibrium diagrams.

A point of interest which arises from the investigations of the reactions between the alkali metal fluorides and group II metal oxides is the apparent absence of formation of compounds of the type $A^{+}_{2}B^{++}F_{4}$. Compounds formulated as K_2MgF_4 and Rb_2MgF_4 are claimed to exist on the basis of thermal analysis data. The elucidation of their structures has however never been attempted. The inability to synthesize these compounds by interaction of the constituent fluorides in the solid state cannot be taken as conclusive evidence of their non-existence for the reason that reactions in the solid state normally give only a single product with all proportions of the reactants (Jander Angew. Chem. 1936, 49, 881).

It is difficult to postulate a general reaction mechanism which would satisfactorily explain the reactions between these metal oxides and fluorides. The reactions are more to be looked upon as a series which occure under conditions of sintering and thereby falls in line with the numerous other such reactions which occur between different classes of inorganic compounds. The apparent individuality of reactions

under conditions of sintering has so far prevented the postulation of a general mechanism which explains all the phenomena normally associated with these reactions. It is probable that the occurrence of several intermediate states in the course of these reactions is responsible for their individuality. The reactions between the alkali metal fluorides and the group II metal oxides show that one other intermediate state of mixed crystal formation has to be added to the diverse phenomena already reported for other systems.

Reactions between alkali metal fluorides and group II metal oxides

Reactants	Lattice constant changes of fluoride.	Minimum reaction. hours. °C		Complete reaction hours. °C		Resultants
LiF + MgO	+ 0.004 kX-units	36	720	-	-	MgF_2 + Li_2O
NaF + MgO	- 0.003 kX-units	72	750	-	-	$NaMgF_3$ + Na_2O
KF + MgO	- 0.004 kX-units	40	680	30	750	$KMgF_3$ + K_2O
RbF + MgO	-	24	650	72	650	$RbMgF_3$ + Rb_2O
CsF + MgO	-	4½	625	48	625	$CsMgF_3$ + Cs_2O
LiF + CaO	+ 0.004 kX-units	24	700	48	800	CaF_2 + Li_2O
NaF + CaO	-	24	600	-	-	CaF_2 + Na_2O
KF + CaO	- 0.003 kX-units	24	760	-	-	$KCaF_3$ + K_2O
RbF + CaO	-	4	650	24	650	$RbCaF_3$ + Rb_2O
CsF + CaO	-	4	600	24	650	$CsCaF_3$ + Cs_2O
LiF + SrO	-	24	550	24	650	SrF_2 + Li_2O
NaF + SrO	-	24	550	24	650	SrF_2 + Na_2O
KF + SrO	- 0.004 kX-units	20	625	30	680	SrF_2 + K_2O
RbF + SrO	-	3	600	24	600	SrF_2 + Rb_2O
CsF + SrO	-	2	600	24	600	SrF_2 + Cs_2O
LiF + BaO	-	2	600	24	650	$BaLiF_3$ + Li_2O
NaF + BaO	-	5	600	24	650	BaF_2 + Na_2O
KF + BaO	-	5	600	24	650	BaF_2 + K_2O
RbF + BaO	-	3	600	20	600	BaF_2 + Rb_2O
CsF + BaO	-	1	500	3	600	BaF_2 + Cs_2O
LiF + ZnO	-	144	825	-	-	ZnF_2 + Li_2O
NaF + ZnO	-	144	825	-	-	$NaZnF_3$ + Na_2O

Reactants	Lattice constant changes of fluoride.	Minimum reaction, hours. °C	Complete reaction, hours. °C	Resultant
KF + ZnO	-	144 600	- -	$KZnF_3$ + K O 3 2
RbF + ZnO	-	96 650	- -	Rb_2ZnF_3 + Rb 3 2
CsF + ZnO	-	96 650	- -	Cs_2ZnF_3 + Cs 3 2

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Part IV The crystallography of the compounds of general formula $A^{+}B^{++}F_3$.

Part IV The crystallography of the compounds of general formula $A^{+}B^{++}F_3$.

(a) Methods employed for indexing monoclinic crystals of the type $a = b = c$ and $\beta \simeq 90^{\circ}$ from powder data.

1. Potassium magnesium fluoride and potassium calcium fluoride.

The compounds potassium magnesium fluoride and potassium calcium fluoride were obtained as reaction products in the reactions of magnesium oxide and calcium oxide with potassium fluoride. A preliminary attempt at indexing the X-ray data of potassium magnesium fluoride showed that the compound was apparently cubic in its lattice type. A few "extra" lines of relative intensities ranging from 3 to 1 present on the X-radiogram of this compound could not however be explained on the assumption of a cubic structure. Repeated attempts to synthesize a specimen of this compound which did not produce these "extra" lines when subjected to X-ray diffraction were a failure. The high crystallinity of the specimens produced in these experiments was evident from the excellent quality of the X-radiograms. The interplanar spacings of the unexplained lines were in addition not characteristic of either of the individual fluorides which were employed in the synthesis. It appeared very probable therefore that the spectra were characteristic of the compound obtained.

Potassium calcium fluoride presented a similar problem.

The crystallinity of this compound was however not of the quality of that of the magnesium compound when prepared by sintering a stoichiometric mixture of the constituent fluorides for twenty four hours at 650°. Diffraction patterns of specimens of this compound which had been heated for fourteen days at 700° in a sealed, evacuated vitreosil tube showed no improvement over those obtained with specimens synthesised directly. Potassium calcium fluoride has apparently a high melting point as the compound was found to fuse only in the flame of a Meker burner which may explain the degree of crystallinity of the material previously obtained. Specimens quenched at 700° in carbon tetrachloride produced X-radiograms identical with those of the specimens subjected to slow cooling. It was evident however that the crystal structures of these compounds were more complex than cubic and attempts were therefore made to explain all the characteristic X-ray spectra of these compounds.

The X-ray data of potassium magnesium fluoride have been indexed as cubic by van Arkel (Physica 1925, 5, 167) who tabulates the $\sin^2\theta$ values for sixteen lines and suggests the presence of a "perovskite" structure on the basis of the relative intensities of the spectra. Frevel (Ind. Eng. Chem. Anal. Ed. 1942, 14, 693) has tabulated a set of cubic isomorphs in which the perovskite structure is claimed to

give a simple cubic pattern with the three strongest sets of lines indexed as 110, 200 and 100, and 211 and 220 respectively. A definite advancement in indexing data of compounds of this type was made by Megaw (Proc. Phys. Soc. 1946, 58, 133). No fluoride structures have however been described by her. Náray-Szabo (Muegyetemi Kozlemenyek 1947, No.1, 36) lists this compound as monoclinic with a = b = c = 8.00 kX-units and $\beta = 90^{\circ}$. He limits his discussion to the oxygen compounds and postulates that monoclinic symmetry is introduced by the tilting of the oxygen octahedra relative to one another. The actual parameters of such compounds have only been determined for perovskite (calcium titanium oxide) by Náray-Szabo (Naturwissenschaften 1943, 31, 203). The detailed crystallography of this class of compounds is evidently far from complete.

The explanation of the individual spectra of potassium magnesium fluoride was attempted by the application of first principles and the drawing of parallels from the work already reported on oxide structures. Use was first made of the $\sin^2\theta$ values to refer the lines as far as possible to an elementary pseudo-cubic cell. The introduction of monoclinic symmetry by the tilting of fluorine octahedra relative to one another would then necessitate the doubling of all three cell edges for the production of an unit cell. On this argument, it was found that lines 2, 5, 7 and 9 in the data given for potassium magnesium fluoride could be

explained as being due to doubled cell edges. The fact that three of these lines had one or more unit indices could be taken as evidence to justify the assumption of the doubling of all the cell edges. Lines 3 and 11 could not however be accounted for on the assumption of doubled cell edges which implied that these lines were produced not by planes of indices so far unknown but by the possible introduction of an angle. The lines were therefore referred to the lines closest to them on the K-radiogram. Line 3 was paired with 4 and line 11 with 12. Pairing in this fasion was considered essential for obtaining an angle closest to 90° as the general character of the K-radiogram suggested only small deviations from this value. Line 4 was found to be indexed as 110 on the pseudo-cubic unit cell. The pair of lines 3 and 4 were therefore assumed to be "split" lines with indices $20\bar{2}$ and 202 or 202 and 220 on the basis of a monoclinic cell with doubled cell edges. The same assumptions were made with lines 11 and 12. All that was then necessary was to calculate a possible angle which explained the data of these pairs of lines. It has been shown that for a monoclinic unit cell

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2/a^2 + l^2/c^2 - 2hl\cos\beta/ac}{\sin^2\beta} + \frac{k^2}{b^2}\right)}}$$

(C.W. Bunn Chemical Crystallography, Oxford University Press, 1949 p.136).

Then assuming that $a = b = c$

$$d^2 = \frac{a^2 \sin^2\beta}{h^2 + l^2 - 2hl\cos\beta + k^2\sin^2\beta}$$

For a pair of lines with interplanar spacings d_1 and d_2 and indices hkl and hKO respectively and $h = K = 1$

$$d_2^2\cos^2\beta - 2d_1^2\cos\beta - 2(d_2^2 - d_1^2) = 0$$

A solution of this quadratic equation with the data obtained from the X-radiogram gave a value of $\beta = 85^\circ$ which appeared to be unsuited for the type of distortion postulated here. In addition, an attempt to calculate a lattice constant value on the assumption of an angle of 85° with the data of the high angle lines showed that no constant value could be obtained. The possibility of the lines being due to h 0 l and h K 0 planes was thereby eliminated.

Megaw (Proc. Phys. Soc. 1946, 58, 141) has shown that when $a = b \neq c$, two lines with indices hkl and hkl̄ with a mean spacing d have

$$\frac{d_{hkl} + d_{hk\bar{l}}}{d} = -\frac{2hl}{N}\cos\beta$$

where $N = h^2 + k^2 + l^2$ for the pseudo-cubic unit cell. This expression is also applicable when $a = b = c$ and it was found that application of this relationship to the pairs of lines 3 and 4 and 11 and 12 gave angles of $\beta = 91.4^\circ$ and 91.2°, respectively. These values are in keeping with values obtained by Megaw for distorted oxide structures

e.g. $\beta_{CaTiO_3} = 90^\circ 40'$; $\beta_{CaZrO_3} = 91^\circ 43'$; $\beta_{CaSnO_3} = 91^\circ 30'$. Furthermore, the assumption of a value of $91^\circ 16'$ for the angle β made possible the determination of a lattice constant for the compound. The indices employed for determining this value are listed in the relevant table. It was found that potassium magnesium fluoride was monoclinic with $a = b = c = 8.00$ kX-units and $\beta = 91^\circ 16'$. A more accurate value for the lattice constant could be determined by successive approximations of the value of the angle β. It was however felt that the large number of calculations involved in such a process would hardly justify the result eventually obtained. Potassium calcium fluoride was found to be monoclinic with $a = b = c = 8.30$ X-units and $\beta = 92^\circ 36'$ by a method strictly analogous to that employed for the evaluation of the constants of potassium magnesium fluoride.

X-ray data of potassium magnesium fluoride ($KMgF_3$). Copper $K\alpha$ radiation.

Line No.	I	θ	$\sin^2\theta$	pseudo-cubic indices	doubled cell edge	indices for lattice constants	a	d
1	3	11.213	0.03783	100				3.96
2	2	13.356	0.05335		211			3.33
3	3	15.161	0.06829	}				2.94
4	9	15.855	0.07460	110 }	calculated β = 91.4°			2.82
5	3	18.703	0.10260		311			2.40
6	9	19.547	0.11198	111				2.30
7	3	21.220	0.13104		321			2.13
8	10	22.757	0.14961	200				1.989
9	1	26.992	0.20611		332			1.697
10	7	28.273	0.22427	211				1.625
11	1	31.604	0.27457	}				1.468
12	9	33.171	0.29927	220 }	calculated β = 91.2°			1.406
13	5	37.693	0.37398	310				1.258
14	5	39.893	0.41145	311				1.198
15	5	42.048	0.44858	222				1.150
16	α_1 4	46.313	0.52290			231	3.99	1.063
	α_2 2	46.404						
17	α_1 2	50.639	0.59797	400		400	3.98	0.994
	α_2 1	50.774						
18	α_1 3	55.039	0.67163	{ 411		141	3.99	0.938
	α_2 2	55.220		{ 330				

X-ray data of potassium magnesium fluoride ($KMgF_3$). Copper K_α radiation.

(continued.)

Line No.	I	θ	$\sin^2\theta$	pseudo-cubic indices	doubled cell edge	indices for lattice constants	a	d
19	α_1 2 α_2 1	57.406 57.541	0.70908	331		331	3.99	0.912
20	α_1 4 α_2 3	59.742 59.903	0.74598	420		420	3.98	0.890
21	α_1 2 α_2 1	65.001 65.197	0.82141	332		332	4.00	0.848
22	α_1 5 α_2 3	71.120 71.557	0.89526	422		242	4.00	0.812
23	α_1 3 α_2 2	79.982 80.456	0.97039	510 431		431	4.00	0.780

Potassium magnesium fluoride is monoclinic with

$a = b = c = 8.00$ kX-units

and $\beta = 91^\circ 18'$

X-ray data of potassium calcium fluoride ($KCaF_3$).

Copper K_α radiation.

Line No.	I	θ	$\sin^2\theta$	pseudo-cubic indices	doubled cell edges	indices for lattice constants	a	c
1	2	10.134	0.03097	100				4.37
2	2	12.185	0.04455		$\bar{2}11$			3.64
3	3	13.762	0.05658	110	calculated $\beta = 92.6^\circ$			3.23
4	10	14.410	0.06192					3.09
5	4	17.016	0.08561		311			2.63
6	4	17.768	0.09310	111				2.52
7	2	19.243	0.10872		321			2.33
8	10	20.629	0.12419	200				2.18
9	2	24.423	0.17096		332			1.861
10	9	25.570	0.18625	211				1.783
11	1	28.565	0.22060	220	calculated $\beta = 92.3^\circ$			1.609
12	7	29.875	0.24813					1.545
13	1	31.442	0.27212		531			1.475
14	5	33.878	0.31076	310				1.386
15	1	37.523	0.37095	222				1.263
16	4	41.289	0.43542	321				1.166
17	1	44.813	0.49668	400				1.092
18	1	46.589	0.52772	322 410				1.059

X-ray data of potassium calcium fluoride ($KCaF_3$).

Copper K_α radiation (contd.)

Line No.	I	θ	$\sin^2\theta$	pseudo-cubic indices	doubled cell edges	indices for lat. const.	a	d
19	(α_1 4	48.365	0.55852	{330 411		141	4.38	1.029
	(α_2 2	48.486						
20	(α_1 2	51.995	0.62096	420		420	4.38	0.976
	(α_2 1	52.191						
21	(α_1 2	55.923	0.68596	332		332	4.40	0.928
	(α_2 1	56.148						
22	(α_1 2	59.433	0.74138	422		242	4.40	0.893
	(α_2 1	59.751						
23	(α_1 3	64.056	0.80866	{431 510		431	4.39	0.855
	(α_2 2	64.401						
24	(α_1 3	74.613	0.92956	521		521	4.40	0.797
	(α_2 2	75.348						

Potassium calcium fluoride is monoclinic

with

$a = b = c = 8.80$ kX-units

$\beta = 92^\circ 36'$

2. Rubidium magnesium fluoride.

Rubidium magnesium fluoride was found as a reaction product in the investigation of the reaction between magnesium oxide and rubidium fluoride. The compound was synthesised by heating a stoichiometric mixture of the constituent fluorides for twenty four hours at 650° in nitrogen.

An X-radiogram of a specimen of this compound showed an obvious "splitting" of several of the lines on visual examination. The "split" lines were furthermore characterised by their occurrence in equal relative intensities e.g. lines 5 and 6, 11 and 12, 14 and 15 etc. in the data listed for this compound. Careful examination of the X-ray data obtained from this powder photograph showed that approximate cubic indexing was possible with all the split lines. The assumption of doubled cell edges for the pseudo-cubic unit cell obtained by the preliminary indexing of the data made possible the explanation of the remainder of the lines. Calculation of a possible value for the angle β gave a value of 88.5° which was employed for determining the lattice constant of the compound. It was found that rubidium magnesium fluoride was monoclinic with $a = b = c = 8.17$ kX-units and $\beta = 89° 30'$. Evaluation of these constants to a greater degree of accuracy by successive approximation, was not attempted for reasons stated previously. The X-ray

data for this compound are listed in a manner which makes the indexing of the compound self-explanatory.

X-ray data of rubidium magnesium fluoride ($RbMgF_3$). Copper K_α Radiation.

Line No.	I	θ	$\sin^2\theta$	approximate cubic indices	cubic increments	doubled cell edges Σh^2	inc.	indices for L.C. determination	a	d
1	3	13.322	0.0531			6	.00885			3.34
2	10	15.430	0.0708	110	0.03	54	indexed as 110 and			2.89
3	7	15.656	0.0727		0.03	64	101 with β = 88.3°			2.85
4	1	18.157	0.0972			11	.00885			2.47
5	6	19.001	0.1060	111	0.03	53	indexed as 111 and			2.36
6	6	19.303	0.1092		0.03	64	$11\bar{1}$ with β = 88.7°			2.33
7	8	20.581	0.1236			14	.00883			2.19
8	8	22.075	0.1413	200	0.03	53	16	.00883		2.05
9	7	22.786	0.1501			17	.00883			1.986
10	2	24.179	0.1677			19	.00883			1.878
11	1	24.818	0.1762	210	0.03	52	indexed as 120 and			1.833
12	1	25.224	0.1816		0.03	63	201 with β = 88.4°			1.805
13	1	26.801	0.1932			22	.00878			1.750
14	7	27.334	0.2107	211	0.03	51	indexed as 211 and			1.675
15	7	27.831	0.2179		0.03	63	$21\bar{1}$ with β = 88.6°			1.648
16	4	29.185	0.2378			27	.00880			1.577
17	2	30.880	0.2634			30	.00878			1.499
18	8	31.975	0.2805	220	0.03	51	indexed as 220 and			1.452
19	8	32.538	0.2893		0.03	62	202 with β = 88.5°			1.430
20	4	34.162	0.3152			36	.00876			1.370
21	2	35.230	0.3328			38	.00876			1.333
22	4	36.315	0.3508		0.03	51	indexed as 301 and			1.299
23	4	37.008	0.3624		0.03	62	$30\bar{1}$ with β = 88.5°			1.278

X-ray data of rubidium magnesium fluoride ($Rb\ MgF_3$). Copper K_α radiation.

(contd.)

Line No.	I	θ	$\sin^2\theta$	approximate cubic indices	cubic increments	doubled cell edges Σh^2	inc.	indices for L.C. determination	a	d
24	5	38.439	0.3865	311	0.035 1	indexed as 311 and				1.237
25	5	39.178	0.3992		0.036 3	$31\bar{1}$ with β = 88.3°				1.218
26	1	40.413	0.4203	222	0.035 0	indexed as 222 and				1.187
27	1	41.257	0.4349		0.036 2	$22\bar{2}$ with β = 88.5°				1.167
28	1	41.973	0.4472			51	.00877			1.150
29	1	43.370	0.4716			54	.00873			1.120
30	α_1 4 α_2 2	44.422 44.482	0.4898	321	0.035 0	56	.00875			1.098
31	α_1 2 α_2 1	45.386 45.446	0.5068			58	.00873			1.080
32	α_1 2 α_2 1	45.937 46.015	0.5167			59	.00876			1.070
33	α_1 2 α_2 1	48.535 48.626	0.5616	400	0.035 1	64	.00875			1.026
34	α_1 2 α_2 1	49.982 50.072	0.5865			67	.00876			1.004
35	α_1 2 α_2 1	51.398 51.504	0.6108			70	.00873			0.983
36	α_1 2 α_2 1	52.513 52.619	0.6296	330 411	0.035 0	72	.00874			0.969
37	α_1 2 α_2 1	53.669 53.820	0.6490			74	.00877			0.955
38	α_1 2 α_2 1	54.713 54.864	0.6663	331	0.035 0	76	.00876			0.942
39	α_1 2 α_2 1	55.609 55.742	0.6810			78	.00873			0.932

X-ray data of rubidium magnesium fluoride ($RbMgF_3$). Copper K_α radiation.

(continued.)

Line No.	I	θ	$\sin^2\theta$	approximate cubic indices	cubic increments	doubled cell edges obs	Σh^2	inc.	indices for I.C. determination	n	d
40	α_1 3 α_2 1	56.763 56.958	0.6993	420	0.03	50	80	.00874	804	8.17	0.919
41	α_1 3 α_2 1	57.200 57.410	0.7066				81	.00873	474	8.17	0.912
42	α_1 3 α_2 2	58.269 58.455	0.7234				85	.00872	753	8.18	0.904
43	α_1 3 α_2 1	61.253 61.479	0.7807	332	0.03	50	88	.00874	664	8.17	0.877
44	α_1 3 α_2 1	63.136 63.393	0.7959				91	.00874	913	8.17	0.862
45	α_1 3 α_2 1	66.979 67.280	0.8471				97	.00873	656	8.17	0.835
46	α_1 4 α_2 2	69.871 70.292	0.8816				101	.00873	674	8.17	0.819
47	α_1 4 α_2 2	72.238 72.735	0.9079				104	.00873	826	8.18	0.807
48	α_1 4 α_2 2	73.157 73.624	0.9161				105	.00873	854	8.17	0.803
49	α_1 4 α_2 2	75.703 76.245	0.9390				108	.00870	666	8.17	0.793

Rubidium magnesium fluoride is monoclinic with

$a = b = c = 8.17$ kX-units

$\beta = 88^\circ\ 30'$

(b) The crystallography of the double fluorides of the perovskite type.

Chemical crystallography has shown the existence of several compounds with very similar lattice types which cannot however be classified as identical. Such structures with slightly different lattice types have been styled "sister structures" by Barth-Dana (Naturwissenschaften 1943, 31, 466). An example of a family of "sister structures" is that of the perovskite type which is classified as E 21 in the Strukturbericht. Oxides of the formula ABO_3 where A is a divalent cation and B a tetravalent cation possess either a corundum-ilmenite or perovskite type of structure. The corundum-ilmenite structure has a rhombohedral unit cell which was however not found in any of the double fluorides investigated crystallographically. The double fluorides represented by the formula $KMgF_3$, $KZnF_3$ and $KNiF_3$ have been shown to be of the perovskite type and the adoption of this structure for the representation of the double fluorides of the alkali and group II metals was found to be most satisfactory in the explanation of their structures.

The perovskite type has been defined by Megaw (Proc. Phys. Soc. 1946, 58, 134) to include structures which retain a pseudo-cell derived from that of the ideal cubic structure E 21 by small distortions of either the cell edge or the cell angle. The true cell may therefore require

(a) doubling of one or more of the cell edges or (b) reference to different axes. In the ideal type the atomic parameters are as follows

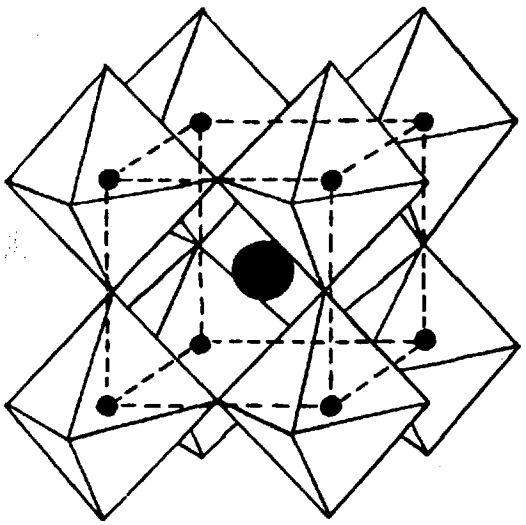
$$A \quad \tfrac{1}{2} \quad \tfrac{1}{2} \quad \tfrac{1}{2}$$

$$B \quad 0 \quad 0 \quad 0$$

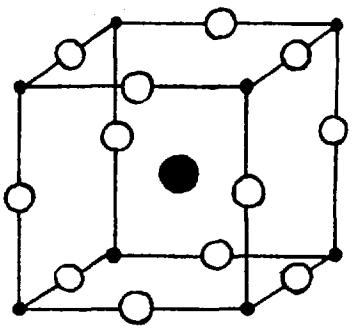
$$F \quad \tfrac{1}{2}\,0\,0\,,\ 0\,\tfrac{1}{2}\,0\,,\ 0\,0\,\tfrac{1}{2}$$

This gives a structure in which the B cations are surrounded by regular octahedra of fluorine ions which are linked together by their corners to form a three-dimensional framework. A representation of this structure is given in fig. 5a. It would then be seen that the A cations occupy the large holes between the octahedra and are each surrounded by twelve fluorine ions. The A - F and B - F electrostatic bond strengths are therefore $\tfrac{1}{12}$ and $\tfrac{1}{3}$ respectively (L. Pauling, The Nature of the Chemical Bond, Cornell University Press, 1949 page 384). There are no bond strengths equal to or greater than 1, which means that the bonds are all qualitatively comparable. Chemically this implies that the compounds must be described as double fluorides and not by terms analogous to the zirconates, titanates etc. which are sometimes employed as a nomenclature for the oxide structures.

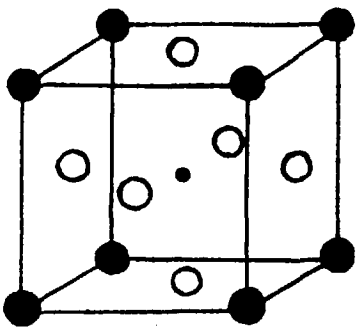
It would be seen that for an ideal perovskite structure, the sum of the ionic radii $r_A + r_F$ must be equal to $\sqrt{2}\,(r_B + r_F)$. Goldschmidt (Geochem. Vert. d. Elem. 1927,



(a) Ideal Perovskite Structure



(b) Environment of A ions



(c) Environment of B ions

● = A (large monovalent) ions

• = B (small divalent) ions

○ = Fluorine ions

Fig. 5.

VIII) showed empirically that structures having the generalised perovskite type occur when a "tolerance factor" t which is equal to $\frac{r_A + r_F}{\sqrt{2}\,(r_B + r_F)}$ lies between 0.80 and 1.00 for the oxide structures. Lower values of t were associated with a corundum-ilmenite structure in the case of the oxides. Naray-Szabo (Muegyetemi Kozlemenyek 1947, No.1, 36) has shown that a classification of the various sub-types of the perovskite class of compounds is possible on the basis of these tolerance factors and the polarisabilities of the cations. The application of these principles governing the oxide structures to the data of the double fluorides investigated in this research was therefore of extreme interest.

For this purpose, a calculation of the tolerance factors of all the possible alkali metal-group II metal double fluorides were made. The values for the ionic radii were the same as the "crystal radii" given by Pauling (loc. cit. p.346). A correction for twelve co-ordination was made by assuming the value of $n = 9$ for the Born exponent (Pauling loc. cit. pages 339 and 368). The results obtained are tabulated on page 270 . A survey of the tolerance factors of the theoretically possible double fluorides shows that no compound formation occurs below a value of $t = 0.808$. On the other hand, values as high as $t = 1.125$ are found for the caesium compounds. It is

important to note that these factors are based on ideal ionic radii and a co-ordination of twelve in the case of the alkali metal cations. Corrections for the polarizabilities of the cations and the ionic radii for twelve co-ordination cannot as yet be applied with any degree of certainty. The empirical rule of the formation of perovskite type compounds in the tolerance factor range 0.80 to 1.00 however applies to the double fluorides as well. The range for these compounds may be quoted as 0.80 to 1.13 for the series of compounds investigated. The absence of formation of strontium and barium compounds leads to more interesting conclusions. It would be seen that some of the possible theoretical compounds e.g. $CsSrF_3$ and $CsBaF_3$, have tolerance factors of $t = 0.909$ and $t = 0.835$ repectively. The values are within the range for the formation of perovskite type compounds which are however not formed. An explanation of this phenomenon is found on consideration of the radius ratio $\rho = r_{D^{++}} / r_{F^-}$ (Pauling loc. cit. p.352). It is found that the radius ratio of strontium to fluorine ions is $\rho = 0.831$. The corresponding value for barium and fluorine ions is 0.993. The limits of 6-co-ordination which is manifested by the divalent cations within the fluorine octahedra are however 0.414 to 0.732. It is evident therefore that the criterion of the formation of double fluoride perovskite type structures is the ability of the divalent cation to be 6-co-ordinated within the fluorine octahedra.

The radius ratio values of magnesium, calcium and zinc confirm that the formation of compounds is primarily determined by the value of the radius ratio. The values of the tolerance factors would then determine the geometrical possibilities of the actual existence of any particular compounds. The stronger B - F electrostatic bond strength of $^{1}/_{3}$ in comparison to the A - F bond strength of $^{1}/_{12}$ adds support to the view that the stability of the octahedra and the divalent cations contained within are the primary determinants of the possibility of structure formation of the type ABF_3. This view has been expressed by Hagaw (loc. cit.) for the oxide structures. Emphasis of this concept is however essential in the discussion of these fluoride structures as the structure of potassium magnesium fluoride described in current text-books is attributed to the possibility of a cubic close-packed arrangement between potassium ions with r_{K^+} = 1.33 A and fluorine ions with r_{F^-} = 1.36 A (Pauling loc. cit. p. 376). This arrangement it would be seen is purely fortuitous and only incidental to the principles governing the formation of perovskite type structures.

The explanation of the formation of different lattice sub-types of this class of compounds is more difficult. The sub-types which occur may be listed as

(a) small cubic unit cells e.g. $RbCaF_3$.

(b) large monoclinic cell e.g. MgF_3.

(c) large tetragonal cell e.g. MgF_3.

The postulation of the existence of directed bonds in barium titanium oxide by Megaw (Proc. Roy. Soc. 1947, A 189, 272) may be regarded as a definite advancement in the attempts to explain the formation of lattice sub-types in a group of "sister structures."

Tolerance factors of possible double fluorides of the formula $A^{+}B^{++}F_3$.

Theoretical compound	tolerance factor	radius ratio $r_{B^{++}} : r_{F^-}$	observations
$LiMgF_3$	0.707		no compound
$NaMgF_3$	0.844		tetragonal unit cell
$KMgF_3$	0.989	0.478	monoclinic unit cell
$RbMgF_3$	1.045		monoclinic unit cell
$CsMgF_3$	1.125		tetragonal unit cell
$LiCaF_3$	0.603		no compound
$NaCaF_3$	0.722		no compound
$KCaF_3$	0.845	0.728	monoclinic unit cell
$RbCaF_3$	0.894		cubic unit cell
$CsCaF_3$	0.963		cubic unit cell
$LiSrF_3$	0.571		no compounds
$NaSrF_3$	0.682		
$KSrF_3$	0.798	0.831	
$RbSrF_3$	0.844		
$CsSrF_3$	0.909		

Theoretical compound	tolerance factor	radius ratio $r_{B^{++}} : r_{F^-}$	observations
$LiBaF_3$	0.525		special instance discussed separately
$NaBaF_3$	0.626		
$KBaF_3$	0.733	0.993	no compounds
$RbBaF_3$	0.775		
$CsBaF_3$	0.835		
$LiZnF_3$	0.677		no compound
$NaZnF_3$	0.868		
$KZnF_3$	0.946	0.544	tetragonal unit cells
$RbZnF_3$	1.000		
$CsZnF_3$	1.078		

(c) The structure of barium lithium fluoride.

It has been shown in the preceding section, that the formation of a perovskite type of structure is determined primarily by the possibility of 6-co-ordination of the divalent cation in the fluorine octahedra. The existence of barium-alkali metal double fluorides was therefore not to be expected. It was however found that a double fluoride of the formula $BaLiF_3$ could be prepared by sintering a stoichiometric mixture of the requisite proportions of the constituent fluorides for twenty-four hours at 650° in nitrogen.

Barium lithium fluoride was found to have a simple cubic structure with a lattice constant of $a = 3.988 \pm 0.001$ kX-units. The general character of the X-radiogram was of such good quality that it may be described as "ideal". There was no doubt therefore of the crystallinity of the specimen and consequently of its homogeneity. A feature of added interest in this X-radiogram was the apparent equality of the intensities of all the spectra. A single line however had a relative intensity of 4 and was indexed as being due to a 400 reflection. A diminishing of the intensity of a line with indices 400 is however to be expected in a simple cubic lattice as it represents a fourth order reflection from a 100 plane. The production of such an X-ray spectrum suggested that diffraction was only representative of a particular atomic species in the lattice. It was evident from considerations of the

diffracting powers of barium, lithium and fluorine that the spectra were due to diffraction by planes containing barium atoms. The situation was similar to that reported to occur in the X-radiograms of tungsten and molybdenum borides by Kiessling (Acta Chem. Scand. 1947, 1, 905) and in those of the double fluorides of sodium and potassium, with uranium and thorium (Zachariasen J. Am. Chem. Soc. 1948, 70, 2147).

The symmetry of a single ionic species in a crystal lattice is however the same as those of the remaining species. A structure had therefore to be postulated for barium lithium fluoride in which barium, lithium and fluorine ions were individually in simple cubic lattices. Such an arrangement in compounds of the general formula $A^{+}B^{++}F_3^{-}$ is found in the perovskite type of structure. The environments of the individual ionic species A^{+} and B^{++} in a perovskite lattice are represented in figs 5 (b) and (c) respectively. The tolerance factor for a compound of the formula $LiBaF_3$ has however been shown to be 0.529 which makes the existence of a normal perovskite lattice impossible. Comparison of the ionic radii of barium and fluorine however showed that the values are almost identical ($r_{Ba^{++}} = 1.33$; $r_{F^{-}} = 1.36$). This would make possible a cubic close-packed arrangement of barium and fluorine ions in a crystal lattice. It appeared very probable, therefore, that in this compound the divalent ions occupy the

positions of twelve co-ordination in the large holes between the fluorine octahedra. A calculation of the unit cell dimensions on the assumption of a barium ion occupying position A in fig.5(b) gave a value of a = 4.00 A which is comparable to the value of a = 3.988 kX-units obtained experimentally for the compound. The slight discrepancy between the two values is to be expected as the calculation makes no correction for the polarizability of the barium ion and employs only an approximate value for its 12 co-ordinated radius. The assumption of this position is further justified by the fact that the radius ratio of lithium to fluorine is 0.440, which makes 6-co-ordination of the lithium in the fluorine octahedra highly probable. A calculation of the lattice constant on the assumption of lithium ions being placed in position B in fig. 5 (c) gave a value of a = 3.92 A which is again in keeping with the experimentally obtained value of a = 3.988 kX-units. The greater divergence of this value from that obtained experimentally when compared to that in the previous considerations of the position of the barium ion, indicates that the stability of the structure is apparently governed by the cubic close-packed arrangement of the barium and fluorine ions. It is possible, therefore, that under these conditions, the lithium ion has more space within the fluorine octahedron than it actually requires. The production of a lattice thereby, in which the lithium ions can "rattle" in their fluorine octahedra would be analogous to the

tetravalent ions in some oxide structures e.g. barium titanium oxide. The compound is, in addition, insoluble in and undecomposed by water. Measurements of its dielectric properties may give interesting results.

The fact that the analogous strontium compound does not exist limits the extension of this class of double fluorides. Radium, however, has been reported to have an ionic radius of 1.43 A (I. Naray-Szabo Kristalykemia, Budapest, 1944, p.39) and it would be of interest to investigate the possible existence of the compound radium lithium fluoride.

Naray-Szabo has postulated that in barium cerium oxide ($BaCeO_3$) the cerium ion is so much smaller than the barium that it probably occurs in the position of 6-co-ordination. It is of interest to note, however, that in oxides of the perovskite type such a choice of the positions of the cations is only empirical. Furthermore, the tetravalent cation is invariably smaller than the divalent, with the result that the choice of position is on the relative "smallness" of the ions. The structure postulated for barium lithium fluoride is, on the other hand, unique, in that no alternative form is possible. It represents a perovskite structure in which the doubly charged cation is very much larger than the singly charged cation. In keeping with the recognised formulation of the type ABF_3, barium lithium fluoride should be represented by the formula $BaLiF_3$ and

written as such. It very probably represents a distinct perovskite sub-type which may be termed "Inverted" perovskite structures. The acceptance of such a structure would add further evidence to the correctness of the postulate of Goldschmidt and his school that the crystal structures of compounds are determined more by the relative ion sizes of the constituents and the possibilities of geometrical arrangement than by the valencies of the individual ions.

Part V General Discussion.

Part V. General Discussion.

The investigations of the reactions between metal oxides and fluorides have been attempted on three distinct lines of research which may be enumerated as follows.

(1) Study of the reactions between the oxide contents of beryl and sodium silicofluoride and potassium ferric fluoride and correlation of the results of these investigations with the decomposition of beryl by the same fluorides.

(2) Study of the reactions between the alkali metal fluorides and some group II metal oxides.

(3) Powder crystallography of the reaction products found in (2).

The discussions have been restricted to the relevant sections for the purpose of pointing out the more direct problems pertaining to the individual research projects.

There are however some wider aspects of reactions between metal oxides and fluorides which have a bearing on the observations of more than one section. It has been seen, for instance, that the reaction between magnesium fluoride and ferric oxide at 1200° results in the liberation of ferric fluoride which immediately attacks the mullite furnace tube with the liberation of silicon tetrafluoride. Sintering of mixtures of potassium ferric fluoride and aluminium oxide and silica separately, however showed no interaction between the components of the mixtures. The properties of complex fluorides such as potassium ferric fluoride therefore appear to differ widely from

those of the constituent fluorides for the reason that ferric fluoride in combination with an alkali metal fluoride produces a compound which does not attack silica under experimental conditions. It appears probable that it is the change in properties of two individual fluorides by complex fluoride formation which is exploited for the selective decomposition of minerals like beryl. In this decomposition process with potassium ferric fluoride, the combination of ferric fluoride with an alkali metal halide presents a convenient form of reagent for the execution of the process. The decomposition process, in this instance, then follows a direct sintering reaction between the beryllium oxide content of the ore and the reagent, which can be represented by a stoichiometric equation. The existence of double fluorides such as potassium calcium fluoride and sodium magnesium fluoride points to the possibility that such compounds may serve as decomposition reagents for particular minerals.

The investigations of the reactions between metal oxides and fluorides have, in addition, shown that under conditions of sintering, complex fluorides and fluorides both react with individual oxides to produce a single reaction product which is independent of the composition of the mixtures. The same conclusion has been drawn by Jander (Angew. Chem. 1936, 49, 881) for the interaction of the components of oxide mixtures. This phenomenon is

of fundamental interest for the reason that such reactions can be utilized for the preparation of pure compounds by solid-phase reactions in instances where lack of relevant thermal analysis data may prevent the production of the compounds by fusion.

The choice of suitable refractories for reactions with various fluorides has been made by trial and error. The results should prove useful in the actual manipulation of such processes. Aluminium oxide (Al_2O_3) is apparently the most suitable material for the fluorides which have been investigated. The attack of mullite ($Al_6Si_2O_{13}$) by ferric and zirconium fluoride vapours at 1000° shows that considerable experimentation is needed before the final choice of refractory materials, in processes which involve the production of fluoride vapours, is made. The study of the conversion of fluorides to oxides is, in addition, of some interest. Such a conversion was found to occur at as low a temperature as 600° in the case of potassium ferric fluoride. The adoption of nitrogen as an inert atmosphere has been found to be most suitable for the reactions investigated. The comparative volatility of the alkali metal fluorides under continuous evacuation and the conversion of fluorides to oxides by ignition in air necessitates the adoption of an inert gas entrainment technique for the study of all reactions involving the use of fluorides at temperatures above 600° .

The reactions between metal oxides and fluorides

investigated, were all found to be comparatively slow. This property of these reactions may be described as being contradictory to the usual suggestion of reactivity associated with the word fluoride. The occurrence of this phenomenon however had its advantages in that it afforded the possibility of isolating intermediate states of mixed crystal formation between oxides and fluorides. These states apparently have in themselves some bearing on the reactions which succeeded their occurrence. More important, perhaps, is the fact that the existence of any extensive mixed metal-oxygen-fluorine lattices, which are a theoretical possibility on consideration of the relative ionic radii of oxygen and fluorine, can be denied in the instances of the oxides and fluorides investigated. The failure for the formation of such lattices probably has its explanation in the different polarisabilities of the individual ions. Reactions such as that of magnesium fluoride and ferric oxide where a volatile reaction product is evolved from the reaction mass, further, offer a possible method for the study of the kinetics of such sintering processes.

The degree of precision in the X-ray methods adopted for the study of these reactions necessitated the determination of standard structural constants for the reactants employed. The co-ordination and correction of values which were found necessary in these determinations showed that apparently simple compounds such as the fluorides of potassium, caesium, rubidium, magnesium, strontium and zinc

have not been examined by X-ray methods in recent years. Perhaps, more striking, is the fact that thermal analysis data for the binary systems of alkali metal and alkaline earth metal fluorides is far from complete and apparently incorrect in one of the instances reported. The impetus given recently by the Russian school of workers in this direction is however encouraging, though as has been pointed out in the relevant section, the use of supplementary X-ray methods may have led to more correct interpretations of the data reported.

An attempt has been made to give some explanation as to the formation of double fluorides between the alkali metal fluorides and those of group II metals. It is fortunate that the assignment of the compounds investigated, to respective crystal classes, was possible. The method itself involved the interpretation of X-radiograms by processes which may be described as being of systematic "trial and error". This was necessitated by the incidence of large unit cells which have apparently some connection with the distortions produced by deviations from the ideal perovskite structure. The success in the interpretation of the monoclinic compounds has to be regarded as being of significance for the reason that quantitative extents of distortion in fluoride structures have not been previously reported. The application of Pauling's concepts of radius ratio and electrostatic bond strengths and Goldschmidt's empirical rule of tolerance

factors have made an explanation of the existence of these compounds possible. The principle underlying the formation of these structures is apparently the possibility of 6-coordination of a divalent cation within fluorine octahedra. The compound barium lithium fluoride has, in this connection, to be regarded as unique in that the similarity of the ionic radii of barium and fluorine makes possible the existence of such a compound. The compound itself has to be categorized as an "Inverted" perovskite structure and will probably remain the only example of such a lattice arrangement. The absence of the formation of any rhombohedral structures for the possible double fluorides of the formula $A^{+}B^{++}F_3$ which have a tolerance factor less than 0.80 shows that such structures are not favoured by highly ionic lattices. The X-ray luminescent property of caesium calcium fluoride and the probability ~~ability~~ of interesting electrical properties in barium lithium fluoride merit further investigations. A study of the electrical properties of the double fluorides should, in any case, give valuable information on the bonding and polarization forces operating in lattices of this type.

The absence of mixed crystal formation in the solid state, between the alkali metal and alkaline earth metal fluorides indicates the absence of extensive mixed metal-fluorine lattices between these compounds. The same conclusions were drawn from the results of the investigations of sintered products of double fluorides with an excess of one of the constituent fluorides. The crystal lattices of the

fluorides apparently maintain their individuality under the experimental conditions employed. This is to be expected on consideration of the high electronegativity of fluorine. The same conclusions could be drawn for the lattices of the oxide structures investigated.

A survey of the literature of reactions promoted by sintering powder mixtures shows that only a very general picture of the mode of occurrence of these reactions can be drawn. (Cohn Chem. Rev. 1948, 42, 561). The principles underlying the reaction processes have often to be based on circumstantial evidence derived from the results of several investigators with widely different types of compounds. Several intermediate states have been shown to exist in sintering reactions. Attempts at a more detailed study of sintering processes by charting the changes of a number of physical properties in the reacting systems are however being made by Ward and his co-workers in America (J.Am. Chem. Soc. 1946, 68, 2085). The existence of intermediate mixed crystal states in the reactions between metal oxides and fluorides should provide an additional physical manifestation which has so far not been studied in any detail in such processes.

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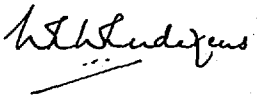

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