STUDIES ON PREPARATION OF SOLUBLE FLUORIDES DIRECTLY FROM CALCIUM FLUORIDE

Part 1.—From Pure Calcium Fluoride

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The reaction between calcium fluoride and various alkali salts in the aqueous medium at atmospheric and high pressure was studied. No reaction is observed at atmospheric pressure. Reaction at 50–125 lb/in² pressure was observed only with alkali carbonates suggesting the usefulness of this method for industrial utilization for the preparation of alkali fluorides. Quantitative conversion on fusion of calcium fluoride and alkali carbonates was also observed.

Fluorine and its compounds find an important place in industrial chemistry. For detailed information reference may be made to Bartley.[1,2,3]

The two sources of fluorine are the mineral fluorspar in which fluorine is present as calcium fluoride, and rock phosphate from which it is recovered as a by-product. The rock phosphate being used in Pakistani industry is of foreign origin containing an average of 3% fluorine.[4,5] However no effort is presently being made to recover the valuable byproduct. Flurospar has been reported to occur in Koh-i-Maran Range in Kalat District and in Hazara District.[6]

The starting point for fluorine chemicals is the manufacture of hydrofluoric acid according to the reaction:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
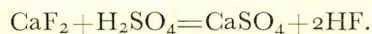
Acid grade fluorspar required for this purpose must contain a minimum of 95% CaF_2.[7]

Safdar and his co-workers[8] attempted to employ this reaction *in situ* for the frosting of glass. They noted that when fluorspar was used the reaction was too slow to be of any direct practical utility. In view of the considerable importance of soluble inorganic fluorides it was considered desirable to study the feasibility of by-passing the preparation of hydrofluoric acid. The present communication describes the investigation made with pure calcium fluoride.

Experimental

A.R. calcium fluoride and other chemicals were used.

Fusion experiments were performed in an electric muffle furnace in iron crucibles. Aqueous reactions were carried out at atmospheric pressure at 90°C.

A gas-heated steel autoclave of working pressure up to 125 lb/in² was used for pressure experiments. The time of autoclaving taken into account was counted from the time the particular pressure was achieved.

The fluoride rendered soluble was estimated gravimetrically by precipitating fluoride as lead chlorofluoride[9] between the limit 0.01 to 0.10 g.

Discussion

Fusion Experiments.—Fusion of calcium fluoride was carried out with sodium, potassium and lithium carbonates at temperatures ranging from 900 to 1200°C, keeping the carbonate content constant and varying the calcium fluoride content. The results are shown in Figs. 1, 2 and 3 which show that in each case almost the theoretically calculated molar yields are obtained. The maximum conversion to alkali fluorides was obtained at 1200°C. At higher temperatures no further increase was evident which could possibly be due to the volatlization of alkalies.

In terms of precentage molar yields the maximum amounts to 93.87 for lithium, 94.97 for sodium and 95.58 for potassium fluoride. It will thus be seen that although a definite trend according to the alkali ion present in the order K > Na > Li is observed, the effect of the alkali metal ion is not appreciable. KF, NaF and LiF have an electronegativity of 4.8, 4.9 and 5.0 respectively and the yields, however, follow the reverse trend.

Aqueous Reaction.—Safdar and Safdar[10] observed that calcium sulphate and ammonium carbonate, and ammonium sulphate and magnesium carbonate react quantitatively in the aqueous medium. The reaction of calcium fluoride with carbonates, halides, sulphates, sulphites, sulphides, oxalates, tartrates, chromates, nitrates and acetates, were studied at atmospheric pressure at 90°C. No soluble alkali fluorides were found in any of these cases.

The above-mentioned reactions were subsequently attempted at pressures of 50 lb/in². Soluble fluorides of sodium, potassium and lithium were found only when the carbonates of the alkali were used. In the case of ammonium salts no ammonium ions were detectable after autoclaving, indicating its probable loss by volatilization.

In view of the above-mentioned results further work was confined to the carbonates of potassium, sodium and lithium, at pressures up to 125 lb/in² in all these experiments the amount of calcium fluoride was varied keeping the alkali carbonate constant. The results are shown in Figs. 4–7. In all cases a typical pattern is apparent.

It is observed that with an increase in pressure a corresponding increase in reaction takes place. Maximum conversion was observed at 125 lb/in² (the limit of the autoclave) which was fairly close to the theoretical conversion. It was also observed that on varying the time of reaction from 30 minutes to 2 hours the increase in conversion was negligible. This fact has to be borne in mind for any industrial adaptation of the process.
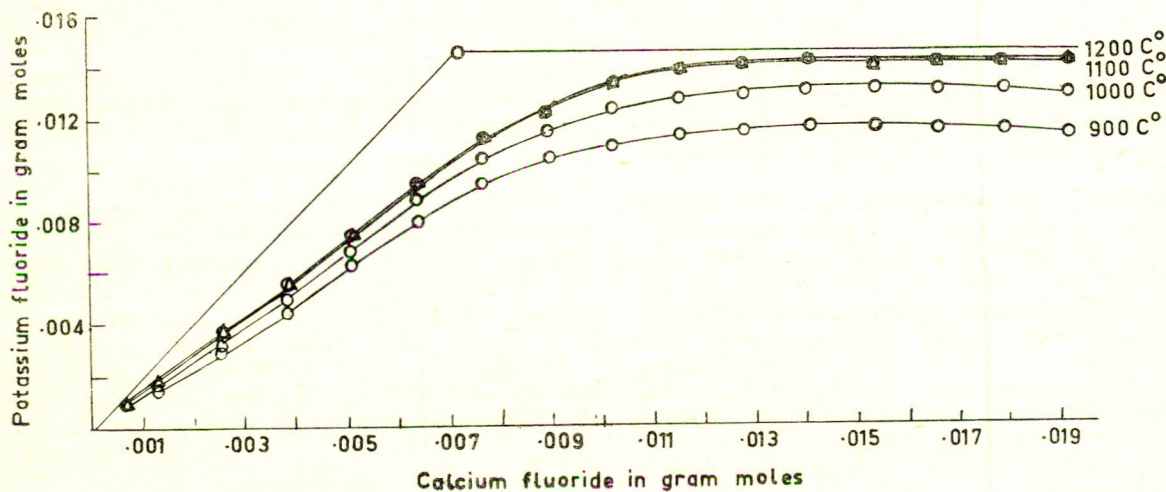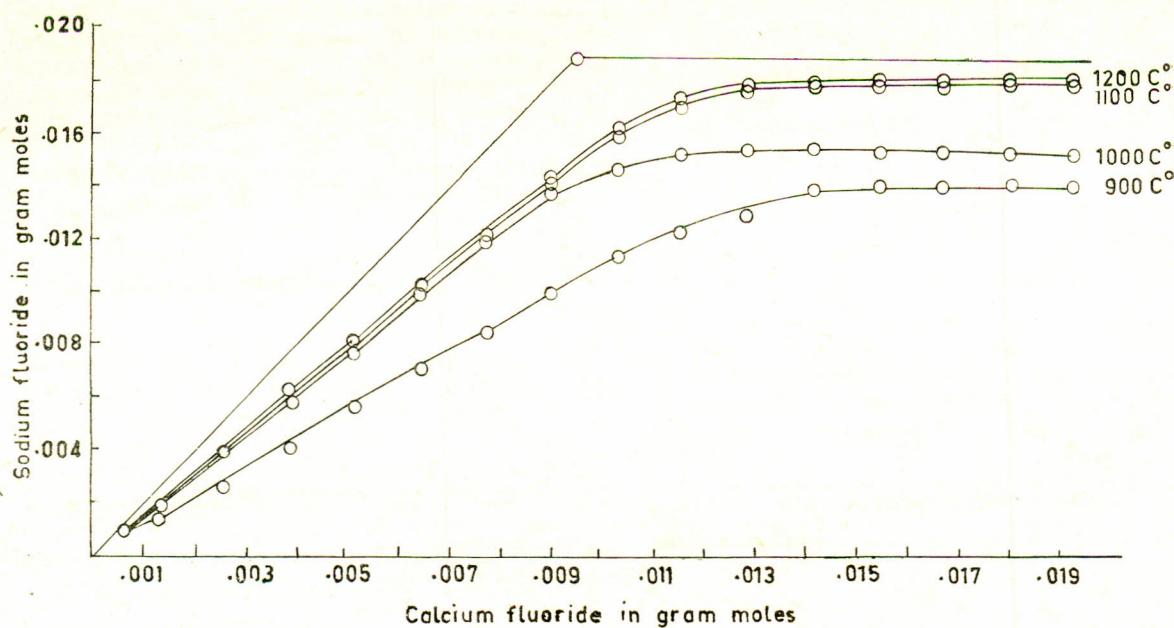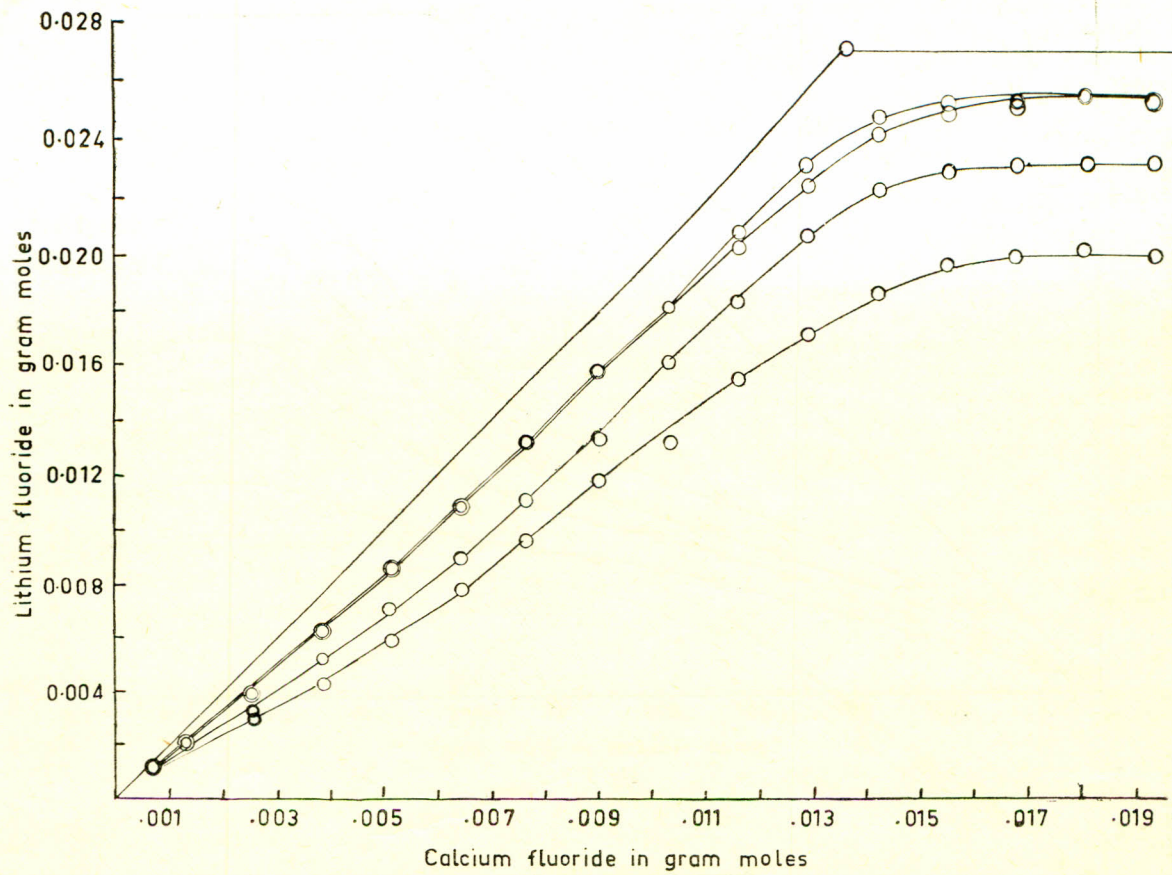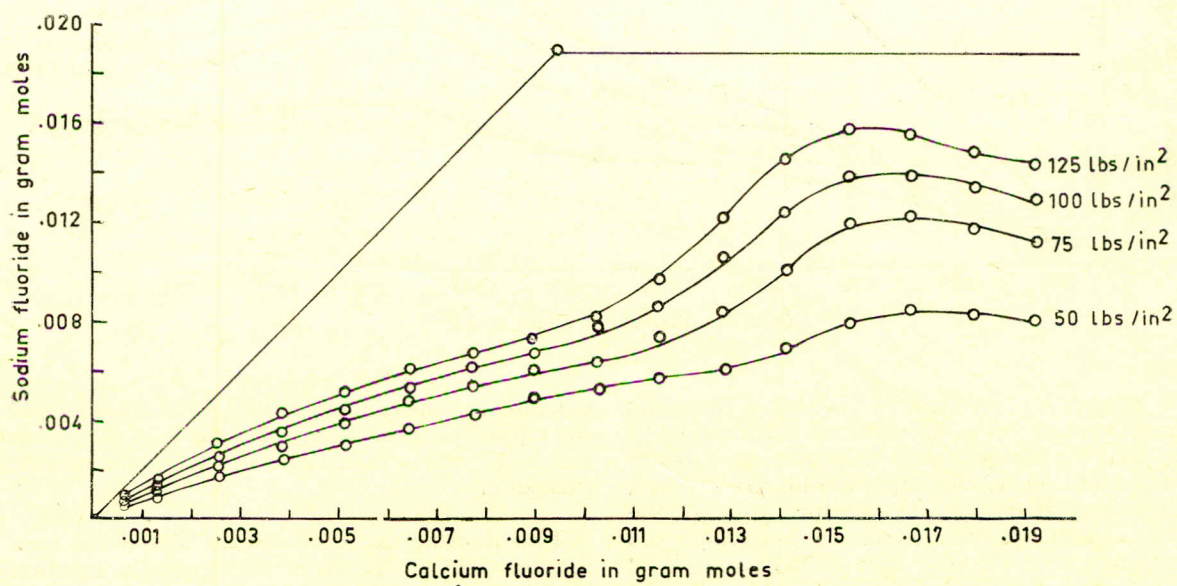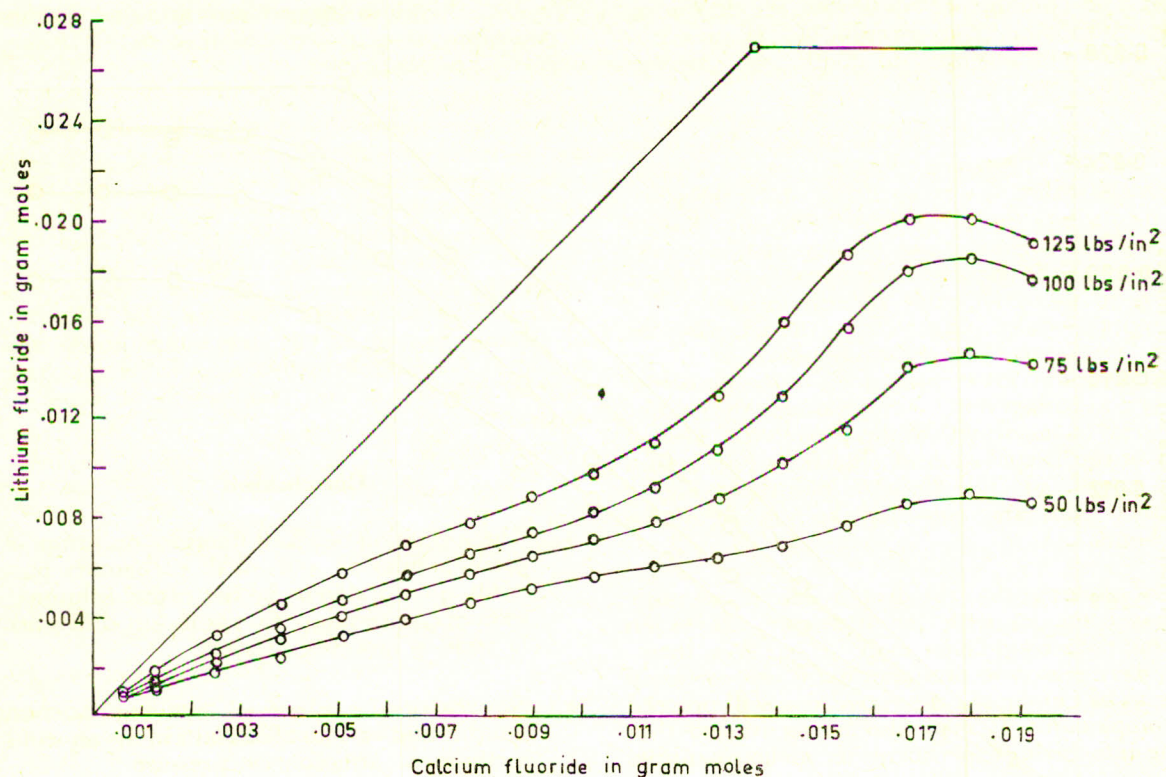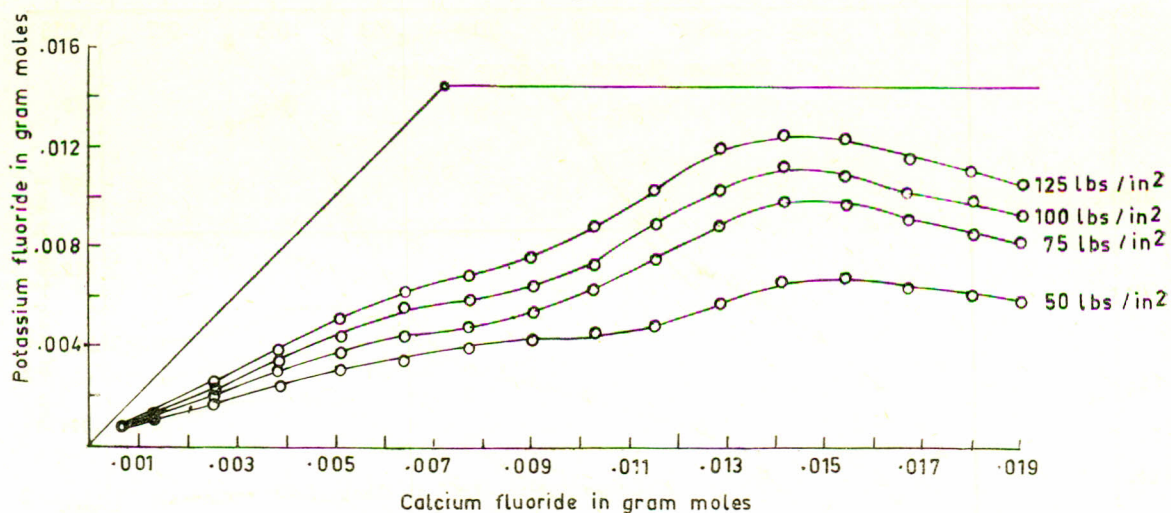

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

A progressive increase of the alkali fluorides formed is observed in all cases till a certain stage after which a sharp decline in conversion on continued addition of calcium fluoride takes place. This change is denoted by the humps in all the curves. A striking difference in behaviour deserves mention. In the case of potassium and sodium this hump is formed considerably after the calcium fluoride content of the system has exceeded the equimolar ratio whereas in the case of lithium this hump starts soon after the equimolar ratio is exceeded.

Two possible explanations are considered here for the sudden change in the apparent reaction in the region of the hump.

(a) The equilibrium conditions are dependent on pressure and concentration.[11]   In this case the shift is probably caused due to the increase of calcium fluoride in the system.

(b) It was observed that in the reaction to the right of the hump considerably greater etching of the glass container takes place.   It is, therefore, assumed that the concentration of the fluoride beyond this region causes proportionally greater corrosion of the glass container and a consequent loss of the soluble fluoride actually formed.   This assumption is also supported by the fact that the hump formation is more pronounced at higher pressures where greater corrosion of the glass container is also observed.   As an example the etching (in terms of loss in wt) of the 250 'Pyrex' beaker used in the preparation of potassium fluoride for two hours   at   125   lb/in^2 is plotted in Fig. 7 together with the corrosion at 125 lb/in^2 for two hours.

It is apparent that the drop in conversion more or less coincides with the increased   corrosion making the second factor more likely.   We, therefore, have reason to presume that if this corrosion were to be eliminated the conversion will proceed to completion.   It may also be mentioned that in the autoclaving experiments the molar quantities

of soluble fluorides formed was lithium < sodium < potassium as observed earlier with the fusion experiments.

An interesting observation made in the case of the study on pressure reaction was that any particular reaction proceeded to the right only when the reaction product of calcium expected to be formed has a solubility lower than that of calcium fluoride.   This hypothesis appeared to be valid in the present study with the sole exception of oxalate.   As insufficient data on the solubility of calcium oxalate at elevated temperatures and pressures, is available further work is being carried out on this aspect and results will be reported separately.

Conclusion

1. The formation of alkali fluorides on fusion of calcium fluoride and alkali carbonates proceeds quantitatively in the order lithium < sodium < potassium. No significant difference in yield is however noticed.

2. No reaction is observed between calcium fluoride and various alkali salts in the aqueous medium at atmospheric pressure.

△ = Conversation of KF at 125 lbs P.S.I. for 2hrs
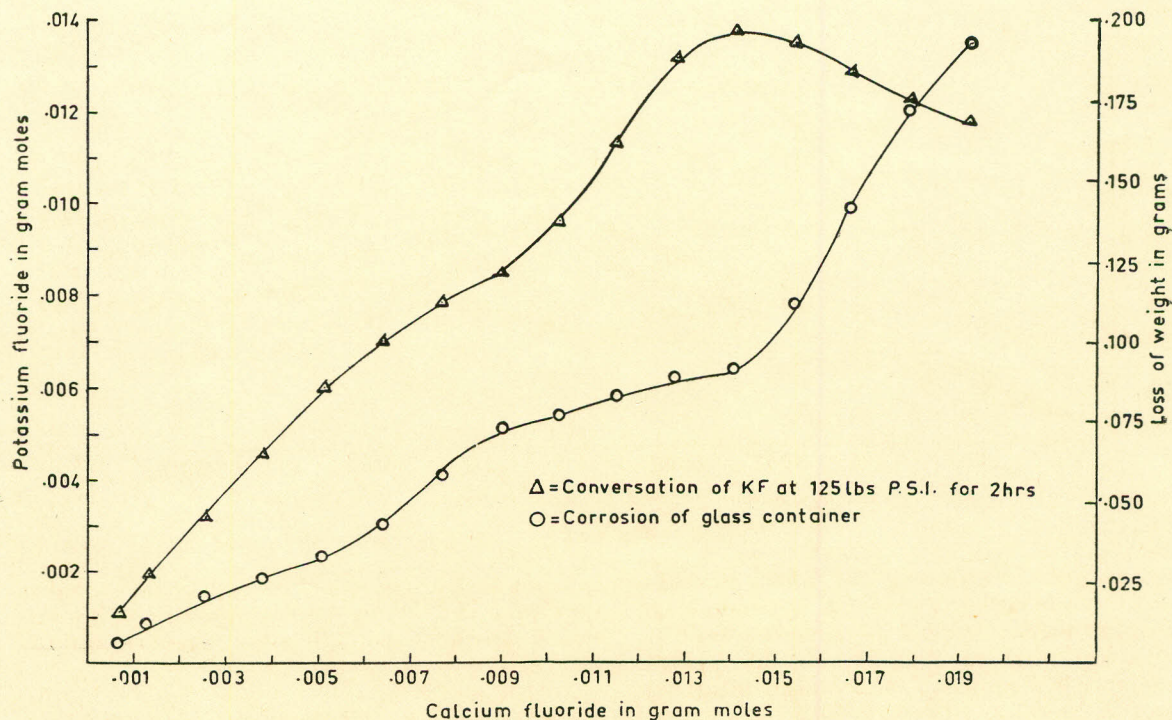○ = Corrosion of glass container

Fig. 7

3. Calcium fluoride quantitatively reacts with the alkali carbonates under pressures of 50–125 lb/in² to form the corresponding alkali fluoride, the reactivity again being lithium < sodium < potassium.

4. No reaction under pressure is observed between calcium fluoride and other alkali salts.

References

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