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ALKALI METAL FLUOROHALOGENATES

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I. INTRODUCTION

Compounds of fluorine with all the elements are known. Until recently the noble gases constituted an exception, but advances in the chemistry of inorganic fluorides in recent years led to the synthesis of the fluorides of these elements too in a pure state[1,2]. The interest in fluorine is largely due to its unusual "extreme" position in the Periodic System—its unusual chemical reactivity. The extremely high oxidising power of fluorine led to its wide application in the preparation of compounds of many elements in their highest valence states[3-7]. These compounds are in turn important in practice, being used in many branches of the new engineering, in the first place in the technology of the processing of nuclear fuel[8-10].

Certain highest fluorides, which are solids, are also powerful fluorinating agents, but considerably inferior to elemental fluorine. As an example, one may mention the difluorides of silver and mercury[11-13], the trifluorides of cobalt and manganese[11,14-16], lead tetrafluoride[17], and others[18-22].

The compounds of fluorine with the other halogens constitute the most interesting class of inorganic fluorides because they are unusual and highly reactive compounds. They can be synthesised relatively easily, many of them are liquids under normal conditions, and they all behave as very powerful fluorinating agents. Halogen fluorides can be arranged in the following series in terms of their reactivity:

$$ClF_5 > ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > IF_3 > IF$$

The reactivity of chlorine trifluoride approaches almost that of elemental fluorine, and with certain inorganic and organic substances ClF_3 actually reacts more vigorously[23]. For example, even before the discovery of halogen fluorides, it was noted that the addition of small amounts of chlorine to fluorine enhances the activity of the latter[24]. There is no doubt that this is associated with the formation of chlorine fluorides.

Chlorine pentafluoride ClF_5 was not obtained in a pure form until 1966,[25] its chemical properties have not been investigated, and, in view of the lack of experimental data, its oxidising power can only be inferred from general relations governing the activity series of halogen fluorides. However, it is quite evident that ClF_5 is a most powerful oxidising agent and an extremely active fluorinating agent, approaching elemental fluorine in these properties.

Chlorine trifluoride, like fluorine itself, can oxidise many metals to their highest valence, but it has an important advantage over elemental fluorine in that it is easy to

handle, can be relatively readily stored, can be transported, and can be used in the liquid state. Chlorine trifluoride converts silver chloride and fluoride into the difluoride and cobalt difluoride into the trifluoride[26,27], and as mentioned above, these compounds are some of the most powerful solid fluorinating agents used. Not only many transition metals, but also oxides are fully converted into the highest fluoride when acted upon by chlorine or bromine trifluoride[28-32].

The above remarks account for the great interest in the chemistry of halogen fluorides. The methods for their synthesis and their physical and chemical properties are being investigated very vigorously and a number of extensive reviews have been published on these topics[20-23,33-37]. There is no doubt that inorganic fluorides, which may be somewhat inferior in their oxidising power to elemental fluorine and halogen fluorides but are solid under normal conditions, are of great practical interest and can find wide application as powerful fluorinating agents. From this point of view, alkali metal fluorohalogenates, the most active of which have been synthesised literally in the last 2–3 years and whose chemistry has developed enormously at the present time, are the most promising.

Table 1 lists all the alkali metal fluorohalogenates known at present and includes for comparison the data for

TABLE 1. Conditions of synthesis and certain physical properties of alkali metal fluorohalogenates, halogen fluorides, and elemental fluorine.

Compound	Fluorine content, wt. %	Synthetic reaction	Temperature of synthesis, °C	M.p., °C	Decomposition temperature, °C
$NaClF_2$	39.38	$NaF+NOClF_2=NaClF_2(?)+NOF$	150	—	—
$KClF_2$	33.75	$MF+NOClF_2=MClF_2+NOF$	150	—	237
$RbClF_2$	23.90	or	25—230	—	248
$CsClF_2$	18.41	$MF+ClF=MClF_2$	175	—	262
$KClF_4$	50.46	$MF+ClF_3=MClF_4$	100	—	~200
$RbClF_4$	38.58	or		~100—200	~250—300
$CsClF_4$	31.10	$MCl+2F_2=MClF_4$	90—300	—	~350—400
NH_4ClF_4	58.69	$NH_4F+ClF_3=NH_4ClF_4(?)$	25		~0—5
$NaBrF_4$	42.48	$NaF+BrF_3=NaBrF_4$	120	—	80
$KBrF_4$	38.97	$MF+BrF_3=MBrF_4$		~330	~330
$RbBrF_4$	31.48	or		—	>330
$CsBrF_4$	26.32	$MBr+2F_2=MBrF_4$	90—250	—	>330
NH_4BrF_4	43.70	$NH_4F+BrF_3=NH_4BrF_4(?)$	25	—	>0
$NaBrF_6$	52.55		140	—	—
$KBrF_6$	48.92		100	—	—
$RbBrF_6$	40.80	$MF+BrF_5=MBrF_6$	100	—	—
$CsBrF_6$	34.88		100	—	>300
NH_4BrF_6	53.80	$NH_4F+BrF_5=NH_4BrF_6(?)$	25		>6
KIF_4	31.40	$MF+IF_3 \xrightarrow{CH_3CN} MIF_4$ or	—45	—	<70
$RbIF_4$	26.35	$MI+IF_5=MIF_4+I_2$ or	20	—	70
$CsIF_4$	22.63	$MI+2F_2=MIF_4$	15—250	—	>120
KIF_6	40.71	$KF+IF_5=KIF_6$ or	100.5	~200	~200
		$KNO_3+IF_5=KIF_6+\cdots$ or	100.5		
		$KF\cdot HF+IF_5=KIF_6+\cdots$	20		
$RbIF_6$	34.92	$RbF+IF_5=RbIF_6$	100.5	—	—
$CsIF_6$	30.50	$CsF+IF_5=CsIF_6$ or	100.5	—	—
		$CsI+3F_2=CsIF_6$	15—250	—	—
NH_4IF_6	44.03	$NH_4F+IF_5=NH_4IF_6(?)$	20	—	—
$KICl_3F$	6.50	$2MF+I_2+3Cl=2MICl_3F$		—	—
$RbICl_3F$	5.61	or			
$CsICl_3F$	4.92	$ICl_3+MF \xrightarrow[pH<7]{H_2O} MICl_3F$	25	172	300
NH_4ICl_3F	7.00			194	300
CsIBrF	5.30	$CsF+IBr=CsIBrF$	120	—	—
ClF	34.86	$Cl_2+F_2=2ClF$	250—400	—154	—
ClF_3	61.62	$Cl_2+3F_2=2ClF_3$	250—400	—77	—
ClF_5	72.80	$ClF_3+F_2=ClF_5$	30	—93	—
BrF	19.19	$Br_2+F_2=2BrF$	10	~—33	50
BrF_3	41.60	$Br_2+3F_2=2BrF_3$	15—50	7.9	—
BrF_5	54.28	$Br_2+5F_2=2BrF_5$	200	—61.7	>460
IF	13.02	$IF_3+I_2 \xrightarrow{CCl_3F} 3IF$	—78	—	>0
IF_3	30.00	$I_2+3F_2 \xrightarrow{CCl_3F} 2IF_3$	—78	—	>—35
IF_5	42.79	$I_2+5F_2=2IF_5$	20—25	9.6	>400
IF_7	51.15	$IF_5+F_2=IF_7$	250—300	5	—
F_2	100.00	$KF\cdot 2HF: \begin{matrix}2HF_2^- \\ 2F^-\end{matrix} \begin{matrix}+2e=H_2+4F^- \\ =F_2+2e\end{matrix}$	100	—218	—

halogen fluorides and elemental fluorine. It is noteworthy that alkali metal fluorofluorates, i.e. compounds of the type $M[F(F_2)]$, where M is an alkali metal, would be most promising from the point of view of their employment as highly active fluorinating agents, but repeated attempts to synthesise such compounds have been unsuccessful so far[38-45]. Nevertheless, similar compounds of chlorine, bromine, and iodine are known, have been isolated in a pure state, and have been investigated in fair detail; their stability increases in the series Cl–Br–I.[46-50]

Evidently the analogous fluorine compounds also exist but, in conformity with the general tendency of halogens, alkali metal fluorofluorates must be very unstable; in all probability this is why their synthesis and isolation present considerable experimental difficulties, which unfortunately have not been overcome as yet.

The advantages of alkali metal fluorohalogenates as fluorinating agents are as follows: (a) high oxidising power of the compounds, greatly exceeding that of all known solid fluorinating agents; (b) the possibility of carrying out reactions at elevated temperatures without the development of a high pressure in a closed system, which means that fluorination can be performed in relatively simple apparatus; (c) the use of purer fluorinating agents than is the case when elemental fluorine or halogen fluoride are used for this purpose; (d) ease of handling of the solid substances; (e) the achievement of complete fluorination (by virtue of the higher temperatures used) of the compounds for which this is impossible in the presence of halogen fluorides, for example.

The last finding is confirmed by the data of Table 2, where compounds which are only partially fluorinated by bromine trifluoride even under severe conditions are listed. On the other hand, when potassium tetrafluorobromate(III) $KBrF_4$ is used, the reaction goes to completion after a relatively short time[51].

Apart from the possibility of using alkali metal fluorohalogenates as fluorinating agents, it is interesting to note that their application for analytical purposes to determine oxygen, and also in isotopic geology, for the removal of oxygen from minerals[51], is also promising.

Alkali metal fluorohalogenates are not only of great practical value but they also constitute a class of inorganic compounds which is of considerable theoretical interest. It has been established[52,53] that halogen fluorides are ionisable solvents, which dissociate according to the equation

$$2XF_n \rightleftarrows XF_{n-1}^+ + XF_{n+1}^-.$$

Consequently these substances are amphoteric solvents and their behaviour can be most readily understood on the basis of the acid–base theory of non-aqueous solvents[33,52-59]. The fluoride ion plays a role analogous to that of the proton, namely the addition of a fluoride ion is equivalent to the loss of a proton [sic (Ed. of Translation)].

TABLE 2. Fluorination of certain oxides with potassium tetrafluorobromate(III).

Compound	Fluorination temperature, °C	Time required for complete fluorination, h	Compound	Fluorination temperature, °C	Time required for complete fluorination, h	Compound	Fluorination temperature, °C	Time required for complete fluorination, h
Nd_2O_3	350	1	ZrO_2	350	1	NiO	500	2
CeO_2	350	1	MnO_2	500	1	Fe_2O_3	500	5
ThO_2	400	2	Al_2O_3	400	1	CaO	500	16

By considering halogen fluorides as ionisable solvents, it is easy to show that certain groups of compounds will react in them as acids and bases, and therefore it is possible to have compounds both with the cation XF_{n-1}^{+} and with the anion XF_{n+1}^{-}. The former are acids and the latter bases. The synthesis of such complex compounds is a direct demonstration of the mechanism of the self-ionisation of halogen fluorides and comprehensive study of the compounds extends greatly our knowledge of the chemistry of complex compounds involving a complex ion consisting entirely of halogens.

A large number of acids with the complex cation XF_{n-1}^{+} are known[60-72]. Among compounds with the complex anion, bases of Group I and Group II elements are known; compounds with alkali metals, in the first place potassium, rubidium, and caesium and, to a lesser extent sodium and ammonium, are most widely represented. So far lithium fluorohalogenates have not been isolated in a pure form, although hypotheses have been put forward concerning the possibility of their existence, at least in an unstable state; this can be fully accounted for by the low radius of the cation which sets up in its vicinity a powerful electric field coordinating the most electronegative ligands of the complex anions and thereby disrupting the latter.

Among alkaline earth metals, compounds with calcium, strontium, and barium are known. The bases with beryllium and magnesium have not been synthesised so far. This is probably also to be accounted for by steric factors. Complex compounds where Ag^{+}, NO^{+}, and NO_2^{+} serve as the cations are also known[33,72-75].

The relative ease of preparation of the complex compounds of KF, RbF, and CsF, compared with other alkali metal and alkaline earth metal fluorides, should be noted. It is interesting that similar behaviour is also characteristic of the anion ClF_3O^{-}.[76]

Among the compounds of alkali metals of small dimensions, the more stable are fluorohalogenates containing a larger halogen. This conforms to the general rule which determines the stability of polyhalogenates[77]: symmetry, the presence of a cation with a large molar volume, and the location of a large electropositive atom in the centre of the anion with all other atoms electronegative.

From this standpoint, it is clear why rubidium and caesium fluorides are more readily converted into the hexafluorobromates(V) $MBrF_6$ (M = Rb, Cs) than into the tetrafluorochlorates(III) $MClF_4$ (M = Rb, Cs) and why sodium tetrafluorochlorate(III) $NaClF_4$ does not exist while small amounts of sodium tetrafluorobromate(III) $NaBrF_4$ have been detected.

Many problems involving alkali metal fluorohalogenates have remained unsolved so far and the available information is usually restricted to purely experimental data. The first serious and successful attempt to give a systematic account of alkali metal fluorohalogenates was the review of Stepin et al.[75], but these authors, who examined alkali metal anionohalogenates in general, were of course unable to systematise sufficiently widely and completely the results of studies of fluorohalogenates in particular. Furthermore, as a result of the vigorous development of precisely this branch of inorganic chemistry, many most interesting and important data were obtained in very recent investigations and were therefore of course not included in the review of Stepin et al.[75]

The present review deals with the methods of synthesis and physicochemical properties of alkali metal fluorohalogenates—compounds which are very interesting theoretically and very important in practice in view of the possibility of their employment as highly effective solid fluorinating agents.

II. ALKALI METAL FLUOROCHLORATES

The first information about the preparation of alkali metal fluorochlorates was obtained in 1950, when Bode[39,40] established that, in the interaction of elemental fluorine with potassium, rubidium, and caesium chlorides or fluorides, powerful fluorinating agents are formed, to which the author assigned the formula MF_x (M = K, Rb, Cs; $x \simeq 3$). It was suggested[78] that compounds of this type can have the formula $M^{I}[M^{III}F_4]$. None of these data were confirmed subsequently. Evidently in this case the tetrafluorochlorates(III) of potassium, rubidium, and caesium ($MClF_4$), markedly contaminated by the initial fluorides, were obtained for the first time. Chemical analysis of the synthesised compounds did not reveal the presence of chlorine, which can be explained by the fact that tetrafluorochlorates(III) form chlorate and not chloride ions on interaction with water. This was demonstrated experimentally more than ten years later[79,80] and therefore reliable data on alkali metal fluorochlorates, the methods of their synthesis and their properties, derive from publications of the last 3–5 years.

1. Alkali Metal Difluorochlorates(I)

Chlorine monofluoride is only very slightly ionised in solution, according to the equation

$$2\,ClF \rightleftarrows Cl^{+} + ClF_2^{-},$$

which is confirmed by the very low electrical conductivity of liquid ClF.[52] However, at the present time compounds have been synthesised which contain both the cation Cl^{+} [65] and the anion ClF_2^{-}.[81,82]

In 1965 it proved possible to obtain for the first time a complex compound with the anion ClF_2^{-} by the reaction of nitrosyl fluoride with chlorine monofluoride[81]:

$$NOF + ClF = NO^{+}ClF_2^{-}.$$

Nitrosyl difluorochlorate(I) $NOClF_2$ is stable in the solid state only at low temperatures. Similar salts, stable at room temperature, were synthesised by the same worker with the cation NO^{+} replaced by potassium, rubidium, and caesium[82]. The preparation of potassium, rubidium, and caesium difluorochlorates(I) was achieved by two possible reactions:

$$NO^{+}ClF_2^{-} + MF = M^{+}ClF_2 + NOF \quad \text{or}$$
$$ClF + MF = M^{+}ClF_2^{-}.$$

In the synthesis of alkali metal difluorochlorates(I) various conditions (temperature, reaction time, pressure) were used. The starting materials were the corresponding fluorides, chlorine monofluoride, and nitrosyl fluoride. The latter behaved, strictly speaking, as a catalyst for the reaction, ensuring the synthesis of $NO^{+}ClF_2^{-}$ and its further interaction with the alkali metal fluoride; the latter process liberated NOF in a free state again and it was therefore not consumed in the reaction. In some experiments caesium fluoride was subjected to a preliminary

treatment with CF_3COCH_3, which, however, did not improve the reaction and the treatment was subsequently abandoned.

The best method for the synthesis of potassium, rubidium, and caesium difluorochlorides(I) proved to consist in the direct interaction of chlorine monofluoride with the corresponding fluorides. It is noteworthy that the higher the pressure and temperature the more complete is the conversion of the fluoride into the difluorochlorate(I), but in none of the cases described was 100% conversion achieved, with synthesis of a pure substance (Table 3). On the other hand, further increase in temperature, which, it would seem, should reduce the reaction time and should ensure that the reaction goes to completion, is restricted to 230°C (the temperature limit of the thermal stability of the substances synthesised).

Attempts to prepare lithium and sodium difluorochlorates(I) by a similar method at temperatures between 25° and 150°C and pressures of the order of 140 atm were unsuccessful. Chlorine was not detected in the reaction products and X-ray diffraction studies failed to reveal the presence of substances other than the initial fluoride.

Ammonium fluoride does not react with gaseous chlorine monofluoride[83] and the use of high temperatures and pressures was not undertaken; however, even this would probably not lead to success, since ammonium difluorochlorate(I) should exist only at low temperatures, if at all.

Potassium, rubidium, and caesium difluorochlorates(I) are solid white salts with relatively high thermal stability (the decomposition temperatures of $KClF_2$, $RbClF_2$, and $CsClF_2$ are respectively 237°, 248°, and 262°C). The decrease of the size of the cation and the increase of polarisation on going from Cs^+ to Li^+ are consistent with the stability of alkali metal fluorochlorates(I). As oxidising and fluorinating agents, these compounds are somewhat inferior to the corresponding tetrafluorochlorates(III).

Infrared spectroscopic studies on caesium difluorochlorate(I)[82] revealed the presence of an absorption band at 636 cm^{-1}, which is consistent with the data obtained earlier for $NO^+ClF_2^-$ (635 cm^{-1}) and corresponds to the asymmetric vibration to the ClF_2^- anion. It is suggested that in nitrosyl difluorochlorate(I) this anion has a linear structure. A similar structure is probably typical for ClF_2^- also in alkali metal difluorochlorates(I).

X-Ray diffraction studies on potassium, rubidium, and caesium difluorochlorates(I) showed the presence of very intense lines corresponding to the α-modification of the bifluoride impurity[84], while the difluorochlorate(I) itself gives rise only to lines of low intensity or is altogether amorphous to X-rays[82].

The infrared spectroscopic data, confirming the linear configuration of the ClF_2^- anion, can be accounted for by one of the following models: (a) the hybridisation model[85], permitted mainly by the sp^3d hybridisation of the atomic orbitals of chlorine, which leads to a trigonal bipyramid with two fluorine atoms at the apex, the chlorine atom in the centre, and three free electron pairs in the remaining corners; (b) the more probable molecular orbital model[85], incorporating mainly the $p\sigma$-atomic orbitals which are used to form semi-ionic bonds.

In conclusion it should be noted that at the present time no alkali metal difluorochlorate(I) has been obtained in a pure form. The results of chemical analysis (Table 3) have been calculated from the increase in the weight of the starting material and on the assumption that the final product is a mixture of only two substances— the alkali metal fluoride and the corresponding difluorochlorate(I). However, X-ray diffraction data fail to confirm this, showing the presence of the bifluoride; furthermore, there is a possibility of a definite amount of impurities due to reaction with the walls of the vessel. Therefore the above chemical identification cannot be regarded as sufficiently reliable. On the other hand, the thermal data, the fluorinating properties of the synthesised mixtures, and also the infrared spectroscopic data (which have been obtained unfortunately only for $CsClF_2$) definitely characterise the new compounds as the difluorochlorates(I) of potassium, rubidium, and caesium.

There is no doubt that the next problem to be solved involves the finding of ways to separate the difluorochlorate(I) from the unreacted fluoride or conditions in which the reaction is successfully taken to completion with formation of a pure product. Only then will it be possible to consider further reliable and comprehensive chemical and physicochemical studies of alkali metal difluorochlorates(I).

TABLE 3. Synthesis of the difluorochlorates(I) of potassium ($KClF_2$), rubidium ($RbClF_2$), and caesium ($CsClF_2$).

Starting materials, moles			Reaction temp., °C	Duration of reaction, h	Reaction pressure, atm	Degree of conversion of initial mixture into $MClF_2$, %	Calc., %			Found, %		
fluoride	ClF	NOF					metal	Cl	F	metal	Cl	F
KF												
0.069	0.390	0.031	150	14	154.7	27	58.5	8.5	33.0	58.2	8.5	33.7
RbF												
0.047	0.200	0.047	25	24	77.3	49	68.1	10.9	21.0	68.1	10.8	20.7
0.036	0.220	—	230	60	91.4	73	61.4	16.3	22.4	60.6	15.0	22.3
0.028	0.240	0.015	230	60	112.5	87	57.4	19.4	23.2	58.2	8.2	22.4
CsF												
0.200	0.700	—	175	48	56.3	53	74.8	9.4	15.8	73.6	9.1	16.0
0.035	0.210	0.012	175	48	77.3	80	69.0	13.7	17.2	69.5	8.7	17.4

2. Alkali Metal Tetrafluorochlorates(III)

In 1961 Asprey et al.[79] showed, having repeated the experiments of Bode[39,40], that the reaction of elemental fluorine with potassium, rubidium, and caesium chlorides does not result in the formation of polyfluorides MF_x ($x \simeq 3$) but tetrafluorochlorates(III), according to the following equation:

$$MCl + 2F_2 = MClF_4.$$

Since the reaction is strongly exothermic, a temperature exceeding the thermal stability of the synthesised tetrafluorochlorate(III) is readily attained and the decomposition is accompanied by the formation of the fluoride:

$$MClF_4 = MF + ClF_3.$$

For this reason, tetrafluorochlorates(III) are very difficult to obtain in a pure form, and the substances synthesised usually contain a certain amount of the corresponding fluoride as a impurity. On the other hand, when the temperature of the synthesis is reduced, the reaction does not go to completion and the impurity is then the initial chloride.

Potassium, rubidium, and caesium tetrafluorochlorates(III) were synthesised in the temperature range 90–250°C.[79] It is noteworthy that Bode and Klesper[43], having

repeated, simultaneously with Asprey et al.[79], their earlier experiments on the fluorination of rubidium chloride with elemental fluorine and having carried out a more comprehensive identification of the substances synthesised, virtually abandoned their earlier findings concerning the formation of polyfluorides[39,40] and arrived at a conclusion analogous to that of Asprey et al.[79] They isolated[43] a substance with the composition Rb_3ClF_6 which was shown by X-ray diffraction to contain no rubidium fluoride. This compound is the double salt $2RbF.RbClF_4$.

Kelly et al.[80] investigated the reaction of alkali metal chlorides with elemental fluorine as a function of temperature (up to 300°C) and pressure (up to 4000 atm). The reaction between potassium chloride and fluorine leads to the formation of potassium tetrafluorochlorate(III) $KClF_4$ only at elevated temperatures and pressures (Table 4). At room temperature only part of the initial potassium chloride is converted into KF even at a pressure of 4000 atm, and potassium tetrafluorochlorate(III) does not form (Table 4, experiment 1).

An increase of temperature leads to the formation of $KClF_4$, the yield being higher the higher is the temperature and pressure. At 300°C and 3400 atm the starting material is completely absent from the final product, but up to 10% of potassium fluoride remains as an impurity and pure $KClF_4$ cannot be obtained (Table 4, experiment 4). Potassium tetrafluorochlorate(III) was identified chemically and by X-ray diffraction. Total chlorine, total fluorine, and potassium were determined for the chemical identification. The calculations were based on the equations

$$\%\ KF = \left(\frac{\%\ K}{39.1} - \frac{\%\ Cl}{35.5}\right) \times 58.1$$

$$\%\ KClF_4 = \frac{1}{4}\left(\frac{\%\ F}{19.0} - \frac{\%\ KF}{58.1}\right) \times 150.6$$

$$\%\ KCl = \left(\frac{\%\ Cl}{35.5} - \frac{\%\ KClF_4}{150.6}\right) \times 74.6\ .$$

Such chemical identification is undoubtedly not free from disadvantages and of course the next problem is to obtain pure potassium tetrafluorochlorate(III). X-Ray diffraction study of the substances synthesised (Table 4, experiments 3 and 4) showed the absence of potassium chloride and the presence of potassium fluoride together with a new phase—potassium tetrafluorochlorate(III).

When elemental fluorine was allowed to react with rubidium chloride (300°C, 1500 atm), a white powder containing 56.7% Rb, 30.9% F, and 11.3% Cl formed. These data and also the results of X-ray diffraction analysis show that under the conditions indicated a mixture with the composition 62.5% $RbClF_4$ + 36.2% RbF was synthesised.

The reaction of elemental fluorine with caesium chloride (300°C, 1250 atm) yielded a powder, amorphous to X-rays, the chemical analysis of which showed the presence of 61.3% Cs, 28.3% F, and 10.0% Cl (calculated for $CsClF_4$: 54.4% Cs, 31.1% F, 14.5% Cl), i.e. evidently in this case a mixture of caesium tetrafluorochlorate(III) and caesium fluoride was obtained.

TABLE 4. Synthesis of potassium tetrafluorochlorate(III) $KClF_4$ by the reaction $KCl + 2F_2 = KClF_4$.

No. of experiment	Maximum temperature, °C	Maximum pressure, atm	Results of chemical analysis, wt. %			Compounds present, wt. %		
			K	F	Cl	KCl	KF	$KClF_4$
1	25	4000	56.8	9.8	33.8	70.0	30.0	—
2	175	3600	42.9	39.8	17.3	8.7	35.4	55.9
3	300	2800	30.2	47.9	21.9	1.9	9.0	89.1
4	300	3400	28.4	50.3	21.3	—	9.6	90.4

The attempts to prepare sodium and lithium tetrafluorochlorates(III), even in a mixture with the corresponding fluoride, by the reaction of elemental fluorine with the corresponding chlorides were unsuccessful. In all cases (even at high temperatures and pressures) only the fluorides of these metals formed. The attempt to carry out the reaction of potassium fluoride with elemental fluorine (300°C, 3000 atm) to prepare potassium polyfluoride KF_n ($n > 1$) also failed.

The method of preparation of alkali metal tetrafluorochlorates(III) based on the reaction of elemental fluorine with the corresponding alkali metal chlorides at high temperatures and pressures is experimentally very difficult and leads to the formation of substances with a large amount of impurities. A more promising procedure is based on the use of chlorine trifluoride[86]. The solvolysis of alkali metal fluorides in liquid chlorine trifluoride yields the corresponding tetrafluorochlorates(III). The reaction can be described by the equations

$$2\,ClF_3 \rightleftarrows ClF_2^+ + ClF_4^-,$$

$$MF + ClF_3 = M^+ + ClF_4^-.$$

The self-ionisation of chlorine trifluoride results in the formation of the complex anion ClF_4^- which gives rise to the base $M^+ClF_4^-$ on interaction with the alkali metal.

Chlorine trifluoride free from the F_2, Cl_2, and ClF impurities and also alkali metal fluorides of high purity, which had been subjected to preliminary heat treatment to remove traces of moisture, were used in the reaction. The syntheses were achieved in a vacuum system made from Monel and nickel. The degree of conversion of the fluoride into the tetrafluorochlorate(III) was determined from the increase in weight after complete removal of excess ClF_3. Chemical analysis involved the determination of total chlorine and total fluorine. The results of the study on the behaviour of alkali metal fluorides in chlorine trifluoride are compiled in Table 5.

The data in Table 5 are completely consistent with the results of earlier work[79,80] and show that lithium and sodium tetrafluorochlorates(III) are not formed even when chlorine trifluoride is used. The conversion of potassium, rubidium, and caesium fluorides into the corresponding tetrafluorochlorates(III) with the aid of chlorine trifluoride is more complete and takes place at lower temperatures than in the reaction between elemental fluorine and the corresponding chlorides. The degree of conversion depends on the nature of the cation and is higher the greater is the size of the alkali metal cation, which is consistent with the general rule governing the stability of polyhalides[77]. The stability series for alkali metal tetrafluorochlorates(III) should evidently be as follows: Cs > Rb > K. The size of the cations NH_4^+ and K^+ (1.48 Å for NH_4^+ and 1.33 Å for K^+)[87] suggests that the conversion of NH_4F into NH_4ClF_4 in the reaction with chlorine trifluoride should be possible. However, the substance formed is unstable and decomposes with explosion when an attempt is made to isolate it in a pure form[86]. N_2, Cl_2, and NF_2Cl in various proportions were found in the explosion products[83].

It is interesting to examine the interaction in ternary systems of the type HF–MF–ClF_3 (M is an alkali metal)[86]

TABLE 5. Synthesis of alkali metal tetrafluorochlorates(III) using chlorine trifluoride*.

Fluoride	Molar ratio ClF_3:MF	Results of chemical analysis, wt. %		Results of analysis
		Cl	F	
LiF	8	–	–	Does not react
NaF	8	–	–	Does not react
KF	8	14.7	46.7	A white crystalline substance forms, 56.5% of the initial KF being converted into $KClF_4$. Calculated for the composition $KClF_4.0.8KF$: 18.2% Cl; 46.5% F.
RbF	7	15.4	37.3	A crystalline solid substance forms, 85.2% of the initial RbF being converted into $RbClF_4$. Calculated for the composition $RbClF_4.0.2RbF$: 16.5% Cl; 36.9% F.
CsF	8	14.4	30.8	A solid crystalline substance forms, 91% of the initial CsF being converted into $CsClF_4$. Calculated for the composition $CsClF_4.0.1CsF$: 13.7% Cl; 30.0% F.
NH_4F	–	–	–	$NH_4F + ClF_3$ mixture explodes on heating above 0°C. The unstable ammonium tetrafluorochlorate(III) NH_4ClF_4 probably forms.

* The reactions were carried out at 100°C.

in order to test the possibility of synthesising alkali metal tetrafluorochlorates(III) in this way. Chlorine trifluoride was added to solutions of the alkali metal fluoride in liquid hydrogen fluoride, the molar ratio MF : HF being chosen so that the alkali metal fluoride was completely dissolved. With lithium fluoride and sodium fluoride, only the bifluorides were obtained. On the other hand, when potassium fluoride, rubidium fluoride, and caesium fluoride were used, the products were solvated bifluorides. Thus in all cases the compounds obtained were the same as those synthesised earlier in the binary systems HF–MF;[88-92] there was no addition of ClF_3, and chlorine was completely absent from the products. These results contradict the data concerning the existence of complexes of HF and ClF_3 [93,94] but are consistent with later data, according to which chlorine trifluoride behaves in hydrofluoric acid as a strong base[95], which favours the formation of stable bifluoride ions[96]:

$$2\,HF + ClF_3 \rightleftarrows ClF_2^+ + 2\,HF_2^-,$$

i.e. its behaviour is analogous to that of alkali metal fluorides in liquid hydrogen fluoride:

$$MF + HF \rightleftarrows M^+ + HF_2^-.$$

It now becomes quite clear why tetrafluorochlorates(III) were not obtained under these conditions. The concentrations of the alkali metal fluorides in liquid hydrogen fluoride solutions correspond to their solubilities[97,98]:

$$CsF > RbF > KF > NaF > LiF.$$

Potassium, rubidium, and caesium tetrafluorochlorates(III) are white crystalline substances which melt at about 100–200°C and decompose into the alkali metal fluoride and gaseous products on heating in a vacuum or in an inert medium at 350–400°C.[86] According to infrared spectroscopic data, the gaseous products are ClF_3 and ClF. The infrared spectrum of solid potassium tetrafluorochlorate(III) showed the presence of the 1970, 1830, 1225, and 970 cm^{-1} frequencies. Caesium tetrafluorochlorate(III) is diamagnetic.

X-Ray diffraction study of potassium tetrafluorochlorate(III) led to its assignment to the tetragonal system with the lattice constants $a = 6.18$ and $c = 10.94$ Å. The type of the unit cell is evidently that of potassium perchlorate, but the crystallisation of alkali metal tetrafluorochlorates(III) is not entirely similar to that of the corresponding perchlorates. Rubidium tetrafluorochlorate(III) crystallises in the cubic system with $a = 4.30$ Å and the unit cell is tentatively assumed to be of the caesium chloride type. As mentioned above, caesium tetrafluorochlorate(III) is amorphous to X-rays.

Potassium tetrafluorochlorate(III) decomposes at about 200°C, while caesium tetrafluorochlorate(III) can be heated for several hours at 300°C without decomposition. As regards thermal stability, rubidium tetrafluorochlorate(III) is intermediate between the tetrafluorochlorates(III) of potassium and caesium.

The densities of potassium and caesium tetrafluorochlorates(III), containing a certain amount of the fluorides as impurities, are as follows[86]:

$$d_4^{25} = 2.58 \text{ for } KClF_4.0.8KF,$$

$$d_4^{24} = 3.40 \text{ for } CsClF_4.0.1CsF.$$

The densities of pure potassium and caesium tetrafluorochlorates(III) can be calculated on the basis of additivity (assuming that the specimens are $MClF_4 + MF$ mechanical mixtures)—the corresponding values are 2.61 and 3.39.

The high oxidising power of alkali metal tetrafluorochlorates(III) must be regarded as their main chemical property[86]. They react vigorously with water, the reaction resulting in the evolution of oxygen and the formation of chlorate ions.

Iodates are oxidised by tetrafluorochlorates(III) to iodine. The chemical reactivity of the compounds is inversely proportional to their stability, which can be represented by the following general scheme:

$$\xrightarrow{\text{increase of stability}}$$
$$K—Rb—Cs$$
$$\xleftarrow{\text{increase of chemical reactivity}}$$

It is known that Pyrex glass does not react with chlorine trifluoride free from hydrogen fluoride, but a solution of an alkali metal fluoride in ClF_3 breaks down Pyrex glass very vigorously, which is evidently due to the increased self-ionisation of chlorine trifluoride as a result of the shift of the equilibrium

$$2\,ClF_3 \rightleftarrows ClF_2^+ + ClF_4^-.$$

Thus it may be suggested that solutions of alkali metal fluorides in chlorine trifluoride can serve as fluorinating agents more powerful than liquid chlorine trifluoride.

Alkali metal tetrafluorochlorates(III) char wood and paper on contact and react explosively with many organic substances.

As a result of their low vapour pressure, alkali metal tetrafluorochlorates(III) can be used in fluorination reactions at temperatures up to 500°C without the development of a high pressure in a closed system, i.e. these compounds find application as convenient sources of fluorine in those reactions where it is difficult to use liquid or gaseous chlorine trifluoride and other halogen fluorides.

In view of their unusual nature, high oxidising power, and high fluorine content, alkali metal tetrafluorochlorates(III) are the most interesting compounds among all the fluorohalogenates known at the present time. It is interesting to examine the behaviour of these compounds as bases and

their interaction with various acids and to investigate the mechanism of the hydrolysis, fluorination processes, etc. However, it should be noted that the chemistry of alkali metal tetrafluorochlorates(III) has been investigated very little and that all the problems enumerated above remain unresolved so far. Information about the physical properties is also very limited. Furthermore, alkali metal tetrafluorochlorates(III) free from the fluorides as impurities have not been synthesised and the nature of the impurities has not been established (i.e. whether these substances are present as mechanical mixtures or whether they are compounds of the double salt type). All these are the most interesting and promising problems awaiting solution in the further study of alkali metal tetrafluorochlorates(III).

As regards alkali metal fluorochlorates in general, it should be noted that the most promising and important task at the present time is the synthesis of hexafluorochlorates(V) with the general formula $MClF_6$, where M is the alkali metal. The information about chlorine pentafluoride is limited to three brief communications[25,99,100] and the reliable synthesis of chlorine pentafluoride was developed as late as 1966.[25] Evidently, as for other fluorochlorates[52,53], the phenomenon of self-ionisation in solution is characteristic of chlorine pentafluoride:

$$2\,ClF_5 \rightleftarrows ClF_4^+ + ClF_6^-$$

which means that there is a possibility of the formation of acids and bases containing the corresponding complex ions. Bases of this type should be the most powerful solid fluorinating agents among those known at the present time.

III. ALKALI METAL FLUOROBROMATES

The reaction leading to the formation of alkali metal fluorobromates was first achieved by Moissan[101], who observed the formation of a compound of fluorine and bromine on fluorination of potassium bromide with gaseous fluorine. Potassium tetrafluorobromate(III) $KBrF_4$ was probably obtained but the compound was not isolated in a pure state; under the experimental conditions used $KBrF_4$ decomposed into potassium fluoride and bromine trifluoride, which was in fact the new, hitherto unknown compound of fluorine and bromine.

The following compounds of bromine and fluorine are known[102-105]: bromine monofluoride BrF, bromine trifluoride BrF_3, and bromine pentafluoride BrF_5. Bromine monofluoride has not yet been isolated in a pure form: it is the least stable compound of the three enumerated above, which is why it has not been well characterised physicochemically. Its chemical properties have not been much investigated either, since it is difficult to separate it from BrF_3, BrF_5, and Br_2 which are in equilibrium with it. Evidently this is the reason why alkali metal difluorobromates(I) have not been isolated so far. Analogous derivatives of BrF_3 and BrF_5 have been successfully synthe- and their properties have been vigorously investigated in recent years.

Banks et al.[52] observed experimentally a considerable difference (by a factor of about 100) between the electrical conductivities of bromine trifluoride in the solid and liquid state; they believe that this is evidence of the ionic character of the conductivity of bromine trifluoride. In view of this and also a number of chemical properties of bromine trifluoride, self-ionisation according to the following equation has been suggested:

$$2\,CrF_3 \rightleftarrows BrF_2^+ + BrF_4^-\,.$$

The analogous behaviour of bromine pentafluoride is also quite evident:

$$2\,BrF_5 \rightleftarrows BrF_4^+ + BrF_6^-\,.$$

Thus successful synthesis of two types of alkali metal fluorobromates, containing the anions BrF_4^- and BrF_6^-, was to be expected. Representatives of both classes are in fact known: alkali metal tetrafluorobromates(III) and hexafluorobromates(V).

1. Alkali Metal Tetrafluorobromates(III)

The determination of the nature of liquid bromine trifluoride and its solutions served as a basis for the successful synthesis of alkali metal tetrafluorobromates(III).[52,53,106-109] Bromine trifluoride can behave both as a donor and acceptor of electrons. The data on the solubility of alkali metal halides in bromine trifluoride are very important for the elucidation of the conditions in which alkali metal tetrafluorobromates(III) can be synthesised. The solubility is of the ionic type. On dissolution in bromine trifluoride, alkali metal fluorides are almost completely dissociated into ions, the solubility increasing sharply with the atomic weight of the metal[110]. When an alkali metal fluoride dissolves, the anion BrF_4^- forms in accordance with the equation

$$MF + BrF_3 = M^+[BrF_4^-]\,.$$

Thus bromine fluoride behaves in this case as an acceptor of fluoride ions. It is interesting that similar behaviour is also characteristic of hydrogen fluoride:

$$MF + HF = M^+[HF_2^-]\,.$$

Sharpe and Emeléus[107] investigated the reactions of bromine trifluoride with alkali metal halides. With lithium chloride, double decomposition results in the formation of lithium fluoride, which is sparingly soluble in an excess of bromine trifluoride. When sodium fluoride is dissolved in bromine trifluoride and when the excess of the latter is removed in a vacuum, a compound with the composition $NaF.0.97BrF_3$ forms. Evidently sodium tetrafluorobromate(III) with an admixture of sodium fluoride is obtained in this case. Potassium chloride is appreciably soluble in bromine trifluoride, the dissolution involving more profound transformations than is the case with lithium fluoride; this is confirmed by the isolation of the reaction product in a pure state. When the excess solvent is removed (vacuum 130°C), a white crystalline substance remains, whose composition corresponds to the formula $KBrF_4$. Sharpe and Emeléus[107] also point out the possibility of preparing the analogous rubidium and caesium salts; however, it was not possible to isolated these compounds in a pure state.

The data for ammonium fluoride show that the compound NH_4BrF_4 is unstable and decomposes explosively. However, ammonium tetrafluorobromate(III) NH_4BrF_4 should be much more stable than ammonium tetrafluorochlorate(III) NH_4ClF_4, and it is quite evident that its isolation in a pure form is possible. So far this compound has not been isolated and investigated. There are only data showing that the interaction of ammonium fluoride with bromine trifluoride yields a white solid product with the tentative composition NH_4BrF_4.[86] Apart from the reaction between alkali metal fluorides or chlorides with liquid bromine trifluoride, alkali metal tetrafluorobromates(III) can be prepared by a "dry" method involving the reaction

$$MBr + 2\,F_2 = MBrF_4\,.$$

The tetrafluorobromates(III) of potassium, rubidium, and caesium were obtained in this way[79]. This method was first used by Bode[39,40], but the latter incorrectly identified the reaction products, as in the case of the chloride.

Thus potassium, rubidium, and caesium tetrafluorobromates(III) have so far been isolated in a pure form, sodium tetrafluorobromate(III) has been obtained together with impurities, and it has been suggested that ammonium tetrafluorobromate(III) may be obtained.

Alkali metal tetrafluorobromates(III) are white crystalline involatile substances. For example, when potassium tetrafluorobromate(III) was placed in a quartz tube and evacuated at room temperature for 6 h, the weight loss was only 0.5%. At 158°C the vapour pressure of $KBrF_4$ is 20 mmHg and at 356°C it is only 90 mmHg. In the above temperature range the vapour pressure is described by the equation

$$\lg P_{mm} = 3.38 - \frac{890}{T}.$$

When potassium tetrafluorobromate(III) is heated at 200°C for 5 min, the weight loss is 30%, while sodium tetrafluorobromate(III) decomposes completely under these conditions; furthermore, rapid decomposition of $NaBrF_4$ is observed even at 80°C. This is one of the reasons for the difficulty of synthesising pure sodium tetrafluorobromate(III).

The melting point of $KBrF_4$ has been determined approximately–it is near 330°C. When the substance is heated above 330°C, the vapour pressure rises sharply, which can be explained by the decomposition of $KBrF_4$ with evolution of gaseous BrF_3.

Thermal decomposition of potassium tetrafluorobromate(III) is accompanied by the evolution of BrF_3 and the formation of potassium fluoride. Similar thermal decomposition is in general characteristic of analogous compounds, i.e. the more electronegative halogen remains in a compound with the alkali metal. This rule is also evident in the thermal decomposition of $KICl_4$ and $RbICl_3F$. The thermal decomposition of these compounds is accompained by the evolution of ICl_3 and the formation of potassium chloride and rubidium fluoride respectively[111,112].

This general tendency in the decomposition of polyhalogenates is explained by the fact that the lattice energy of the alkali metal halides decreases on going from the fluorides to iodides and therefore the formation of the halides involving the most electronegative halogen is favoured by the energy change.

There are no data on the thermal stability of rubidium and caesium tetrafluorobromates(III). The stability series should however be the same as for the tetrafluorochlorates(III), i.e. Cs > Rb > K > Na > Li. The data for $KBrF_4$ and $NaBrF_4$ fully confirm this hypothesis. The first views concerning the structure of potassium tetrafluorobromate(III) were put forward by Sharpe and Emeléus[107]. It was suggested that $KBrF_4$ has a structure analogous to that of $KICl_4$, which was found to consist of the cation K^+ and a planar anion $[ICl_4^-]$.[113] Potassium fluoride lines are absent from the powder diffraction pattern. If the $[BrF_4^-]$ anion has a configuration analogous to that of $[ICl_4^-]$, then the first is much smaller than the second, because the Br–F distance should be 1.78 Å and the I–Cl distance 2.34 Å. Subsequently a complete investigation of the crystal structure of $KBrF_4$ was made[51,114] and it was shown that the compound crystallises with a tetragonal unit cell ($a = 6.174$, $c = 11.103$ Å), the space group being $I4/mcm$. Experimental determination of the density (3.06) showed that 4 molecules are present in the unit cell, which is in good agreement with the density calculated from the X-ray diffraction data. The fluorine atoms are disposed tetrahedrally with respect to each bromine atom, with a Br–F distance of 1.81 Å. The F–F distances in the $[BrF_4^-]$ anion are 2.81 and 3.03 Å. Each potassium atom is linked to eight fluorine atoms, the K–F distances being 2.84 Å. These results were obtained from powder diffraction patterns of potassium tetrafluorobromate(III).

Sly and Marsch[115] believe that the more likely configuration is a square $[BrF_4^-]$ anion. The fluorine atoms give rise to approximately square symmetry with respect to potassium atoms. The interatomic distances in this case are as follows: Br–F 3.30, K–F 2.74, and F–F 2.70 Å. However, the authors themselves note[115] that, on the basis of the available experimental data, it is difficult to establish reliably the validity of one of the two proposed structures. The experimental results correspond with approximately the same precision to both the tetrahedral and the square configuration of the $[BrF_4^-]$ anion. The final determination of the structure of $KBrF_4$ will evidently be possible after studies on single crystals. There have been no investigations of the structures of other alkali metal tetrafluorobromates(III).

Potassium tetrafluorobromate(III) is a very reactive substance which reacts vigorously with water. The reaction products are bromine, hydrobromic and hydrofluoric acids, oxygen, and potassium fluoride. The first stage of the reaction can be represented by the equation

$$K^+BrF_4^- + 2H_2O = K^+ + HBrO_2 + 3H^+ + 4F^-\,\dagger$$

with subsequent decomposition of $HBrO_2$ into Br_2, HBr, and O_2.

$KBrF_4$ does not react with carbon tetrachloride, acetone, and dioxan and does not dissolve in them, whereas BrF_3 reacts very vigorously, usually explosively. On the other hand, even boiling BrF_3 does not react with platinum, while $KBrF_4$ does react with platinum on heating, with formation of K_2PtF_6.

$AgBrF_4$ and $Ba(BrF_4)_2$ are known to be more reactive than $KBrF_4$, due to their lower stability and the greater ease of evolution of BrF_3, which is the active principle in the reaction of these compounds. Consequently sodium tetrafluorobromate(III) should be more reactive and rubidium and caesium tetrafluorobromates(III) less reactive than potassium tetrafluorobromate(III), but no experimental data are available for these compounds.

It must be emphasised that the available experimental data refer in the first place to $KBrF_4$. The information about the tetrafluorobromates(III) of other alkali metals is restricted virtually only to the method of synthesis. All other properties can be considered only on the basis of analogies in the series Li–Na–K–Rb–Cs. Therefore so far there has been no reliable and comprehensive physicochemical study of alkali metal tetrafluorobromates(III).

† It is interesting to compare this reaction with the reaction $BrF_3 + H_2O = HBrO_2 + 3H^+ + 3F^-$.

2. Alkali Metal Hexafluorobromates(V)

The hexafluorobromates(V) of potassium ($KBrF_6$), rubidium ($RbBrF_6$), and caesium ($CsBrF_6$) were first obtained in 1964 by Whitney et al.[86] in a detailed study of the solvolysis of BrF_5. The mechanism of the interaction of alkali metal fluorides with BrF_5 involves the reactions

$$2\,BrF_5 \rightleftarrows BrF_4^+ + BrF_6^+,$$

$$MF + BrF_5 = M^+ + BrF_6^-,$$

where M is the alkali metal. The ease of reaction depends on the nature of the cation. Table 6 gives the conditions for the synthesis of alkali metal hexafluorobromates(V).

It is evident from Table 6 that the general rule common to all the alkali metal fluorohalogenates applies to hexafluorobromates(V) as well, i.e. the ease of the reaction $MF \rightarrow MBrF_6$ increases in the series Li–Na–K–Rb–Cs. The pure hexafluorobromate(V) has been obtained only for caesium, while lithium hexafluorobromate(V) does not form and sodium hexafluorobromate(V) has been obtained only as a small amount of impurity in the bulk of sodium fluoride which has not reacted.

Alkali metal hexafluorobromates(V) are white crystalline substances. They are unusually stable to heat, compared with alkali metal polyhalides without fluorine. For example, it has been shown that $CsBrF_6$ can be heated to 300°C for several hours without appreciable decomposition. The density of $CsBrF_6$ is 3.68, the density of the composition $RbBrF_6 \cdot 0.1RbF$ is 3.59, and the value calculated for pure $RbBrF_6$ on the basis of additivity is 3.58.

Alkali metal hexafluorobromates(V) are very reactive, their hydrolysis involving the formation of bromate ions predominantly. These compounds are very powerful fluorinating agents, and since they are stable on heating to at least 300°C, their employment in high-temperature fluorination processes appears to be highly desirable.

The most important problems involving fluorobromates are those that have already been noted for fluorochlorates, i.e. they include the search for methods of synthesis of these compounds in a pure form, the determination of the nature of the mixtures synthesised, containing a definite amount of the initial alkali metal fluoride, a comprehensive physicochemical investigation of the compounds, and also the development of methods for the synthesis of alkali difluorobromates(I), which have not been obtained so far.

TABLE 6. Synthesis of alkali metal hexafluorobromates(V) using bromine pentafluoride*.

Fluoride	Molar ratio BrF_5 : MF	Results of analysis, wt. %		Results of synthesis
		Br	F	
LiF	10	–	–	Does not react.
NaF	10	–	–	No reaction observed; sodium hexafluorobromate(V) probably forms at 140°C but the degree of conversion is less than 5%.
KF	10	25.2	43.5	A white crystalline substance forms; 49.4% of the initial KF is converted into $KBrF_6$. Calculated for $KBrF_6 \cdot KF$: 27.3% Br; 45.4% F.
RbF	10	27.3	39.8	A white crystalline substance forms; 90% of the initial RbF is converted into $RbBrF_6$. Calculated for the composition $RbBrF_6 \cdot 0.1RbF$: 27.6% Br; 40.8% F.
CsF	10	24.4	34.8	A white crystalline substance forms; 100% conversion of CsF into $CsBrF_6$. Calculated for $CsBrF_6$: 24.4% Br; 34.8% F.
NH_4F	–	–	–	A white crystalline substance forms, but breaks down on heating above 0°C. Probably NH_4BrF_6.

* The reaction was carried out at 100°C.

IV. ALKALI METAL FLUOROIODATES

Iodine fluorides constitute the most extensive class of halogen fluorides. Iodine monofluoride IF, trifluoride IF_3, pentafluoride IF_5, and heptafluoride IF_7 are known[116–120]. Iodine heptafluoride is the only compound, not only among halogen fluorides but among interhalogen compounds in general, which contains seven atoms of one halogen in the molecule. Iodine is the only halogen which in its reaction with fluorine exhibits the highest valence characteristic of the Group. The capacity to form higher molecular species can be explained by the position of the elements in the Periodic System: the wide separation of the halogens facilitates the preparation of higher interhalogen compounds. The reason is the enhanced difference between the properties of the elements which facilitates their mutual saturation on interaction. The geometrical factor is also important: the large atomic radius of iodine and the small atomic radius of fluorine favour the maximum saturation of iodine by fluorine.

Despite the very wide variety of iodine fluorides, alkali metal fluoroiodates have been investigated least completely, which in the first place is evidently due to the low fluorinating activity of iodine fluorides, compared with chlorine and bromine fluorides.

1. Alkali Metal Tetrafluoroiodates(III)

Alkali metal tetrafluoroiodates(III) were first synthesised in 1960 by Hargreaves and Peacock[121]. The authors used IF_5 for the synthesis instead of iodine trifluoride (evidently because of the low fluorinating capacity of the latter and the low solubility of alkali metal fluoride in it). The use of IF_5 became possible after it had been established that a solution of an alkali metal fluoride in iodine pentafluoride behaves as a reducing agent, capable of reducing, for example, MoF_6 to MoF_6^- and ReF_6 to ReF_6^-.[122,123] Since the I^- ion does not exist in the solution, it is evident that the reducing agent in this case is a new complex, i.e. the tetrafluoroiodate(III) ion $[IF_4^-]$.

In the synthesis of alkali metal tetrafluoroiodates(III) with iodine pentafluoride a large excess of the latter was condensed on to the iodide of the corresponding alkali metal. The interaction was accompained by the evolution of free iodine:

$$5MI + 4F_5 = 5MIF_4 + 2I_2.$$

After the complete dissolution in the cold of the initial solid, the excess solvent was removed in a vacuum and the reaction product was heated in the vacuum to 50°C to remove the residual iodine. Tetrafluoroiodates(III) with the general formula MIF_4 were obtained in this way for potassium, rubidium, and caesium, and also a soluble compound of caesium with the composition $CsIF_4 \cdot IF_5$ (CsI_2F_9) (Table 7).

Alkali metal tetrafluoroiodates(III) were also synthesised using iodine trifluoride[124]. The alkali metal fluoride dissolved in acetonitrile was treated with iodine trifluoride for a long period at −45°C. Chemical analysis of

TABLE 7. Synthesis of alkali metal tetrafluoroiodates(III) using iodine pentafluoride.

Starting materials	Temperature of synthesis, °C	Products	Results of chemical analysis			
			calc., %		found, %	
			F	I	F	I
NaI+IF_5	20	—	—	—	—	—
KI+IF_5	20	KIF_4	31.4	52.5	33.0	45.3
RbI+IF_5	20	$RbIF_4$	26.3	44.1	26.2	43.3
CsI+IF_5	20	CsI_2F_9	30.7	45.5	30.7	46.6
CsI_2F_9	100 (vacuum)	$CsIF_4$	22.6	37.8	24.8	37.9

* Erroneous values were quoted by Hargreaves and Peacock [121] for the calculated iodine content of the tetrafluoroiodates(III): 48.4% for KIF_4, 44.6% for $RbIF_4$, 46.3% for CsI_2F_9, and 38.7% for $CsIF_4$. The corrected results are given in this table. It should be noted that they do not alter fundamentally the experimental data obtained for the tetrafluoroiodates(III) of rubidium and caesium and confirm the successful synthesis of these compounds. Hargreaves and Peacock [121] evidently also obtained potassium tetrafluoroiodate(III) but with considerable admixtures of the hexafluoroiodate(V), which is confirmed by the results of chemical analysis—the low iodine content and the high fluorine content of the substance synthesised.

the resulting colourless finely crystalline powders confirmed the formation of compounds with the composition MIF_4 (Table 8).

It has been stated, without the description of the conditions of synthesis, that the tetrafluoroiodates(III) of potassium, rubidium, and caesium can also be obtained using elemental fluorine to fluorinate the corresponding iodates [79]. It is surprising that the authors [79] obtained under these conditions tetrafluoroiodates(III) and not hexafluoroiodates(V). The latter is the more likely, but, in view of the brevity of the information given and the lack of identification of the products, it is impossible to assess the conclusions with sufficient reliability [79].

The tetrafluoroiodates(III) of lithium, sodium, and ammonium have not been obtained. The known alkali metal tetrafluoroiodates(III) are readily decomposed by atmospheric moisture and water. Their stability depends, as with other fluorohalogenates, on the size of the cation, which is confirmed by data derived from thermal studies. The tetrafluoroiodates(III) of potassium, rubidium, and caesium readily decompose on heating. Potassium tetrafluoroiodate(III) decomposes slowly even at room temperature with evolution of iodine, but caesium tetrafluoroiodate(III) is much more stable to heat and does not undergo appreciable changes on heating in a vacuum to 120°C. Vigorous decomposition is observed on heating below 70°C for KIF_4, below 70°C for $RbIF_4$, below 60°C for CsI_2F_9, and above 120°C for $CsIF_4$. [124] The powder diffraction patterns of potassium, rubidium, and caesium tetrafluoroiodates(III) did not permit the determination of the structures of these compounds, but they confirmed unambiguously that they do not have the same structures as the corresponding tetrafluorobromates(III). [51,114,115]

TABLE 8. Synthesis of alkali metal tetrafluoroiodates(III) using iodine trifluoride.

Compound	Results of chemical analysis					
	calc., %			found, %		
	metal	F	I	metal	F	I
KIF_4	16.1	31.4	52.5	17.3	30.5	52.0
$RbIF_4$	29.6	26.3	44.1	28.8	26.9	44.3
$CsIF_4$	39.6	22.6	37.8	39.8	23.6	36.5

2. Alkali Metal Hexafluoroiodates(V)

Iodine pentafluoride is appreciably inferior as a fluorinating agent to chlorine and bromine trifluorides. However, it too is capable of self-ionisation in solution [52,53,66,125]:

$$2\,IF_5 \rightleftarrows IF_4^+ + IF_6^-,$$

which means that the formation of acids and bases containing the corresponding complex ions is probable.

Sharpe and Emeléus [107] first showed in 1948 that potassium fluoride dissolves in IF_5 (about 1% KF) with the probable formation of potassium hexafluoroiodate(V) KIF_6. Subsequently the same workers [126] successfully achieved the synthesis of KIF_6 and examined the behaviour of other fluorides on dissolution in iodine pentafluoride.

Boiling IF_5 dissolves up to 1% of KF and on cooling white crystals are deposited from the solution. The attempt to remove the solvent at a reduced pressure (< 1 mmHg) did not result in the isolation of potassium hexafluoroiodate(V) in a pure form; phases of variable composition were produced (KF. $0.61IF_5$, KF. $0.91IF_5$). A product of constant composition was obtained by removing the excess IF_5 at 15–20°C and a pressure of 2–5 mmHg. Under these conditions the substance synthesised does not decompose and has the composition KIF_6. Potassium hexafluoroiodate(V) can also be obtained on prolonged boiling of potassium nitrate in iodine pentafluoride with subsequent removal of the excess of the latter in a vacuum at 20°C. [127]

When equimolar amounts of IF_5 and KF.HF are dissolved in anhydrous hydrogen fluoride, a deposit forms, whose composition has not been established accurately, but chemical analysis suggests that in this case too the product is KIF_6, contaminated with the initial KF.HF. [66] It is interesting to note 40% hydrofluoric acid converts KIO_3 into KIO_2F_2. [128] This compound may be regarded as the product of the partial replacement of fluorine by oxygen in potassium hexafluoroiodate(V). Caesium hexafluoroiodate(I) was obtained, like KIF_6, by crystallisation from solution in iodine tetrafluoride [126,129]. Furthermore, it has been stated that this compound can be obtained by fluorinating caesium iodide with elemental fluorine [79].

As already mentioned, when an alkali metal iodide reacts with cold IF_5, the tetrafluoroiodate(III) forms. On the other hand, the corresponding hexafluoroiodate(V) is produced in hot iodine tetrafluoride [121]. The alkali metal iodide is treated with an excess of IF_5, the solution is boiled for 5 min and then rapidly cooled, and the excess of the solvent is pumped off in a vacuum. The hexafluoroiodates(V) of potassium, rubidium, and caesium have been obtained in this way.

When NH_4F is dissolved in IF_5, a white solid is formed, which probably has the composition NH_4IF_6. In view of its extreme instability, the compound was not isolated in a pure form [85]. From the point of view of finding new ways of synthesising alkali metal fluorohalogenates, it is interesting to examine the interaction of alkali metal fluorides in

TABLE 9. Synthesis of alkali metal hexafluoroiodates(V) using copper pentafluoride.

Compound	Composition			
	calc., %		found, %	
	I	F	I	F
KIF_6	45.3	40.7	45.7	40.2
$RbIF_6$	38.3	34.9	38.3	35.5
$CsIF_6$	33.0	30.5	33.9	30.5

mixtures of halogen fluorides. It is known [130] that ClF_3 dissolves in IF_5 and BrF_5 and is not evolved on heating the mixture appreciably above its boiling point (60–70°C). This is undoubtedly due to interaction in solution. The effect of such complex self-ionisation in solution and the nature of the interaction between the alkali metal fluoride and the mixture of halogen fluorides can be explained on the basis of data for the relative acidities of the pair of halogen fluorides under consideration. In the stronger acids fluoride ions are coordinated to form complex anions of the type XF_n^-. It follows from the data in Table 10 that BrF_5 and IF_5 are stronger acids than ClF_3; the following reactions are involved:

$$\text{(a)}\quad ClF_3 + BrF_5 \rightleftarrows ClF_2^+ + BrF_6^-,$$

$$MF + ClF_2^+ + BrF_6^- \rightleftarrows MBrF_6 + ClF_3,$$

$$\text{(b)}\quad ClF_3 + IF_5 \rightleftarrows ClF_2^+ + IF_6^-,$$

$$MF + ClF_2^+ + IF_6^- \rightleftarrows MIF_6 + ClF_3.$$

The interaction of potassium fluoride with the ClF_3–BrF_5 mixture is an exception. In this case the tetrafluorochlorate(III) forms instead of the expected potassium hexafluorobromate(V). No explanation has so far been found for this phenomenon. When alkali metal fluorides are dissolved in ClF_3–BrF_3 mixtures, the reaction products should be the hexafluorobromate(III), and this is confirmed by the study of fluorine isotope exchange between ClF_3 and BrF_3 [93] which has shown that in this case chlorine trifluoride is a base and bromine trifluoride an acid:

$$ClF_3 + BrF_3 \rightleftarrows ClF_2^- + BrF_4^-.$$

Thus one of the methods of synthesising alkali metal fluorohalogenates is based on the use of mixtures of halogen fluorides as solvents. This is particularly important in the synthesis of fluoroiodates, in view of the lower fluorinating activity of iodine fluorides compared with chlorine and bromine fluorides.

TABLE 10. Interaction of alkali metal fluorides with ClF_3–BrF_5 and ClF_3–IF_5 mixtures.

Fluoride	Solvent	Temperature of synthesis, °C	Reaction products
KF	ClF_3+BrF_5	25	$KClF_4 \cdot KF$
KF	ClF_3+BrF_5	100	$KClF_4 \cdot 0{,}7\ KF$
RbF	ClF_3+BrF_5	25	$RbBrF_6 \cdot 0{,}5\ RbF$
CsF	ClF_3+BrF_5	25	$CsBrF_6 \cdot 0{,}1\ CsF$
KF	ClF_3+IF_5	100	KIF_6

Potassium hexafluoroiodate(V) KIF_6 is the first fluorohalogenate containing seven halogen atoms in the complex anion whose existence has been reliably established. There are no structural data for potassium hexafluoroiodate(V), but its properties are known and, by analogy with other similar compounds, one can reliably suggest the formula $K^+IF_6^-$. This is also quite evident for the hexafluoroiodates(V) of rubidium and caesium.

The iodine atoms in the complex anion $[IF_6^-]$ should have a valence shell of 14 electrons but only six coordination sites. This distinguishes the $[IF_6^-]$ anion from IF_7. Since $[IF_6^-]$ resembles $[SeF_6]^{2-}$ and $[TeF_6]^{2-}$, [131,132] it is possible that it has an octahedral structure. The configuration of iodine atoms in $[IF_6^-]$ is $5s^25p^25d^46s^2$ and therefore it can be suggested that $[IF_6^-]$ does not resemble other polyhalide anions, where the bond length is the sum of the corresponding radii [133], and that in this case the distance between the halogen atoms should be anomalously large [126].

Structural studies on KIO_2F_2 [128] have shown that the $IO_2F_2^-$ ion is an octahedron or a trigonal bipyramid. The iodine and oxygen atoms lie in one plane, the O–I–O angle is 100°±10°, and two fluorine atoms, forming an angle of 180°, are located in a direction perpendicular to the plane containing the iodine and oxygen atoms. The interatomic distances are 1.93±0.05 Å for I–O and 2.00±0.05 Å for I–F.

Potassium hexafluoroiodate(V) is moderately soluble in cold IF_5 and appreciably soluble in hot IF_5. It is decomposed by water with evolution of heat according to the equation

$$IF_6^- + 3H_2O = 6F^- + IO_3^- + 6H^+.$$

Thermal decomposition is accompanied by the evolution of IF_5 and the formation of KF. The melting point of KIF_6 is about 200°C. The fusion of KIF_6 is accompained by decomposition, since vigorous evolution of iodine pentafluoride is observed. Carbon tetrachloride does not affect KIF_6, while dioxan decomposes it only slightly [126]. All these findings are evidence of the relative stability of potassium hexafluoroiodate(V).

There are no data on the chemical behaviour of rubidium and caesium hexafluoroiodates(V). One can, however, speak of the similarity of their chemical and thermal properties and their greater stability compared with potassium hexafluoroiodate(V).

The question of the existence of alkali metal octafluoroiodates(VII) so far remains open. It is known [134] that, on interaction with iodine heptafluoride and subsequent evaporation of the latter at room temperature, rubidium chloride is only partially converted into rubidium fluoride. Under these conditions sodium, potassium, and rubidium fluorides do not dissolve in IF_7. Schumb and Lynch [134] concluded that compounds of the type MIF_8 cannot form under these conditions. However, this conclusion does not disprove the possibility of achieving the synthesis of similar compounds under other conditions; the compounds are the first representatives of bases containing nine halogen atoms in the complex anion. The synthesis of alkali metal octafluoroiodates(VIII), the search for new methods of synthesising and purifying tetrafluoroiodates(III) and hexafluoroiodates(V), the study of the physical and chemical properties of fluoroiodates, and the determination of their fluorinating capacity are the most important problems which must be solved first in further studies on alkali metal fluoroiodates.

V. ALKALI METAL FLUOROPOLYHALOGENATES

The first note concerning alkali metal fluorohalogenates containing two halogens in addition to fluorine dates back to 1931, when Cremer and Duncan[77] published an extensive paper on alkali metal polyhalogenates. It is interesting that a stability series for polyhalogenates is quoted in this paper, but the series was established only qualitatively. For the same anion the stabilities can be arranged in the following sequence: $Na < K < NH_4 < Rb < Cs$. Cremer and Duncan[77] do not indicate the position of lithium in this series, but there is no doubt that its compounds, if they exist at all, are the least stable. Only one compound containing fluorine is quoted in the paper, namely caesium fluorobromoiodate CsIBrF, which was obtained, by the adsorption of IBr on CsF, in the form of a yellow crystalline compound. The authors do not quote the results of chemical analysis and do not prove that it is indeed a chemically individual compound which, as far as one can judge from the very brief description, was evidently not isolated in a pure form. Later communications describe the syntheses of alkali metal fluorotrichloroiodates $MICl_3F$,[112,135] which have been obtained with potassium, ammonium, rubidium, and caesium in the form of orange-yellow needle-shaped crystals. The authors state that the caesium salt is the most stable and the potassium salt the least stable. In these papers the results of chemical analyses of polyhalogenates containing fluorine are quoted for the first time but fluorine was not determined directly (it was found by difference); the methods chosen by the authors for the determination of the remaining components are not the most reliable and therefore there are not sufficient grounds to believe that these compounds exist at room temperature in a free form. It should be noted that the information about alkali metal fluoropolyhalogenates is limited to the above communications, which are more than thirty years old and the experimental data of which give rise to considerable doubt. Thus at the present time there is no reliable information about this extremely interesting class of inorganic fluorides, although the existence of similar compounds of other halogens has been reliably established and they have been investigated in detail[49,136-140].

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Fluorine compounds have a number of specific properties which make them very interesting objects of study in different branches of chemistry, such as the chemistry of volatile compounds, non-aqueous solvents, complex compounds, etc., in the theory of the chemical bond, and in the study of the structure of matter. Furthermore, fluorine compounds have found considerable application in industry. The range of their application is extremely wide, in the first place because the most active and the most inert substances are to be found among one or other class of fluorine compound. However, these substances are not usually encountered in nature: they are synthesised artificially, and therefore the preparation of fluorinating agents whereby the initial compounds can be converted into fluorides always constitutes a very important problem. Evidently it is essential to have an extensive set of fluorinating agents permitting the synthesis of fluorine compounds in a predetermined manner. Powerful oxidising agents, whereby exhaustive fluorination can be readily carried out, occupy an important place here. Such substances are, in the first place, elemental fluorine, halogen fluorides, and the alkali metal fluorohalogenates examined in the present review.

There is no doubt about the advantages of alkali metal fluorohalogenates in fluorination processes. However, these compounds have not found wide practical application at the present time, which the present author believes is primarily due to the fact that they have not been adequately investigated and that reliable methods of synthesis are altogether lacking for some alkali metal fluorohalogenates, while for others they have been developed only recently. Furthermore, many methods proposed yield the required compounds only with an admixture of the initial fluoride, which is larger the lighter is the alkali metal in the fluorohalogenate synthesised.

The most promising method for the synthesis of alkali metal fluorohalogenates is the one based on the reaction of the corresponding halogen fluorides with alkali metal fluorides. It is in fact this method which yields the purest products. It is based on a reaction in a non-aqueous medium.

At an early stage of the development of inorganic chemistry water was used almost exclusively as the reaction medium, while in modern synthetic inorganic chemistry non-aqueous media are used to an increasing extent[141-144]. Reactions in non-aqueous media can be divided into two types: (a) reactions involving the self-ionisation of the solvent (i.e. solvolysis reactions) or with direct participation of the solvent and (b) reactions which are independent of the solvent. Reactions of the first type are used in the synthesis of alkali metal fluorohalogenates—the solvent itself takes part in the reaction. In this case the correct choice of the solvent and the reaction conditions is of primary importance. The task in further studies on alkali metal fluorohalogenates on these lines consists in a comprehensive investigation of binary systems of the type alkali metal fluoride–halogen fluoride which will lead to the discovery of the most rational methods of synthesising alkali metal fluorohalogenates and will permit the investigation of their most important property—their fluorinating capacity.

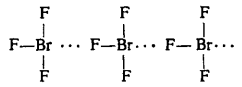
While in the initial period water was used as the sole medium in synthetic inorganic chemistry and then non-aqueous solvents, nowadays there is a tendency to use mixed non-aqueous solvents[145,146]. The most interesting results under these conditions are in fact to be expected for alkali metal fluorohalogenates; the most complete information about the conditions of the synthesis and the properties of the compounds obtained can be derived from studies of the corresponding multicomponent non-aqueous systems by methods of physicochemical analysis; this is one of the most important tasks in the further development of methods for the synthesis of alkali metal fluorohalogenates.

In the reactions considered, where aprotic solvents such as halogen fluorides are used, one may apply Gutmann and Lundqvist's definition of acids and bases[147]. Alkali metal fluorides are donors of fluoride ions and behave as bases in halogen fluorides:

$$\overset{F^-}{\overbrace{KF + ClF_3}} \rightleftarrows K^+ + ClF_4^- .$$

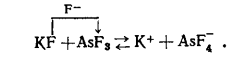
The possibility of fluoride ion transfers is determined by the structure of the compounds: for example, the BrF_3 molecule has a T-shaped configuration[148-151] while the BrF_4^- ion has a planar square structure[115,152]. The formation of fluoride bridges in pure solvents with corresponding fluoride ion transfers takes place without appre-

ciable structural changes; probably association takes place via fluoride bridges [153]:



Further structural studies should show whether the BrF_4^- ions or fluoride bridges exist in this case.

It has been shown by ^{19}F nuclear magnetic resonance that continuous fluorine exchange takes place in the KF–AsF_3 system [154]:



The ^{19}F nuclear magnetic resonance of SbF_5 solutions in AsF_3 also reveals the exchange of fluoride ions bound in fluoride bridges [154]. Consequently the presence of fluoride ions and fluoride ion coordination are characteristic of covalent solvents, which include halogen fluorides. The processes occurring in the synthesis of alkali metal fluorohalogenates using halogen fluorides should in fact be examined from these standpoints.

Thus comprehensive investigation of the reactions between halogen fluorides and alkali metal fluorides will greatly extend our knowledge about reactions in non-aqueous media, will lead to the development of reliable methods for the synthesis of alkali metal fluorohalogenates, will enable the investigation of their behaviour as oxidising agents, and will place at the disposal of theoretical and applied science new highly effective fluorinating agents.

In view of their practical value and the advances in the chemistry of alkali metal fluorohalogenates, a considerable future can be forecast for this class of inorganic fluorides.

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THE REACTIONS OF ACTIVE NITROGEN WITH ORGANIC MOLECULES

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1. INTRODUCTION

The fixation of nitrogen continues to be the subject of extensive studies in organic chemistry, biochemistry, photochemistry, electrochemistry, and radiation chemistry. This problem is vitally important, and at the same time difficult to solve. Molecular nitrogen is characterised by an unusual chemical inertness, which makes it impossible for nitrogen to react chemically with the great majority of chemical substances under ordinary conditions. The dissociation energy of nitrogen is 225.96 kcal mole^{-1} (at 298°K), the greater part of this energy (~ 125 kcal mole^{-1}) being required for the rupture of the first bond. These values are so large that they generally cannot be compensated by the liberation of energy on formation of new bonds. For example, the energies of the bonds formed by the nitrogen atom with a number of other elements have the following values (kcal mole^{-1})[1]:

N—H	N—C	N—Si	N—O	N—S	N—P	N—Sb	N—F	N—Cl	N—Br
84	195	105	152.3	116	164.9	111	61	62	70

It is clear that most fundamental reactions involving the rupture of the bonds (or even one bond) in the nitrogen molecule cannot take place spontaneously, without preliminary excitation of the molecular nitrogen. This last requirement is not simple either, however, since all the first excitation levels of molecular nitrogen are relatively high. For example, the excitation of molecular nitrogen to the first vibrational level requires an energy quantum of 0.43 eV. Thus this process will take place to a significant extent only at temperatures of the order of several thousand degrees. The energy required for the electronic excitation of N_2 amounts to not less than 6.167 eV, and that required for photochemical excitation is 8.546 eV.[2] The ionisation potential of N_2 is 15.6 eV.[1] Thus electronic excitation of nitrogen is difficult and requires extremely severe conditions. The central problem in the fixation of nitrogen is therefore the conversion of molecular nitrogen into a chemically active state. There are in principle two possibilities: (1) transfer to the nitrogen molecule of sufficient energy to bring about its electronic or vibrational excitation, dissociation, or even ionisation; (2) mild activation of molecular nitrogen; the mechanism of this process has not been elucidated, but it takes place in the fixation of nitrogen in biological systems. The second possibility has led to search for chemical systems providing models of these biological systems, and encouraging results have already been obtained[3-7]. Possible routes to chemical activation of N_2 in these systems have been examined[3,5]. Significant excitation of molecular nitrogen is achieved in the photochemical and radiation-chemical fixation of nitrogen, and also in discharge reactions. Here we are dealing with energy-rich nitrogen species such as atoms, electronically excited molecules, ions, etc. Routes to the fixation of nitrogen by organic molecules by the irradiation of these systems with hard radiation have recently been indicated[8]. In order to understand the mechanism of these complex reactions, it is important to know how the various active nitrogen species react with organic molecules. A considerable amount of factual material on these problems (particularly concerning nitrogen atoms) has accumulated, and we have tried to summarise this material in the present paper. Generally speaking, the reactions of energy-rich nitrogen species with organic molecules lead to the formation of a wide range of products. Since the present paper is concerned with the problem of nitrogen fixation, however, we shall consider here only the nitrogen-containing products of these reactions.

2. REACTIONS OF NITROGEN ATOMS

The reactions of nitrogen atoms with organic molecules will be examined chiefly on the basis of data obtained in the study of active nitrogen, that is nitrogen withdrawn from an electric discharge. The composition of active nitrogen has been the subject of detailed study since its discovery[9]. Up to the present, the following species have been identified, in addition to non-excited nitrogen molecules: $N(^4S)$, $N(^2P)$, $N(^2D)$, vibrationally excited $N_2(X^1\Sigma_g^+)$, $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $N_2(C^3\Pi_u)$, and $N_2(a^1\Pi g)$.

The presence of nitrogen atoms in active nitrogen has been proved by a number of direct physical methods. The ultraviolet range of the absorption spectrum of active nitrogen shows the transitions $NI(^4S \rightarrow 2p^4P)$, $(^4S \rightarrow 3s^4P)$, $(2p^32D \rightarrow 3s^2P)$, and $(2p^32P \rightarrow 3s^2P)$[10].

The forbidden $NI(^2P)$ line ($\lambda = 3466$ Å) can be observed in the emission spectrum of active nitrogen at pressures