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Metal† Hydrogen Fluorides

A.A.Opalovskii and T.D.Fedotova

The review deals with the available information on metal hydrogen fluorides. The methods of synthesis of hydrogen fluorides and their physical and chemical properties are examined and studies on the hydrogen bonds in hydrogen fluorides and their structures are discussed. The principal trends in the research in this field have been outlined on the basis of these data.
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I. INTRODUCTION

Fluorine is a very reactive element and forms compounds with all other elements. Its high electronegativity and small ionic radius are largely responsible for the wide variety of the properties of fluorine-containing compounds and their large number. Among fluorine compounds one may mention interesting classes of substances such as halogen compounds of fluorine[1-4] and noble gas fluorides[5-7], the development of the studies of which is related to the general advances in the chemistry of inorganic fluorides achieved in the last decades.

Since fluorine is known to form numerous complex compounds in which it behaves as the ligand[8,9], it is interesting to examine the interaction of inorganic fluorides with fluorine-containing solvents. Among these mention should be made in the first place of hydrogen fluoride, the specific properties of which are the reason for the increasing interest in it as a solvent[9].

The high dielectric constant and low viscosity of hydrogen fluoride make it a good ionising solvent. It is an associated liquid and its self-ionisation takes place via the mechanism[10]

$$(HF_m) \xrightarrow[+]{F^-} (HF)_n \rightleftarrows H_mF^+_{m-1} + H_nF^-_{n+1}.$$

The equilibrium constant for this process at 0°C [9] is 2.07×10^{-11}.

Reactions in anhydrous hydrogen fluoride normally involve the participation of the solvent itself. The unusual properties of hydrogen fluoride are responsible for the wide variety of compounds formed when fluorides react with hydrogen fluoride and its solutions[11].

A characteristic feature of the reaction of many fluorides with anhydrous hydrogen fluoride is their solvation by HF molecules. This process is not characteristic solely of hydrogen fluoride but occurs also with halogen compounds of fluorine, for example. Thus it is known

† Including ammonium hydrogen fluorides (Ed. of Translation).

that these compounds undergo self-ionisation in the liquid state[12-15]:

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

and numerous studies in recent years have shown that their interaction with many inorganic fluorides is due to the presence of the above ions in solution and the formation of the fluorohalogenates MXF_{n+1} ($MF.XF_n$) can itself be regarded as the solvation of fluorides by the halogen fluoride[16,17].

The solvating capacity of hydrogen fluoride is well illustrated by the data of Jache and Cady[18], who established that highly soluble fluorides exhibit a greater capacity for combining with hydrogen fluoride. However, they quote only the approximate composition of the solid phase in the saturated solutions of fluorides in hydrogen fluoride after centrifugation and therefore their results cannot be regarded as final proof of the existence of definite solvates as individual compounds.

The most complete information about processes involving the solvation of inorganic fluorides by hydrogen fluoride was obtained by the physicochemical analysis of binary and ternary systems containing hydrogen fluoride and metal fluorides. The results of studies on fusion diagrams for $HF-MF_m$ systems and on isothermal solubility in $HF-MF_m-H_2O$ systems indicate the formation in such systems of individual compounds with the composition $MF_m.nHF$, which are called the acid fluorides or hydrogen fluorides of the corresponding elements.

The formation of metal hydrogen fluorides in anhydrous hydrogen fluoride may be explained as follows. Hydrogen fluoride is an extremely active acidic solvent and ionic fluorides are strong bases in relation to HF, since they dissociate in it with formation of fluoride ions[19]. This leads to a displacement of the self-ionisation equilibrium of hydrogen fluoride towards the formation of the polymeric anions $H_nF_{n+1}^-$, which combine with metal cations to form metal hydrogen fluorides. It is noteworthy that the high tendency of hydrogen fluoride to solvate the F^- anion is due to the fact that the fluorides of many metals are dissociated in hydrogen fluoride to a greater extent than their hydroxides in water, although the dielectric constants of the two solvents are similar[20]. From this point of view, it becomes understandable why metal hydrogen fluorides are formed primarily by univalent and divalent metals, the dissociation of the fluorides of which in hydrogen fluoride differs from that of the fluorides of polyvalent elements, which exhibit molecular solubility in hydrogen fluoride[21,22] or have acidic properties in this solvent, i.e. behave as acceptors of fluoride ions[23,24].

The formation of metal hydrogen fluorides is also possible in aqueous solutions of hydrogen fluoride since here there is a possibility of an autocomplex-formation process:

$$H_2O + (n+1)\,HF \rightleftarrows H_3O^+ + H_nF_{n+1}^- .$$

The number of HF molecules added to the metal hydrogen fluorides formed increases as the concentration of water in the solution falls.

It is interesting to note that solvation by hydrogen fluoride is observed not only for simple fluorides but is also characteristic of certain complex fluorides, provided that they are stable in anhydrous hydrogen fluoride and its highly complicated solutions. Thus in a study of ternary systems of the type $HF-H_2MF_6-H_2O$ (M = Ge or Sn) it was established that rubidium, caesium, and ammonium hexafluorogermanates and rubidium and caesium hexafluorostannates form the solid solvates $H_2MF_6.nHF$.[25-27]

The first studies on metal hydrogen fluorides were undertaken primarily in connection with their practical applications. The most important application of these compounds is in the preparation of fluorine by electrolysis. This method, used in 1886 by Moissan[28], was subsequently developed and improved and is now the main industrial procedure for the manufacture of elemental fluorine, since it yields this important chemical industrial product in a fairly pure form and in a high yield[29-31]. Among other examples of the application of metal hydrogen fluorides, mention should be made of the use of potassium hydrogen difluoride for the preparation of pure anhydrous hydrogen fluoride[32-34]. Sodium hydrogen difluoride has found extensive application for the synthesis of anhydrous hydrogen fluoride from aqueous solutions[35] and for the elimination of hydrogen fluoride from fluorine in the industrial process[29,30].

The studies on metal hydrogen fluorides are of interest from the standpoint of the development of our knowledge of fluorine chemistry, since they are associated with important theoretical problems concerning the mechanism of the solvation of fluorides by fluorine-containing solvents, the structure of metal hydrogen fluorides, and the nature of their chemical bonds.

However, so far the only reviews of studies on metal hydrogen fluorides are restricted to chapters in monographs by Simons[36] and Ryss[8]. The publications which have appeared in the last 10–15 years on this problem and also the general progress in the development of the chemistry of inorganic fluorides make it possible in many cases to reassess the value of the earlier investigations and to draw new conclusions and generalisations. This review deals with the data available at present on the methods for the synthesis of metal hydrogen fluorides and their physical and chemical properties, structure, and the nature of their chemical bonds and the prospects of further research in this field of chemistry are discussed. The problems of the industrial utilisation of metal hydrogen fluorides are not considered, since they are dealt with in the specialist literature.

II. SYNTHESIS OF METAL HYDROGEN FLUORIDES

The first communication on the synthesis of alkali metal hydrogen fluorides was by Berzelius[37], who obtained lithium, sodium, and potassium hydrogen difluorides by dissolving the corresponding fluorides in hydrofluoric acid, and ammonium hydrogen difluoride by heating an aqueous solution of the fluoride. Later potassium hydrogen difluoride was synthesised by Fremy[38] from potassium carbonate and a hydrofluoric acid solution and became known as the Fremy salt. Borodin obtained NaF.HF and KF.HF by evaporating solutions of the fluorides in organic acids[39].

Moissan[40] synthesised compounds with the composition KF.2HF and KF.3HF from a solution of potassium hydrogen difluoride in anhydrous hydrogen fluoride. An attempt was made to obtain potassium hydrogen fluoride with the formula $KF.nHF$ by evaporating KF.HF solutions in hydrofluoric acid, but this yielded only KF.2HF contaminated with K_2SiF_6.[41]

The synthesis of the rubidium hydrogen fluorides RbF.HF and RbF.2HF mixed with RbF.3HF was first reported by Eggeling and Meyer[42]. However, subsequent investigations[43,44] showed that the compounds obtained by

Eggeling and Meyer[42] are in fact rubidium hexafluorosilicates; Eggeling and Meyer[42] described the synthesis of RbF.2HF containing a small admixture of Rb_2SiF_6 from a solution of rubidium carbonate in 40% hydrofluoric acid. Webb and Prideaux[41] described the synthesis of the hydrogen fluorides RbF.HF and RbF.2HF from a solution of rubidium fluoride in hydrofluoric acid and of RbF.3HF from anhydrous hydrogen fluoride.

The following acid salts have been reported for caesium fluoride: CsF.HF,[45] CsF.1.5HF, and CsF.2HF (approximate composition)[46], which were synthesised from anhydrous hydrogen fluoride.

According to a number of communications, silver(I) fluoride also forms acid salts. Thus Guntz[47] described the preparation of AgF.HF from a solution of AgF in hydrofluoric acid. A silver hydrogen fluoride with the composition AgF.3HF is formed in hydrofluoric acid solution and also when gaseous hydrogen fluoride acts upon dry silver fluoride at 13°C.[21,48]

In addition to the hydrogen difluoride[49], the acid fluorides with the composition TlF.2HF[50] and TlF.2HF.$0.5H_2O$[51] were obtained for thallium(I), but subsequently it was shown that the latter compound is a hexafluorosilicate[52].

All the investigations enumerated above were concerned with the synthesis of the hydrogen fluorides of univalant metals, the fluorides of which are readily soluble in hydrogen fluoride and its solutions.

Until recently the acid salts of the fluorides of other metals, much less soluble in hydrogen fluoride, were almost unknown. Only barium hydrogen fluoride BaF_2.HF was obtained[53] and the existence of the compound PbF_2.2.5HF on the basis of vapour pressure data[54] for the $HF-PbF_2$ system was suggested. The reports of the existence of the acid fluorides $CaF_2.2HF.6H_2O$[55] and $MF_2.5HF.6H_2O$ (M = Cu, Ni, Co, or Mn)[56] proved to be erroneous; the substances obtained were in fact hexafluorosilicates[57,58]. The earlier report of the synthesis of zinc hydrogen fluoride from a solution of the fluoride in hydrofluoric acid is also doubtful[59].

Although the existence of compounds with the composition $MF_m.nHF$ has been known for a long time and the publications quoted above include reports of their synthesis, it should be noted that a considerable proportion of these data are doubtful. This is mainly due to the fact that the experimental technique available at the time did not allow the early investigators to obtain the hydrogen fluorides in a pure state. As admitted by the authors themselves, the majority of the compounds synthesised contained an admixture of hexafluorosilicates or metal hydrogen fluorides of another composition. Moreover, the individuality of the hydrogen fluorides obtained was established in most cases only on the basis of chemical analysis, which gives rise to particular doubts concerning the composition of the compounds quoted, since most metal hydrogen fluorides are unstable even at room temperature and lose the combined HF molecules. This may also be reflected by the finding that certain physical constants of metal hydrogen fluorides of the same composition differ in various investigations.

The application of the methods of physicochemical analysis to the study of the interaction of metal fluorides with hydrogen fluoride and its solutions yielded accurate information about the composition and conditions of synthesis of metal hydrogen fluorides.

The first studies in this field were those of the fusion diagrams by Ruff and Staub[60] for the system $HF-NH_3$ and by Cady[61] for the system HF–KF. Later the corresponding binary systems with rubidium and caesium fluorides were investigated[62,63]. The results obtained indicate the formation in the HF–MF system of the following individual hydrogen fluorides: KF.nHF (n = 1, 2, 2.5, 3, or 4), RbF.nHF (n = 2, 3, 3.5, or 4.5), CsF.nHF (n = 1, 2, 3, or 6), and $NH_4F.n$HF (n = 1, 2, 3, or 5). Subsequently the data on the $HF-NH_3$ system were significantly revised by Euler and Westrum[64], who reject the existence of the compound $NH_4F.2HF$.

Tananaev's studies[65-67] by isothermal solubility of the ternary systems $HF-MF-H_2O$ (M = Li, Na, or K) were an important stage in the investigation of methods for the synthesis of metal hydrogen fluorides. The value of his results consists in the fact that the possibility of synthesising a whole series of sodium and potassium hydrogen fluorides, NaF.nHF (n = 1, 2, 3, or 4) and KF.nHF (n = 1, 2, 2.5, 3, or 4) from aqueous hydrogen fluoride solutions was demonstrated, which has undoubted advantages compared with the use of anhydrous hydrogen fluoride. The formation of the hydrogen difluoride LiF.HF in the $HF-LiF-H_2O$ system (investigated up to 75% HF) was established, but, because of the slowness of the reaction LiF → LiF.HF in the solid phase, it was recommended that lithium hydrogen difluoride be obtained by crystallisation from a saturated solution of LiF in hydrofluoric acid[65].

In a subsequent reinvestigation of the $HF-NaF-H_2O$ system[68] and part of the HF–NaF system[69], metal hydrogen fluorides were obtained whose composition was similar to that established previously[66].

Further investigations of systems of the type $HF-MF-H_2O$ were undertaken by the authors of this review. In a study of the highly concentrated region of the $HF-LiF-H_2O$ system, including anhydrous hydrogen fluoride, we did not observe any phase transformations of lithium hydrogen difluoride, although its solubility increased appreciably[70]. The results of the study of the $HF-RbF-H_2O$ and $HF-CsF-H_2O$ systems over the entire range of HF concentrations showed that the interaction in these systems leads to the formation of metal hydrogen fluorides with the composition RbF.nHF (n = 1, 2, 3, or 3.5) and CsF.nHF (n = 1, 2, or 3)[71]. In the $HF-CsF-H_2O$ system we did not observe compounds with compositions intermediate between CsF.HF and CsF.2HF, as in the HF–CsF system[63]. Evidently the report of the synthesis of the caesium hydrogen fluoride with the composition CsF.1.5HF is erroneous and Mathers and Stroup[46] must have obtained a mixture.

In a study of the $HF-NH_4F-H_2O$ system, hydrogen fluorides with the compositions $NH_4F.HF$ and $NH_4F.3HF$ were found as the solid phases[72]. The acid salts 3AgF.2HF, AgF.HF, AgF.2HF, AgF.3HF, and AgF.5HF as well as a compound with the somewhat unexpected composition $6AgF.7HF.2H_2O$ were obtained for silver fluoride in the ternary system[23].

The results of studies on binary and ternary systems containing alkali fluorides and hydrogen fluoride reveal certain general features of the solvation of these fluorides by HF molecules and the formation of metal hydrogen fluorides. The solubility of alkali metal fluorides and their capacity for solvation in hydrogen fluoride increase with the ionic radius of the cation, which is evidently due to the decrease of their crystal lattice energy on passing from LiF to CsF. The maximum number of HF molecules added to caesium fluoride is six, while for lithium only the hydrogen difluoride LiF.HF is known. The solubility of ammonium fluoride in hydrogen fluoride also obeys the

above relation. The formation by NH_4F of hydrogen fluorides with a larger number of combined HF molecules than in the case of rubidium fluoride can probably be accounted for by its capacity to form hydrogen bonds of two types: F–H...F and N–H...F.

Bearing in mind the ionic radius of Ag^+, silver(I) fluoride should occupy in the above series a position intermediate between the fluorides of sodium and potassium, but this is not observed, which may be due to different electronic structures of alkali metal and silver cations.

A marked tendency towards solvation would be expected for thallium fluoride, which has the highest solubility in hydrogen fluoride among univalent fluorides. However, the corresponding systems with thallium fluoride have not been investigated and therefore the problem remains unelucidated; at the present time hydrogen fluorides other than TlF.HF and TlF.2HF are unknown.

The possibility of synthesising alkaline earth metal hydrogen fluorides from aqueous hydrofluoric acid solutions was previously considered unlikely[8], although the data of Jache and Cady[18] indicated a tendency by these fluorides to combine with HF. In a study of the HF–MF_2–H_2O systems (M = Ca, Sr, or Ba), Nikolaev and Ikrami[11] obtained metal hydrogen fluorides with the following compositions: $CaF_2.2HF$, $SrF_2.nHF$ (n = 1, 2, or 2.5), and $BaF_2.nHF$ (n = 1, 3, or 4.5). Lead(II) fluoride behaves in hydrogen fluoride and its solutions similarly to alkaline earth metal fluorides, the formation of $PbF_2.2.5HF$ having been established in the HF–PbF_2–H_2O system[74].

The interaction of alkaline earth metal and lead fluorides with hydrogen fluoride obeys the same relation as a function of the ionic radius of the cations as for alkali metal fluorides, the only exception being the anomalously high solubility of strontium fluoride in anhydrous hydrogen fluoride. Comparison of the results of the studies on the HF–MF_2–H_2O (M = Ca, Sr, Ba, or Pb) systems shows that the formation in them of the metal hydrogen fluoride begins as a rule at a higher HF concentration in solution than for univalent metal fluorides, evidently because of the greater stability of the MF_2 crystal lattice.

Recent studies on the HF–MF_2–H_2O (M = Cu, Zn, Cd) systems[75,76] showed that, despite their very low solubility in anhydrous hydrogen fluoride and its concentrated solutions, the fluorides of copper, zinc, and cadmium also form the hydrogen fluorides $CuF_2.3HF$, $ZnF_2.2HF$, and $CdF_2.HF$. This suggests that the hydrogen fluorides of other divalent metals whose fluorides are sparingly soluble in hydrogen fluoride, such as HgF_2, MnF_2, etc., may also be obtained.

We may note that the studies on the systems HF–UF_4–H_2O [77] and HF–ThF_4–H_2O [78], where the fluorides are sparingly soluble over the entire range of concentrations of hydrogen fluoride, established the formation in the solid phase of compounds with the composition $UF_4.4HF$, $ThF_4.HF.H_2O$, and $ThF_4.4HF$, but the properties of these compounds were not investigated and their nature has not been elucidated.

In conclusion of the discussion of the methods for the synthesis of metal hydrogen fluorides, we may note that they reduce to the reaction between the fluorides and a solution of hydrofluoric acid (the conditions of synthesis are determined by the HF–MF_m–H_2O solubility isotherm) or anhydrous hydrogen fluoride (the conditions are determined by the HF–MF_m fusion diagram). One may also point out the possibility of the synthesis of these compounds by the thermal decomposition of metal hydrogen fluorides with a higher HF content. The principal data at present available on the solvation of fluorides by hydrogen fluoride are compiled in Table 1.

Table 1. Solvation of uni- and divalent-metal fluorides by hydrogen fluoride.

Fluoride	Radius of cation according to Belov and Bokii Å	Solubility in anhydrous HF at 0°C wt.%	No. of moles of HF in $MF_m.nHF$	Fluoride	Radius of cation according to Belov and Bokii Å	Solubility in anhydrous HF at 0°C wt.%	No. of moles of HF in $MF_m.nHF$
LiF	0.68	9.36	1	CaF_2	1.04	1.05***	2
NaF	0.98	21.79	1; 2; 3; 4	SrF_2	1.20	12.76***	1; 2; 2.5
KF	1.33	27.68	1; 2; 2.5; 3; 4	BaF_2	1.28	4.52***	1; 3; 4.5
RbF	1.49	56.50	1; 2; 3; 3.5; 4.5	PbF_2	1.26	3.40	2.5
CsF	1.65	66.60	1; 2; 3; 6	CuF_2	0.80	0.008	3
NH_4F	1.43*	29.04	1; 3; 5	ZnF_2	0.83	0.02	2
AgF	1.13	38.20	0.66; 1; 2; 3; 5	CdF_2	0.99	0.20	1
TlF	1.36	81.80**	1; 2				

* According to Goldschmidt.
** –7.8°C.
*** –3.3°C.

Hitherto it has not proved possible to obtain hydrogen fluorides containing two different metals as the cations. In principle their existence might be established by studying the corresponding binary or ternary systems.

The study of isothermal solubility in systems of the type HF–MF–M'F (M and M' are alkali metals)[70] showed that they contain as solid phases the hydrogen fluorides of the same composition as in the HF–M(M')F systems, the compound less soluble in hydrogen fluoride occupying a wide crystallisation field. Solid solutions and binary compounds are not formed in the systems. The type of interaction in them is determined primarily by the difference between the solubilities of the fluorides in HF and their different capacities for solvation.

III. PROPERTIES OF METAL HYDROGEN FLUORIDES

Metal hydrogen fluorides are white crystalline substances. The pyknometric densities of alkali metal hydrogen difluorides[79] and alkaline earth metal hydrogen fluorides[80] have been determined (Table 2).

The solutions of all metal hydrogen fluorides in water are acidic. The hydrogen difluorides of all alkali metals (except LiF.HF) and ammonium and also KF.2HF (at 40°C), RbF.2HF, CsF.2HF, and RbF.3HF are congruently soluble in water, which follows from the results of an investigation of the isothermal solubilities in the systems[65–67,68,71]. The solubilities of sodium, potassium, and ammonium hydrogen difluorides in water increase with temperature[66,67,81–83]. Hydrogen difluorides are insoluble in ethanol[84]. The isotherms for the ternary systems H_2O–KCl–KHF_2,[85] H_2O–NH_4Cl–NH_4HF_2,[86] and H_2O–NH_4F–NH_4HF_2 [87] are of a eutonic type.

The enthalpies of solution of alkali metal and ammonium hydrogen fluorides in water were determined for the first time by Peterson[88], Guntz[89], and de Forcrand[90], the data being revised subsequently[91,92] (Table 3). The standard entropy of the HF_2^- ion (16 cal $mole^{-1}$ deg^{-1}) found by Cox and Harrop[91] differs from the value calculated previously (26 cal $mole^{-1}$ deg^{-1}) [93]. The enthalpies of solution of the hydrogen fluorides $NH_4F.HF$ and $NH_4F.3HF$ in anhydrous

hydrogen fluoride have also been determined (−5.76 and −3.35 kcal mole^{-1} respectively[94]).

The thermal properties of hydrogen fluorides are of interest primarily in connection with their practical applications; they have been most thoroughly investigated for alkali metal and ammonium hydrogen fluorides.

Table 2. Pyknometric densities of metal hydrogen fluorides.

Compound	d_{25}, g cm^{-3}	Compound	d_{25}, g cm^{-3}
LiF·HF	2.05±0.01	BaF_2·HF	4.603±0.004
RbF·HF	3.1±0.2	CaF_2·2HF	2.613±0.004
CsF·HF	3.7±0.2	SrF_2·2.5HF	3.068±0.004
TlF·HF	6.3±0.3	BaF_2·3HF	3.56±0.01
SrF_2·HF	3.999±0.004	BaF_2·4.5HF	2.947±0.004

The melting points of alkali metal fluorides determined in the early studies are in most cases erroneous, owing to the presence of impurities in the test compounds and the deviation of their compositions from stoichiometry. Thus the following melting points were found initially: 227°C [95], 215–225°C [96], and 217°C [97] for potassium hydrogen difluoride, 142°C [46] for caesium hydrogen difluoride, and 105°C [40] and 70°C [98] for KF.2HF. Later the melting points of the hydrogen fluorides were determined with greater accuracy from a study of the fusion diagrams [61-64]. Comparison of these values (Table 4) shows that the melting points of alkali metal hydrogen fluorides decrease from sodium to caesium and with increase in the number of HF molecules combined.

Table 3. Enthalpies of solution of hydrogen fluorides in water (298.16°K).

Compound	LiF·HF	NaF·HF	KF·HF	RbF·HF	CsF·HF	NH_4F·HF	AgF·HF	KF·2HF	KF·3HF
$-\Delta H^\circ$, kcal mole^{-1}	18.60	6.2	6.0	5.31	3.73	4.85	2.0	8.0	8.6

The sodium hydrogen fluoride NaF.3HF melts incongruently[69]. According to Cady's data[61], all the potassium hydrogen fluorides melt congruently. However, in a recent paper[99] it is claimed, on the basis of a thermodynamic calculation for the decomposition reactions of the hydrogen fluorides formed as individual compounds in the HF–KF system[61], that compounds with the composition KF.2.5HF and KF.3HF exist only in the solid state and on fusion decompose according to the mechanisms

$$2K_2H_5E_7 \rightarrow 3KH_2F_3 + KH_4F_5; \quad 2KH_3F_4 \rightarrow KH_4F_5 + KH_2F_3.$$

The enthalpies and entropies of fusion of potassium hydrogen difluoride have been determined as 1.582 ± 0.003 kcal mole^{-1} and 3.09 ± 0.01 cal mole^{-1} deg^{-1} respectively[100,101]. The properties of potassium hydrogen fluoride melts have been investigated by a number of workers in connection with their use in the manufacture of elemental fluorine. It has been established that the addition to the hydrogen fluorides KF.HF and KF.2HF of lithium and sodium fluorides appreciably lowers the melting points despite their low solubility in the melts[61,102,103]. The viscosities and densities of KF–HF melts and the effect of the addition of lithium fluorides on them have been investigated[104].

Table 4. Melting points of hydrogen fluorides.

Compound	M.p., °C	Compound	M.p., °C
NaF·3HF	60.5	RbF·3.5HF	34–40
NaF·4HF	39.8	RbF·4.5HF	23.0
KF·HF	238.7	NH_4F·HF	126.3
KF·2HF	71.7	NH_4F·3HF	23.4
KF·2.5HF	64.3	NH_4F·5HF	−8.2
KF·3HF	65.8	CsF·HF	176.0
KF·4HF	72.0	CsF·2HF	50.2
RbF·HF	204–205	CsF·3HF	32.6
RbF·2HF	51.7	CsF·6HF	−42.3
RbF·3HF	45.0		

On the basis of a study of the densities and viscosities of HF–NH_4F melts, Semerikova and Alabyshev[104] suggested that the electrolytic dissociation of ammonium hydrogen fluorides takes place differently from metal hydrogen fluorides: ammonium hydrogen fluorides are dissociated to only a slight extent, they merely promote the dissociation of hydrogen fluoride. Sudarikov et al.[105], who investigated the $NH_4F-NH_4HF_2$ and $NH_4HF_2-KHF_2$ systems and determined the enthalpies of fusion of NH_4HF_2, disagree with this view on the mechanism of the dissociation of $NH_4F.nHF$. They believe that ammonium hydrogen difluoride dissociates in the melt according to the mechanism $NH_4HF_2 \rightleftharpoons HF_2^- + NH_4^+$, i.e. in the same way as metal hydrogen difluorides, and that the mechanism put forward by Semerikova and Alabyshev[104] is incorrect. The enthalpy of fusion of ammonium hydrogen difluoride is 15.68 kcal mole^{-1} [106]. The entropy of fusion of the hydrogen fluoride $NH_4F.3HF$ has been determined as 16 cal mole^{-1} deg^{-1}.[64]

The studies on the thermal stability of metal hydrogen fluorides are concerned mainly with alkali metal hydrogen difluorides. Wartenberg and Bosse[107] quote the following temperatures of the rapid decomposition of hydrogen difluorides:

LiF·HF	NaF·HF	KF·HF	RbF·HF	CsF·HF
210°	270°	310–440°	500–600°	550–670°

The following decomposition temperatures have been indicated for lithium hydrogen difluoride: 105°C [108] and 27°C [65]. A more accurate value of the decomposition temperature of LiF.HF (129.5°C) was determined by measuring the temperature variation of the vapour pressure of HF over LiF.HF (36–118°C)[79]. According to Cox and Harrop[91], at 25°C the vapour pressure of HF over LiF.HF is 1.89 mmHg. The thermodynamic functions for the dissociation of LiF.HF were determined also in the last two studies (Table 5).

The vapour pressure of HF over sodium hydrogen difluoride has been investigated by numerous workers by various methods in connection with the use of sodium fluoride as an absorber of hydrogen fluoride in many technological processes. Equations have been obtained for the temperature

variation of the vapour pressure of HF and the enthalpy of decomposition of sodium hydrogen difluoride has been determined[109-113]. ΔH_{decomp} for NaF.HF was also calculated from the results of calorimetric measurements[113,114] (Table 6). The decomposition temperature of sodium hydrogen difluoride is 278°C [111]. The entropy change in the decomposition of NaF.HF is 26.35 cal mole^{-1} deg^{-1}.[110] Fisher[113] obtained the following equation for the free energy of dissociation of NaF.HF:

$$\Delta F^0 = 16.11 \cdot 10^3 - 30.17T \ (157-269°) .$$

The enthalpy of decomposition of the hydrogen fluoride NaF.2HF has been found to be 10.3 kcal mole^{-1} [115] and 9.0 kcal mole^{-1}.[64]

Table 5. Thermodynamic functions of the dissociation of lithium and potassium hydrogen difluorides (298.16°K).

Thermodynamic function	LiF·HF	References	KF·HF	References
ΔC°_p, cal mole^{-1} deg^{-1}	0.35	79	0.32	100
ΔS°, cal mole^{-1} deg^{-1}	16.97	91	32.52	100
$\Delta(F^\circ - H^\circ_0)/T$, cal mole^{-1} deg^{-1}	—	—	29.86	100
$\Delta(H^\circ - H^\circ_0)$, kcal mole^{-1}	—	—	0.791	100
ΔF°, kcal mole^{-1}	3.50	79	11.63	100
ΔH°, kcal mole^{-1}	13.7±0.3	79	21.32	79
	13.41±0.05	91	21.1	99

The vapour pressure of HF over potassium hydrogen difluoride was investigated in connection with the problem of the preparation of fluorine with a minimal HF impurity and the use of KF.HF for the preparation of anhydrous hydrogen fluoride. This problem was investigated by Morgen and Hildebrand[116] in the temperature range 230.5-347.5°C. Fredenhagen and Cadenbach[96] found that KF.HF begins to decompose at 400°C and the final elimination of HF terminates at 504°C. They also noted the effect of traces of water in KF.HF on its thermal decomposition. The non-equilibrium nature of the thermal decomposition of potassium hydrogen difluoride has also been pointed out by Yatlov et al.[117], who established that the temperature of the rapid decomposition of potassium hydrogen difluoride is 600-620°C. When sodium fluoride is added to a melt of KF.HF, the vapour pressure of HF initially decreases somewhat and, when the NaF content is in excess of 5%, it increases[118].

Westrum and Pitzer[100] obtained the following relation for the dissociation pressure of KF.HF in the temperature range 196-238.8°C:

$$\lg p \ (\text{mmHg}) = 8.57 - 4000/T$$

and determined the thermodynamic functions for the dissociation process (Table 5).

The vapour pressure of hydrogen fluoride over HF-KF melts of various compositions was studied by Cady[61], who showed that the values of p_{HF} over KF.HF and KF.3HF found previously at 100° and 150°C [119] were erroneous. Cady's data were used subsequently by Sudarikov et al.[99] to establish a relation between the equilibrium hydrogen fluoride vapour pressure and the composition of the HF-KF melt. The enthalpies of decomposition of the hydrogen fluorides were determined:

$$KHF_2 \rightarrow KF + HF \qquad \Delta H = 21.1 \text{ kcal mole}^{-1},$$
$$KH_2F_3 \rightarrow KHF_2 + HF \qquad \Delta H = 14.3 \text{ kcal mole}^{-1},$$
$$KH_4F_5 \rightarrow KH_2F_3 + 2HF \qquad \Delta H = 19.3 \text{ kcal mole}^{-1},$$

The dissociation pressures of rubidium and caesium hydrogen difluorides have not been investigated. The standard enthalpies of decomposition of RbF.HF and CsF.HF were obtained from calorimetric measurements as 21.8 and 25.0 kcal mole^{-1} [114].

Table 6. Thermal stabilities of sodium hydrogen difluorides.

Temperature range, °C	Temperature variation of HF vapour pressure	ΔH_{decomp}, kcal mole^{-1}	References
37—100	$\lg p(\text{atm}) = 6.677 - 3940/T$	18.0	109
40—120	$\lg p(\text{mm}) = 11.19 - 4292/T$	19.6	110
100—250		14.8	111
126—205	$\lg p(\text{mm}) = 9.97 - 3830/T$	17.5	112
157—269	$\lg p(\text{mm}) = 9.475 - 3521/T$	16.1	113
		17.9	114

The vapour pressure of ammonium hydrogen difluoride was measured in the temperature ranges 70-110°C [94] and 130-237°C [106]. The enthalpy of the reaction NH_4HF_2(solid) → NH_4F(solid) + HF(gas) is 51.9 kcal mole^{-1} (thermochemical data[115]) or 51.1 kcal mole^{-1} (vapour pressure data[94]). The enthalpies of sublimation (17.05 kcal mole^{-1}) and evaporation (1.2 kcal mole^{-1}) of ammonium hydrogen difluoride have been calculated and its enthalpy of decomposition in the vapour phase has been found to be 33.85 kcal mole^{-1}.[106]

Measurements of the vapour pressure of $NH_4F.3HF$ yielded the relation[64]

$$P \ (\text{mmHg}) = -5288/T + 20.97 \ (-10 \text{ to } +23.4°) .$$

The enthalpy of the decomposition reaction $NH_4F.3HF$(solid) → NH_4HF_2(solid) + 2HF(gas) was found to be 17.6 kcal mole^{-1} [115] and 17.1 kcal mole^{-1} [94].

There exist only isolated purely qualitative data on the thermal stabilities of other alkali metal hydrogen fluorides. Thus the hydrogen fluorides NaF.3HF and NaF.4HF are known to be converted at room temperature in air into the hydrogen difluoride[66]. Under these conditions, potassium hydrogen fluorides decompose to KF.2HF, which is converted into potassium hydrogen difluoride at 150°C [67]. RbF.2HF, which is stable at room temperature, begins to split off hydrogen fluoride at 100-110°C [42] and is converted into RbF.HF after prolonged heating at 150-190°C [44].

The thermal stability of the entire series of alkaline earth metal hydrogen fluorides was investigated thermogravimetrically by the authors of this review[120]. The mechanisms of the decomposition reactions of the hydrogen fluorides were established and the intermediates in the reactions, which proceed stepwise, were determined. The existence of the previously unknown compound $BaF_2.2HF$ was discovered in the decomposition of barium hydrogen fluoride. The kinetics of the decomposition of the hydrogen fluorides were investigated and the kinetic parameters for individual reaction stages were determined (Table 7).

According to the HF vapour pressure data for the HF–PbF_2 system, p_{HF} = 0.016 atm and ΔH_{decomp} = 4.5 kcal mole^{-1} for $PbF_2 . 2.5HF$ at 0°C [54].

Table 7. Kinetic parameters of the decomposition reactions of alkaline earth metal hydrogen fluorides.

Decomposition mechanism	Temp. of maximum extent of reaction, °C	Reaction order n	Activation energy, kcal mole^{-1}	Frequency factor, mole^{1-n} × min^{-1}
$BaF_2 \cdot 4.5HF \xrightarrow{-2.5HF} BaF_2 \cdot 2HF$	95	0.50	32.1±0.6	$9 \cdot 10^{18}$
$BaF_2 \cdot 2HF \xrightarrow{-HF} BaF_2 \cdot HF$	100	0.30	12.0±0.5	$3 \cdot 10^{8}$
$BaF_2 \cdot HF \xrightarrow{-HF} BaF_2$	224	0.35	16.7±0.6	$7 \cdot 10^{8}$
$SrF_2 \cdot 2.5HF \xrightarrow{-0.5HF} SrF_2 \cdot 2HF$	82	0.18	12.1±0.4	$8 \cdot 10^{6}$
$SrF_2 \cdot 2HF \xrightarrow{-2HF} SrF_2$	145	0.35	24.7±0.5	$4 \cdot 10^{12}$
$CaF_2 \cdot 2HF \xrightarrow{-2HF} CaF_2$	130	0.34	27.3±0.5	$3 \cdot 10^{14}$

Analysis of the available data on the thermal stabilities of alkali and alkaline earth metal hydrogen fluorides shows that their stability decreases with increase in the number of combined HF molecules and also with decrease of the ionic radius of the cation and increase of its polarising capacity.

Table 8. Thermodynamic functions of hydrogen fluorides (at 298.16°K).

Thermodynamic function	LiF·HF	NaF·HF	KF·HF	RbF·HF	CsF·HF	$NH_4F \cdot HF$	TlF·HF	NaF·2HF	$NH_4F \cdot 3HF$
C_p°, cal mole^{-1} deg^{-1}	16.77	17.93	18.37	18.97	20.86	25.50	21.25	—	—
S°, cal mole^{-1} deg^{-1}	16.97	21.73	24.93	29.70	32.31	27.61	34.92	27.3	79.9
$-(F^\circ - H_0^\circ)/T$, cal mole^{-1} deg^{-1}	7.49	10.54	12.66	15.51	18.22	—	20.47	—	—
$H^\circ - H_0^\circ$, kcal mole^{-1}	2.826	3.334	3.655	3.933	4.201	4.243	4.308	—	—
$-\Delta H_{form}^\circ$, kcal mole^{-1}	224.2	216.6	220.0	217.3	216.1	191.4	—	292.5	337.4
$-\Delta F_{form}^\circ$, kcal mole^{-1}	—	207.2	—	—	—	154.9	—	—	—

Westrum and coworkers [79,98,100,114] carried out a series of studies on the thermodynamic properties of univalent metal and ammonium hydrogen fluorides. Measurements were made of the heat capacities of LiF.HF and NaF.HF (10–298.16°K), KF.HF (20–500°K), RbF.HF, CsF.HF, and TlF.HF (7–305°K), and $NH_4F.3HF$ (200–320°K). Anomalies were discovered in the temperature variation of the heat capacities of NaF.HF and $NH_4F.3HF$. The heat capacity of liquid potassium hydrogen difluoride was determined as 25 cal mole^{-1} deg^{-1}. The thermodynamic functions of the hydrogen difluorides, the standard values of which are listed in Table 8, were calculated from the results of these investigations.

The following equations relating the thermodynamic functions to temperature were obtained for potassium hydrogen difluoride (the α- and β-phases):

at 330–469.2°K:

$$H_T^\circ - H^\circ = 11.353T + 11.56 \cdot 10^{-3}T^2 758 \text{ cal mole}^{-1},$$

$$C_p^\circ = 11.353 + 23.12 \cdot 10^{-3}T \text{ cal mole}^{-1} \text{ deg}^{-1},$$

$$S^\circ = 26.141 \lg T + 23.12 \cdot 10^{-3}T - 46.65 \text{ cal mole}^{-1} \text{ deg}^{-1};$$

at 469.2–500°K:

$$H_T^\circ - H^\circ = 23.96T - 1469 \text{ cal mole}^{-1},$$

$$C_p^\circ = 23.96 \text{ cal mole}^{-1} \text{ deg}^{-1},$$

$$S_0^\circ = 55.17 \lg T - 107.68 \text{ cal mole}^{-1} \text{ deg}^{-1},$$

$$S_{500}^\circ = 41.22 \pm 0.1 \text{ cal mole}^{-1} \text{ deg}^{-1}.$$

There is an appreciable regularity in the temperature variation of the heat capacities and entropies of the hydrogen difluorides MF.HF. Davis and Westrum [101] attempted to correlate the entropies and, using the relation thus obtained between the entropy and the logarithm of the atomic weight of the cation, determined $S_{298.16}^\circ$ for silver hydrogen difluoride as 30.5 cal mole^{-1} deg^{-1}.

IV. THE STRUCTURE OF METAL HYDROGEN FLUORIDES AND THEIR HYDROGEN BONDS

A detailed study has been made of the structures of alkali metal, ammonium, and thallium hydrogen difluorides, which consist of M^+ cations and the linear anion $[F-H-F]^-$ formed by hydrogen bonding (Table 9).

Table 9. Structural data for alkaline earth metal, ammonium, and thallium hydrogen difluorides.

		LiF·HF	NaF·HF	KF·HF	RbF·HF	CsF·HF	$NH_4F \cdot HF$	TlF·HF
Unit cell parameters of α-phase, Å	a	4.72	3.47	5.67	5.90	6.14	8.40	8.58
	b	—	—	—	—	—	8.16	—
	c	13.19	13.76	6.81	7.26	7.84	3.67	—
Density of α-phase, g cm^{-3}		2.22	2.14	2.36	3.27	3.86	1.50	5.08
Conditions of phase transition		—	p=8.5 килобар	T=196°	T=176°	T=61°	—	—
Unit cell parameters of β-phase, Å	a	—	7.240	6.36	6.71	4.21	—	—
	b	—	6.105	—	—	—	—	—
	c	—	3.631	—	—	—	—	—
Density of β-phase, g cm^{-3}		—	—	2.02	2.73	3.81	—	—
F-F distance, Å		2.27	2.264± ±0.003	2.277± ±0.006	2.26	2.26	2.275± ±0.004, 2.269± ±0.004	~2.4

Lithium [121] and sodium [122–124] hydrogen difluorides crystallise in the rhombohedral system. NaF.HF was found to undergo a polymorphic transformation into a phase with rhombohedral symmetry at a pressure of 8.5 kbar [125]. Potassium, rubidium, and caesium hydrogen difluorides have the same structures and have two polymorphic modifications [61,63,126]. The low-temperature modification

crystallises in the tetragonal system[126-128] and the high-temperature modification in the cubic system[126]. The structure of ammonium hydrogen difluoride includes additional N–H...F hydrogen bonds and the substance crystallises in the rhombohedral system[129,130]. At room temperature the crystal structure of thallium hydrogen difluoride has the highest symmetry among the hydrogen difluorides: TlF.HF crystallises in the cubic system and does not undergo a phase transformation even on cooling to the temperature of liquid helium[131].

The phase transition from the tetragonal to the cubic modification of potassium hydrogen difluoride is accompanied by appreciable heat (2.671 kcal mole^{-1}) and entropy (5.69 cal mole^{-1} deg^{-1}) change, the latter exceeding by a factor of almost two the entropy of fusion[99-101]. The study of the structure of the β-phase of potassium, rubidium, and caesium hydrogen difluorides showed an appreciable entropy of phase transition associated with the fact that the HF_2^- ions can occupy with equal probability each of the four sites on the diagonal of the cubic unit cell[126]. The volume of the β-phase also increases appreciably. The coefficients of thermal expansion of α- and β-KHF_2 and the volume change in the $\alpha \rightarrow \beta$ transition have been determined dilatometrically[132].

$$(\partial V/\partial T)_p^0 = 0.0047 \pm 0{,}0005 \text{ cm}^3 \text{ deg}^{-1} \text{ mole}^{-1} \ (20-135^\circ),$$
$$(\partial V/\partial T)_p^0 = 0.015 \pm 0{,}004 \text{ cm}^3 \text{ deg}^{-1} \text{ mole}^{-1} \ (196-259^\circ),$$
$$\Delta V^0_{\alpha\rightarrow\beta} = 4.2 \pm 0.1 \text{ cm}^2 \text{ mole}^{-1}.$$

The phase transition of potassium hydrogen difluoride also leads to a sharp change in its electrical conductivity[101,133]. Davis and Westrum[101] obtained the following equation for the electrical conductivity of β-KHF_2:

$$\lambda = 1.15 \cdot 10^5 \exp(-1.05 \cdot 10^4/T), \ E_{act} = 20.9 \text{ kcal mole}^{-1}.$$

Later studies on the electrical conductivity of KF.HF and KF.DF suggested that the mechanism of conduction in the crystals is associated with the migration of interstitial protons or proton defects, the formation of which involves the following activation energies[133]:

	KF·HF	KF·DF	
E_{act}, kcal mole^{-1}	21.7	23.5	α-phase
	19.8	20.9	β-phase .

The F–F interatomic distances in the HF_2^- ion in the structure of the hydrogen difluorides MF.HF provide information about the strength of the hydrogen bonds in these compounds, but the values found for them initially were determined with a large error and had to be corrected in subsequent studies.

The initial values of r_{F-F} found for sodium hydrogen difluoride (2.50 Å [122] and 2.38 Å [123]) were clearly too high. This interatomic distance was found more accurately in a neutron diffraction study of NaF.HF (Table 9) [124].

Initially the F–F distance in potassium hydrogen difluoride was found to be 2.25 Å [131] and was then corrected to 2.26 Å [128]. The latter value was adopted in all subsequent studies on KHF_2. However, in a neutron diffraction study a somewhat higher value was obtained[134] (Table 9). The studies of the crystal structures of rubidium and caesium hydrogen difluorides[126] led to the conclusion that the F–F interatomic distances in these compounds are the same as in KHF_2 (according to the data of Helmholz and Rogers[128]).

In the ammonium hydrogen difluoride structure the F–F distance was initially found to be 2.37 Å [129]. The theoretical F–F distance for the symmetrical linear HF_2 ion in NH_4HF_2 is 2.32 Å according to Pauling's data[135]. Later it was established that these values are too high and the structure of ammonium hydrogen difluoride contains hydrogen difluoride ions with two different F–F distances[130] (Table 9).

Isotope substitution of the proton in sodium and potassium hydrogen difluorides increases slightly the F–F distance in the crystal[124,136].

Using the available structural data for potassium, rubidium, and caesium hydrogen difluorides (Table 9), Waddington[137] calculated the energies of their crystal lattices as –33.0, –29.6, and –24.7 kcal mole^{-1} respectively. The enthalpy of the process HF_2^-(gas) → HF(gas) + F^-(gas) which he calculated (58 kcal mole^{-1}) and also the F–F distances in the HF_2^- ion in alkali metal hydrogen difluorides obtained from structural studies (Table 9), which are much smaller than in solid hydrogen fluoride (r_{F-F} = 2.49 Å) [138], indicate the presence of a strong hydrogen bond in the hydrogen difluoride ion.

The nature of the hydrogen bond in the hydrogen difluoride ion and in the first place the position of the proton between the fluorine atoms are of interest. The latter may be assymetric as in the O–H...O bond or symmetrical, and for the symmetrical model there are two possibilities: (a) the proton is located at equal distances from the two fluorine atoms; (b) the F–H distances are unequal but the proton oscillates between two positions[139]. To solve the problem of the position of the proton in the HF_2^- ion, many different research techniques were resorted to and in most cases potassium hydrogen difluoride was investigated.

Ketelaar[140] observed in the KHF_2 infrared spectrum absorption frequencies at 1222 and 1450 cm^{-1}, which he assigned to the HF_2^- assymmetric stretching vibration doublet and explained the doublet splitting by the presence of a double potential energy minimum in this ion. However, the results of subsequent studies on KHF_2 were not consistent with this model of the hydrogen difluoride ion.

Polder[141] measured the dielectric constant of KHF_2 and observed a weak temperature variation: $d\epsilon/dT = 2 \times 10^{-4}$ (80–300°K), whereas in the case of a double minimum in the HF_2^- ion the presence of free electric dipoles should give rise to a large temperature coefficient of the dielectric constant. Analogous results were obtained by Pitzer and Westrum[142] in the measurements of ε for KHF_2. On the basis of the heat capacity data for potassium hydrogen difluoride at low temperatures, they also calculated its entropy in the vicinity of the absolute zero, the value obtained (26.17 cal mole^{-1} deg^{-1}) agreeing well with 26.05 cal mole^{-1} deg^{-1} found from direct calorimetric measurements. This indicates the absence of residual entropy, which should be present in the case of a double minimum, as, for example, for the hydrogen bond in ice. Moreover, the experimental dissociation pressures of potassium hydrogen difluoride fall on the line calculated theoretically without taking into account the double minimum[98].

All the above data required a new interpretation of the infrared spectrum of potassium hydrogen difluoride. Halverson[143] explained the presence in the spectrum of the 1222 and 1450 cm^{-1} absorption bands by the splitting of the 1300 cm^{-1} band owing to perturbations of the crystal lattice, but this was not confirmed by subsequent experiments. A more correct explanation was suggested by Westrum and Pitzer[100], who assigned the 1222 cm^{-1} frequency to the deformation vibrations of the HF_2^- ion (ν_2) and the 1450 cm^{-1} frequency to the asymmetric stretching vibration (ν_3), but agreed with Ketelaar[140] that the

5090 cm^{-1} band is due to the $3\nu_3$ overtone, having postulated that there is a marked negative anharmonicity of the levels associated with the ν_3 vibration in the symmetrical hydrogen difluoride ion.

Later investigations of Ketelaar and Vedder[144] of the infrared absorption and reflection spectra of KHF_2 in polarised light and of the low-temperature infrared spectra obtained by Cote and Thompson[145] agree with this frequency assignment. There is a difference in the assignment of the frequencies associated with the overtones in the work of Newman and Badger[146], who suggested a slight positive anharmonicity of the levels in the hydrogen difluoride ion.

Ibers[147] studied the potential function in the region of the stretching vibrations of potassium hydrogen difluoride. Neglecting the interaction between the HF_2^- ions and the lattice vibrations and the interaction between deformation and stretching vibrations, he calculated the force constants and absorption frequencies $[\nu_1, \nu_3(H,D), 3\nu_3(H,D)]$ and the isotope effects on bond lengths. The satisfactory agreement of these quantities with experiment is evidence of a symmetrical linear configuration of HF_2^-.

The Raman spectrum of potassium hydrogen difluoride revealed absorption bands at 595 and 604 cm^{-1}, the positions of which virtually coincided with those predicted by Ketelaar[140] for the symmetrical stretching vibrations of HF_2^-. Initially the appearance of the doublet was accounted for by resonance between two configurations of the HF_2^- ion with a double minimum[148]. However, analysis of the band intensities led the investigators to the conclusion that the splitting is caused by the interaction of individual HF_2^- ions in the crystal[149]. The infrared spectrum of KHF_2 does not show an absorption in the region of 600 cm^{-1}, which can be explained by the selection rules for the linear symmetrical configuration $[F-H-F]^-$ [145]. Thus the results of the infrared spectroscopic studies on potassium hydrogen difluoride support a symmetrical model of the HF_2^- ion.

Peterson and Levy[150] investigated the hydrogen bond in potassium hydrogen difluoride by neutron diffraction and concluded that the proton in the HF_2^- ion occupies a symmetrical position between the fluorine atoms. Later these results were subjected to critical analysis and it was shown that the use of the neutron diffraction method alone does not allow an unambiguous choice between the two models, although the difference between the mean square vibration amplitudes of the hydrogen and fluorine atoms calculated from the spectroscopic data and obtained by the neutron diffraction method is the same, which probably confirms the symmetry and linearity of the hydrogen difluoride ion[134].

An NMR study of potassium hydrogen difluoride yielded best agreement between the experimental resonance absorption line and the line calculated theoretically[151] on the assumption of the symmetrical model for HF_2^-.

However, having analysed numerous investigations of the hydrogen bond in potassium hydrogen difluoride, Blinc[152] believes that some of them are not inconsistent with the model of the HF_2^- ion having a structure intermediate between those of symmetrical and asymmetric ions, i.e. one may suppose that there is a potential barrier between two minima, but it is small.

As mentioned earlier, the energy of the hydrogen bond in the HF_2^- ion is large but the separate contributions to it of the electrostatic interaction and covalent energies are unknown. The energy 47.3 kcal $mole^{-1}$ obtained by Davies[153] for a purely electrostatic interaction is evidently too high. The necessity to take into account the covalent component of the hydrogen bond, which is probably associated with the participation of the excited orbitals of the hydrogen atom, has been emphasised by a number of investigators[154,155]. In an NMR study of deuterated potassium hydrogen difluoride[156] the chemical shift and the screening constant for the ^{19}F NMR signal were determined: the filling coefficient for the *p*-shells of the fluorine atoms and the effective atomic charges were determined on the basis of the theory of Carplus and Das[157]. The estimates obtained agree with the assertion that, in the case of powerful interactions such as those in the HF_2^- ion, all three atoms should make significant contributions to the molecular orbital and the two electron pairs should be delocalised among the three atoms[158].

Apart from the experimental studies on the hydrogen bond in the hydrogen difluoride ion, a number of theoretical calculations of the electronic structure of the HF_2^- ion have been made by quantum-mechanical methods[159-164].

As stated above, the hydrogen bond in potassium hydrogen difluoride was investigated in greatest detail. The studies of the hydrogen bond in the entire series of univalent metal hydrogen difluorides by various physical methods (NMR, infrared spectroscopy, refractometry) were a further development of these investigations.

The NMR spectra of the hydrogen difluorides of alkali metals (except LiF.HF) [151,156,165] and ammonium[165,166] are similar in form with the spectra calculated theoretically for the hydrogen difluoride ion with a linear symmetrical configuration[151] and the absorption lines have similar second moments. This is due to the similarity of the structure of the HF_2^- ion in these compounds. The symmetrical position of the proton in sodium hydrogen difluoride has also been demonstrated by neutron diffraction studies[167]. The NMR data for lithium[156,164] and silver[167] hydrogen difluorides show that the structures of these compounds contain HF_2^- ions with a weaker hydrogen bond than in other hydrogen difluorides. This weakening of the hydrogen bond is also accompanied by a shift of the equilibrium position of the proton from the mid-point between the fluorine atoms.

Table 10. Principal absorption bands in the infrared spectra of hydrogen fluorides.

Compound	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	Compound	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
CsF·HF	—	1230	1480	BaF_2·HF	—	1158—1183	1630—1780
RbF·HF	—	1235	1480	SrF_2·HF	—	1152—1185	1700—1820
KF·HF	600*	1235	1460	CaF_2·2HF	—	1152—1175	1520
NaF·HF	—	1215	1600	SrF_2·2.5HF	—	1165—1190	1500
LiF·HF	400—500	1160	1750	PbF_2·2.5HF	—	1020—1150	1800
NH_4F·HF	—	1208	1600	BaF_2·3HF	—	980, 1150—1170	1650—1850
AgF·HF	—	1160—1190	1600—1800	CdF_2·HF	—	1165—1235	1700
RbF·2HF	480	1025—1070	1780	ZnF_2·2HF	—	1160—1215	1800
KF·2HF	480	1030—1100	1780	HF_{TB}	366	—	3100—3400

* Raman spectrum.

The first data on the infrared spectra of $NaHF_2$ and NH_4HF_2 were quoted in Refs. 168—171. Ketelaar et al.[170] were the first to point out the differences in the positions of the absorption bands in the infrared spectra of sodium, potassium, and ammonium hydrogen difluorides as a function of the method of preparation of the specimens for the recording of the spectra.

In a systematic infrared spectroscopic study of the entire series of alkali metal hydrogen difluorides

MF.HF (M = Cs, Rb, K, Na, and Li) and their deuterated derivatives, we investigated[172,173] the effect of various methods of preparation of the specimens on the quality of the spectrum and established optimum conditions for the recording of the spectra. The absorption frequencies associated with the deformation (ν_2) and asymmetric stretching (ν_3) vibrations of HF_2^- in the spectra of alkali metal hydrogen difluorides (Table 10) show the presence in these compounds of a strong hydrogen bond, which becomes weaker on passing along the series from caesium to lithium. In silver hydrogen difluoride the hydrogen bond is approximately as strong as in $LiHF_2$, in agreement with the NMR data[155,165,168].

In a study of the infrared spectra of sodium and potassium hydrogen difluorides at low frequencies, it was established that the absorption frequencies corresponding to the translational vibrations of the crystal lattice are not altered when the hydrogen difluorides are deuterated[174,175].

Table 11. Refractometric data for hydrogen fluorides.

Compound	Refractive indices				R_D, cm^3	$R_{H\text{-bond}}$, cm^3
	n_g	n_m	n_p	n_{av}		
CsF·HF	—	1.414	1.410	1.413	11.06	0.73
RbF·HF	—	1.373	1.357	1.368	8.57	0.98
KF·HF	—	1.352	1.327	1.344	7.01	0.96
NaF·HF	1.331	1.260	—	1.281	5.08	0.81
LiF·HF	1.408	1.319	—	1.348	4.43	0.55
NH_4F·HF	1.394	1.390	1.385	1.390	8.93	0.83
KF·2HF	1.315	1.311	1.305	1.310	9.18	0.61
BaF_2·HF	1.498	1.467	1.466	1.470	11.8	0.41
SrF_2·HF	1.472	1.473	1.418	1.442	9.6	0.47
CaF_2·2HF	1.415	1.387	1.355	1.388	10.6	0.49
SrF_2·2.5HF	1.400	1.380	1.344	1.374	13.0	0.42
BaF_2·3HF	1.425	1.411	1.394	1.410	16.3	0.38
BaF_2·4.5HF	—	1.360	—	1.360	19.8	0.40

The strength of the hydrogen bond in alkali metal and ammonium hydrogen difluorides can be estimated quantitatively with the aid of the refractometric method[176]. The first data were obtained for potassium and ammonium hydrogen difluorides[177]. Later this method was employed to study the hydrogen bonds in the entire series of hydrogen difluorides[178]. Comparison of the refraction of the hydrogen bonds (Table 11) shows that the strongest hydrogen bonds are characteristic of rubidium and potassium hydrogen difluorides, while in sodium and lithium hydrogen difluorides they are much weaker. An anomalously low refraction of the hydrogen bond was obtained for $CsHF_2$ compared with $RbHF_2$ and KHF_2, while according to the data derived by other methods the hydrogen bonds in these compounds are approximately of equal strength. This can be accounted for by the steric effect of the Cs^+ ion, which has a large ionic radius, or by its deformation[178]. The weakening of the hydrogen bond in the HF_2^- ion in ammonium hydrogen difluoride is caused by the presence in its structure of hydrogen bonds of the type N−H...F.[177]

The problems concerning the structures of alkali metal hydrogen fluorides with the composition MF.nHF ($n > 1$) have been investigated much less completely than for hydrogen difluorides.

There has been only one X-ray diffraction study of these compounds, in which the structure of KF.2HF was considered[179]. This hydrogen difluoride crystallises in the orthorhombic system with the unit cell constants a = 8.52 Å, b = 4.09 Å, and c = 6.69 Å and its density is 2.06 g cm^{-3}. The KF.2HF lattice consists of K^+ ions and the polymeric $H_2F_3^-$ anions formed by hydrogen bonding in which the F−F distance is 2.33 Å and the angles formed by the fluorine atoms are 133° and 139°. It proved possible to determine the F−H distances in $H_2F_3^-$ ions by the NMR method as 1.065 and 1.265 Å[180]. The NMR data for RbF.2HF [156,165] suggest that this compound also contains the polymeric $H_2F_3^-$ anions with the same structure. We may note that potassium and rubidium hydrogen difluorides have similar structures too.

NMR studies of RbF.3HF and CsF.3HF led to the hypothesis that their structures include the polymeric $H_3F_4^-$ anions with an asymmetric hydrogen bond[160,165]. The existence of two modifications has been established for the hydrogen fluoride NaF.3HF (transition temperature 43.1 °C), but their structures are unknown[69].

Further increase of the number of combined HF molecules in the hydrogen fluorides MF.nHF probably also leads to the formation of the polymeric ions $H_nF_{n+1}^-$ by hydrogen bonding, the structure of which approaches the infinite zig zag chains with asymmetric hydrogen bonds in the structure of solid hydrogen fluoride[138]. The presence of such anions has also been suggested for silver hydrogen fluorides with the composition AgF.nHF ($n > 1$)[168].

The low-frequency molecular vibrations in the hydrogen fluorides NaF.2HF and KF.2HF were investigated by a method based on the non-elastic scattering of slow neutrons[181]. An infrared spectroscopic study of the hydrogen fluorides MF.2HF (M = Rb or K) was undertaken for the first time by the present authors[172,173] and it was found that there is a significant difference between the infrared spectra of the MF.HF and MF.2HF compounds, owing to the presence in the structure of the latter of $H_2F_3^-$ ions.

The asymmetric stretching vibrations of the $H_2F_3^-$ ion are shown in the region of 1780 cm^{-1}, while deformation vibrations give rise to a broad band with a maximum at 1025−1100 cm^{-1}. The appearance in the MF.2HF spectrum of an absorption band with a frequency of 480 cm^{-1}, which was assigned to the symmetrical stretching vibration of $H_2F_3^-$, can be explained by the fact that for the $H_2F_3^-$ ion with an asymmetric hydrogen bond this vibration is not forbidden in the infrared spectrum.

Later data[182] on the infrared spectra of KF.2HF and KF.2DF agreed fully with the above absorption frequencies of the $H_2F_3^-$ ion and their assignment. The force constants of $H_2F_3^-$ were also estimated in the above investigation, the results indicating an asymmetric position of the proton in this ion.

Comparison of the infrared spectra of the hydrogen fluorides MF.HF and MF.2HF reveals a weakening of the hydrogen bond with increase in the number of combined HF molecules (Table 10). Comparison of the vibration frequencies in the infrared spectra of KF.HF, KF.2HF, and solid hydrogen fluoride[183] with the F−F and F−H distances in these compounds shows that they vary in parallel.

In a refractometric study of the hydrogen fluoride KF.2HF, the refractions of the $H_2F_3^-$ ion (6.93 cm^3) and its hydrogen bond (0.61 cm^3) were calculated[178]. These values agree well with the regular change in the strength of the hydrogen bond in the hydrogen fluorides with increase in the number of combined HF molecules (Table 11).

Thus the study of the structure of alkali metal hydrogen fluorides by physical methods established the presence in them of complex anions with the composition $H_nF_{n+1}^-$, in which the strength of the hydrogen bond increases with increase in the ionic radius of the cation and with decrease of the number of combined HF molecules.

Ikrami, Ruchkin, and Nikolaev[80,184] and the present authors[156,185] investigated the structure of alkaline earth metal hydrogen fluorides. Using the NMR method, it proved possible to deduce the structures of these compounds. Analysis of the adsorption line form and the second moments of the NMR spectra of the hydrogen fluorides $MF_2.HF$ established that they contain the anions HF_2^- and F^-. An increase in the number of combined HF molecules leads to the formation of two hydrogen difluoride ions in compounds with the composition $MF_2.2HF$. In the hydrogen fluorides $MF_2.3HF$ the additional HF molecule adds to the HF_2^- ion, forming $H_2F_3^-$. Thus the addition of HF to alkaline earth metal fluorides is somewhat different from the addition to the fluorides of univalent elements, since here there is an equal possibility of the formation of a hydrogen bond with each fluoride ion in MF_2. Evidently, solvation takes place with formation of the most symmetrical structures, identical anions being formed when the number of combined hydrogen fluoride molecules is even[156,185]. The structures of the hydrogen fluorides of other divalent metals (lead, copper, zinc, and cadmium[74-76]) may be represented similarly.

The ^{19}F NMR and ^1H NMR spectra of alkaline earth metal hydrogen fluorides indicate some asymmetry in the position of the proton in the hydrogen difluoride ion in their structure, which is quite reasonable, since, although accurate values of the interatomic distances in the $MF_2.nHF$ lattices are unknown, an estimate of r_{F-H} in the HF_2^- ion based on NMR data indicates the presence in them of a much weaker hydrogen bond than in potassium and sodium hydrogen difluorides[156,185].

The first results of studies on alkaline earth metal hydrogen fluorides by infrared spectroscopic[184] and refractometric[80] methods led the investigators to the conclusion that the hydrogen bond in these compounds is much stronger than in hydrogen fluoride but weaker than in potassium hydrogen difluoride and also to the hypothesis that the polymeric ions $H_nF_{n+1}^-$ are formed in metal hydrogen fluorides with the composition $MF_2.nHF$ ($n > 1$). In a reinvestigation of the infrared spectra of calcium, strontium, and barium hydrogen fluorides, we concluded[173] that the spectra of hydrogen fluorides with the compositions $CaF_2.2HF$ and $SrF_2.2.5HF$ may be interpreted in terms of a structure with two hydrogen difluoride ions. On the other hand, the absorption bands in the region 740–750 cm^{-1}, which were assigned[184] to the polymeric ions $H_nF_{n+1}^-$, were found to be due to the decomposition products of the hydrogen fluorides. The characteristic absorption frequencies of the HF_2^- ions in the infrared spectra of $MF_2.nHF$ indicate a steady weakening of the hydrogen bond in alkaline earth metal hydrogen fluorides with decrease of the ionic radius of the cation, as in the case of alkali metal hydrogen fluorides (Table 10).

Thus alkali and alkaline earth metal hydrogen fluorides are formed via hydrogen bonds of the type F–H...F, which lead to the formation of the ions $H_nF_{n+1}^-$. However, in alkaline earth metal hydrogen fluorides the hydrogen bond is on the whole weaker and their structures may include several types of anions.

The hydrogen bond in hydrogen fluoride solutions has not so far been investigated. Studies have been made on aqueous solutions of alkali metal hydrogen difluorides by the NMR method[186-188] in which the concentration dependence of the ^{19}F signal and the chemical shift of the HF_2^- ion were determined. Infrared spectroscopic studies on potassium hydrogen difluoride solutions in water established that the hydrogen bond in the hydrogen difluoride ion is somewhat stronger in solution than in the crystalline state[189]. It was not possible to obtain the Raman spectrum and a KHF_2 solution, which has been explained[190] by the markedly ionic character of the bond in the hydrogen difluoride ion.

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The above data show that until recently the study of metal hydrogen fluorides was restricted to those of alkali metals and among them only the hydrogen difluorides were largely investigated in greater detail. The advances in the chemistry of inorganic fluorides in the last decades, the development of synthetic chemistry, and the advances in experimental techniques greatly expanded our knowledge in this field of fluorine chemistry, which is of theoretical and practical importance. The difficulties in experiments with metal hydrogen fluorides—substances which are frequently extremely unstable and hygroscopic, liberating on decomposition the corrosive hydrogen fluoride—have now been overcome in the majority of cases, ensuring that the experiments are carried out with fairly pure substances of the required composition. In addition, the present level of development of physical research methods undoubtedly promotes a further expansion of comprehensive studies on metal hydrogen fluorides. A characteristic feature of the investigations in recent years is an increasing interest in higher alkali metal hydrogen fluorides $MF.nHF$ ($n > 1$) and divalent metal hydrogen fluorides.

Analysis of the data at present available on metal hydrogen fluorides permits an outline of the principal trends in the development of investigations in this field.

1. Physicochemical study of systems containing hydrogen fluoride and metal fluorides with the aim of synthesising new metal hydrogen fluorides.
2. The study of the physical and chemical properties of metal hydrogen fluorides and their solutions.
3. The study of the thermal stability of metal hydrogen fluorides and the determination of its quantitative characteristics.
4. Thermodynamic study of metal hydrogen fluorides.
5. The study of the crystal structures of metal hydrogen fluorides and their hydrogen bonds by various physical methods.

The development of investigations in the field of metal hydrogen fluorides along the lines indicated above will lead to the preparation of many new compounds of this class and will expand our knowledge of the properties of metal hydrogen fluorides. Moreover, further study of metal hydrogen fluorides will evidently lead to new types of their applications in science and engineering.

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Institute of Inorganic Chemistry,
Siberian Division of the USSR
Academy of Sciences, Novosibirsk