HYDROGEN FLUORIDE AND ITS SOLUTIONS

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The study of hydrogen fluoride is beset with difficulties and dangers, but the valuable results obtained compensate for the obstacles that must be overcome. A more complete knowledge of hydrogen fluoride should add much to chemistry in general, for it is in many respects a unique compound. For instance, it has the ability to form addition compounds, and has the highest heat of formation of the hydrogen halides. Compared with the other hydrogen halides it is a moderately weak acid in aqueous solution, and its boiling and freezing points are not in agreement with the trend of these for the other hydrogen halides. The structures of the molecular species, H_6F_6 and HF_2^-, which have been reported for hydrogen fluoride, are a challenge to our theories of molecular structure and must be explained by any complete picture of chemical compounds.

Solutions in liquid hydrogen fluoride have been studied very little until quite recently. It is probably because the technique of handling anhydrous hydrogen fluoride is different from that of working with other substances that it has been almost neglected by chemists. Glass vessels are not suitable containers for it, and our technique of constructing apparatus entirely of metal and operating it without being able to observe visually the processes that are taking place has not been highly developed.

Hydrogen fluoride was first obtained by Margraff (1) in 1768, but it was Sheele (2) who in 1771 definitely characterized it. A pure and highly concentrated aqueous solution was prepared by Thénard and Gay-Lussac (3) in 1809. Davy (4) in 1813 and the years following worked with hydrogen fluoride and proved that it contained no oxygen. He experimented with passing an electric current through the liquid and also the gas. He actually obtained at the end of the electrolysis a liquid which would not conduct the current, indicating that he had prepared the liquid in a high state of purity. It is reported that he ceased his experiments with this material when he found that they were injurious to his health. Fremy (5) in 1856 was the first to make anhydrous hydrogen fluoride and by the method that is still used, that is, by heating purified and dried potassium hydrogen fluoride. Gore (6) in 1869 also studied hydrogen fluoride. He showed that it would not conduct the electric current, but that it became a conductor when a small amount of water was present. The early history of hydrogen fluoride is perhaps ended with the work of Moissan (7). He prepared a liquid of high purity, found that potassium fluoride was soluble in it to give a conducting solution, and prepared fluorine by the electrolysis of this solution.

THE PREPARATION OF ANHYDROUS HYDROGEN FLUORIDE

The preparation of hydrogen fluoride by the treatment of calcium fluoride with sulfuric acid does not give a material that is pure or anhydrous (8). The difficulties in the method used by Fremy lie chiefly in drying the potassium hydrogen fluoride. Moissan (9) describes the method he used for doing this as follows:

> In order to obtain pure anhydrous hydrofluoric acid, one begins by preparing the fluohydrate of potassium fluoride, taking all the precautions indicated by Fremy. Having obtained this salt in a state of purity, it is dried over the water bath at a temperature of 100°C. and afterwards the capsule containing it is placed in vacuo in presence of sulfuric acid and of caustic potash fused in a silver crucible. The acid and potash are replaced every morning during fifteen days, and the vacuum in the bell jar is always maintained to a pressure of about one centimeter of mercury.
>
> During this desiccation, it is necessary to pulverize the salt from time to time in an iron mortar, in order to expose fresh surfaces. When the fluohydrate no longer contains water, it falls into a fine powder and can then be used for the preparation of hydrofluoric acid. It is to be noted that well-made fluohydrate of potassium fluoride is much less deliquescent than the normal salt.

When the fluohydrate is thoroughly dry, it is quickly transferred to a platinum alembic, which has been dried at a red heat a little while before. It is heated gently for an hour or an hour and a half, in order that the decomposition may begin slowly, and the first portions of the hydrofluoric acid formed, which may contain traces of water remaining in the salt are rejected. . . . .

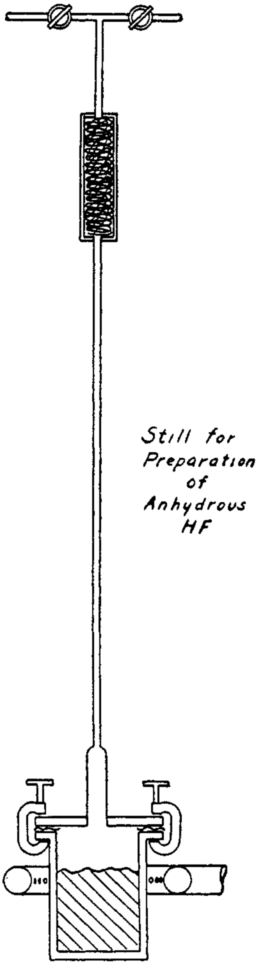

FIG. 1. STILL FOR THE PREPARATION OF ANHYDROUS HYDROGEN FLUORIDE

Fredenhagen and Cadenbach (10) have shown that the acid salt loses hydrogen fluoride gradually until at a temperature of 504°, when about 30 per cent has been lost, the temperature remains constant, and the remainder of the gas is liberated. They have also shown that any small amount of water remaining in the salt comes off with the first portions of hydrogen fluoride distilled at the higher temperatures. They have been able to reduce the residual water in the almost anhydrous liquid by repeated distillations.

The tedious drying of the salt and the equally difficult repeated distillations of the liquid have been eliminated in the method of Simons (11). He completely dehydrates the salt by electrolysis in the fused state. The distillation of the resulting material produces a product that must be completely anhydrous. Fluorine is produced smoothly and in quantity only after all the water has been removed from the salt. This enables one to determine easily when it is completely dry. As the molten salt has a tendency to foam during the distillation, Simons has preferred to use the still shown in figure 1 heated by means of a ring burner. As the electrolysis is carried on in the base of the still, there is no necessity of transferring the material and no danger of absorbing water during such a process.

THE TECHNIQUE OF HANDLING HYDROGEN FLUORIDE

Improvements in the technique of handling anhydrous hydrogen fluoride have been very important in its study. As the anhydrous liquid absorbs water with great vigor, all moisture must be excluded. The liquid acts as a good dehydrating agent, hence any material from which water may be extracted, such as Bakelite, many organic materials, etc., must be avoided. Silicious materials are of course reacted upon, and although the action on quartz is slow, it is, nevertheless, appreciable. Fredenhagen and Cadenbach (12) were, however, able to determine qualitative solubilities in a fused quartz vessel because of the slowness of the action. The reaction or solubility of so many of the inorganic compounds makes them inadequate for use as containers. Even the slight solubility of calcium fluoride would prevent fluorite from being used for quantitative experiments. Sulfur has been used successfully for the insulator separating the electrodes in conductivity experiments by Fredenhagen and Cadenbach. Apparatus constructed for the study of anhydrous hydrogen fluoride should in general be made entirely of metal—preferably of platinum, gold, or silver. Copper may be used, but apparatus made of it should be kept filled with dry nitrogen. Any oxide or other coatings on the metal should be carefully removed, and the apparatus scrupulously dried. Permanent joints can be made with silver solder; others can be made by some sort of metal to metal screw or pressure connections. The apparatus should be sealed directly to the vessel in which the anhydrous liquid is prepared, so that the liquid can be distilled directly into the apparatus.

CHEMICAL PROPERTIES

Although hydrogen fluoride does not react appreciably with most of the elementary metals, it reacts with sodium in the same manner that water does. It does not react with magnesium. With the chlorides, bromides, and iodides of the alkali metals and of the alkaline earth metals, and with ferrous chloride, manganous chloride, and cerous chloride, it liberates the hydrogen halide and forms the fluoride. It reacts in the cold with the hydroxides of the metals and with many of the oxides, such as those of magnesium, calcium, strontium, barium, silver and also with lead monoxide. It reacts slowly with aluminum oxide, silicon dioxide, and cupric oxide. With potassium and barium chlorates, it liberates chlorine dioxide. It liberates hydrogen cyanide from potassium cyanide, and silicon tetrafluoride from potassium fluosilicate. It unites with water with considerable evolution of heat, and freezing point data indicate the crystalline compounds $H_2O \cdot HF$ (13), $H_2O \cdot 2HF$, and $H_2O \cdot 4HF$ (29). With the alkaline fluorides it forms a number of crystalline compounds, as for example $KFHF$, $KF(HF)_2$, $KF(HF)_3$, etc. (14). In these compounds it is probably analogous to water of crystallization. It is a good dehydrating agent and will remove water from many substances. It reacts with acetic anhydride to produce acetyl fluoride and will react with the aliphatic alcohols at high temperatures to produce the fluorides.

PHYSICAL PROPERTIES

The boiling point (15) of hydrogen fluoride is 19.5°; freezing point (16), −83°; heat of fusion, 1090 calories per mole of HF; heat of vaporization (11), 6020 calories per apparent molecular weight in the gas phase; heat of formation (16), 63000 calories per mole; specific conductivity (10), less than 1.4×10^{-5}; dielectric constant (17) 174.8 at −73°, 173.2 at −70°, 134.2 at −42°, 110.6 at −27° and 83.6 at 0°. Its vapor pressure has been shown to fit the equation

TABLE 1

Comparison of the properties of hydrogen fluoride with those of related compounds

	FREEZING POINT	BOILING POINT	MOLAR HEAT OF FUSION	MOLAR HEAT OF VAPORIZATION	DIELECTRIC CONSTANT
	°C.	*°C.*	*calories*	*calories*	
HF	−83	19.5	1.09×10^3	6.02×10^3	83.5 (0°)
HCl	−114	−85.8	0.50×10^3	3.6×10^3	4.60 (27.7°)
HBr	−86	−67.1	0.62×10^3	4.0×10^3	3.82 (24.7°)
HI	−53.6	−36.0	0.72×10^3	4.4×10^3	2.9 (21.7°)
H_2O	0	100	1.34×10^3	9.72×10^3	80 (20°)
H_2S	−85.5	−61.8			5.75 (10°)
H_2Se	−64	−42			
H_2Te	−48	−1.8			
NH_3	−77	−38.5	1.84×10^3	5.6×10^3	14.9 (24.5°)
PH_3	−132.5	−86.4			2.71 (−25°)
AsH_3	−113.5	−54.8			2.05 (15°)
SbH_3	−91.5	−18			2.58 (−50°)
HCN	−13.8	26.5		5.7×10^3	95 (21°)

$$\log P = 7.37 - \frac{1315}{T},$$

where P is the pressure in millimeters of mercury and T is the temperature in degrees K.

A comparison of the physical properties of hydrogen fluoride with those of the other hydrogen halides and with water, ammonia, and hydrogen cyanide is shown in table 1. It is apparent that hydrogen fluoride does not follow the properties of the other hydrogen halides in the expected manner; it shows greater similarity to water and to hydrogen cyanide, than it does to the halides. Its melting point, freezing point, heat of vaporization, and heat of fusion, instead of being lower than those of hydrogen chloride, are higher. It is interesting that the relation between the properties of water and those of hydrogen sulfide, hydrogen selenide, and hydrogen telluride, and the relation between the properties of ammonia and those of phosphine, arsine, and stibine is the same as the relation between the properties of hydrogen fluoride and those of the other hydrogen halides.

MOLECULAR STRUCTURE

In order to account for the peculiar properties of water, it has been assumed that it is polymerized or associated in the liquid state. Some investigators have assumed definite molecular species, such as $(H_2O)_2$, $(H_2O)_3$, etc. and have considered them to exist in equilibrium with one another. Others have considered chain molecules of indefinite and indeterminable size from which the single molecules are continually being gained and lost. One might also assume that instead of definite polymers being formed, the simple molecules exert unusually large attractive forces upon one another. This must be true in any case, as seen by the large electric moment of the water molecule. Polymerization has also been assumed for hydrogen fluoride in the liquid state in order to account for its peculiar properties.

Its structure is, therefore, a matter of considerable interest. The formula H_2F_2 is generally seen in text-books, despite the fact that investigators are now in agreement that this molecular species has never been found. This formula has come into our literature, because at warm room temperature and atmospheric pressure the density of the gas corresponds to the density which the formula H_2F_2 would give. An early worker, Mallet (18), made this determination, assigned the formula, and it has been retained. A variation of temperature changes the apparent molecular weight considerably, as shown by Thorpe and Hambly (19); in fact, just above the boiling point the density is much greater than H_2F_2 would give. A variation of pressure also varies the apparent molecular weight. These results indicate that if H_2F_2 exists at all, it is certainly not the only or even the major molecular species. There is another argument that has been used in favor of H_2F_2, and that is that the salts KFHF and NaFHF exist as crystalline compounds. This is of course a very weak argument, for the crystalline compounds $KF(HF)_2$ and $KF(HF)_3$ also exist. This is the same reasoning one would use in assigning the formula for water on the basis of the number of molecules of H_2O that are retained as water of crystallization in a particular compound. There is fairly good evidence for the existence of the HF_2^- ion in aqueous solutions, but this does not indicate the existence of H_2F_2. In fact, the experimental data give no indication of this molecular species, although it has been looked for.

Simons and Hildebrand (20) were able to obtain apparent molecular weights for gaseous hydrogen fluoride as high as 87.4, showing that there must be a molecular species containing more than four HF molecules. They did this by comparing the vapor pressure determined by the static method by Simons (11) with that determined by the dynamic method. In the dynamic method of determining vapor pressure, the value of the molecular weight must be assumed in order to calculate the number of moles taken through the apparatus per mole of the carrier gas. When the vapor pressure is known, the molecular weight becomes the unknown factor and can be calculated from the experimental data. By assuming an equilibrium between two molecular species in the gas phase according to the equation

$$n\,\mathrm{HF} = (\mathrm{HF})_n$$

with the equilibrium constant K expressed in terms of the partial pressures of these species p and p_n, by the equation $K = \frac{p_n}{p^n}$, they have been able to account for their determinations of apparent molecular weight which extend from −39° to +16° over which range the vapor pressure of HF changes from 56.2 mm. to 661 mm. of Hg, and also the extensive vapor density determinations of Thorpe and Hambly (19), which at constant pressure extend from 26.5° to 88.2° and at constant temperature extend from 353 mm. up to atmospheric pressure. Thorpe and Hambly used two methods of reducing the pressure: one by reducing the total pressure in the apparatus, and the other by diluting the hydrogen fluoride with air. These results checked, and they carried out the constant temperature experiments at two different temperatures. Various values of n were tried, and an agreement with the experimental data was found with $n = 6$. Figure 2 shows the good agreement of the theoretical and experimental values for apparent molecular weight, as the pressure is varied with the temperature constant at 305°K. At this temperature the equilibrium constant equals 2.91×10^{-15}. By treating the equilibrium constant in the usual way, the effect of temperature upon it is given by the equation:

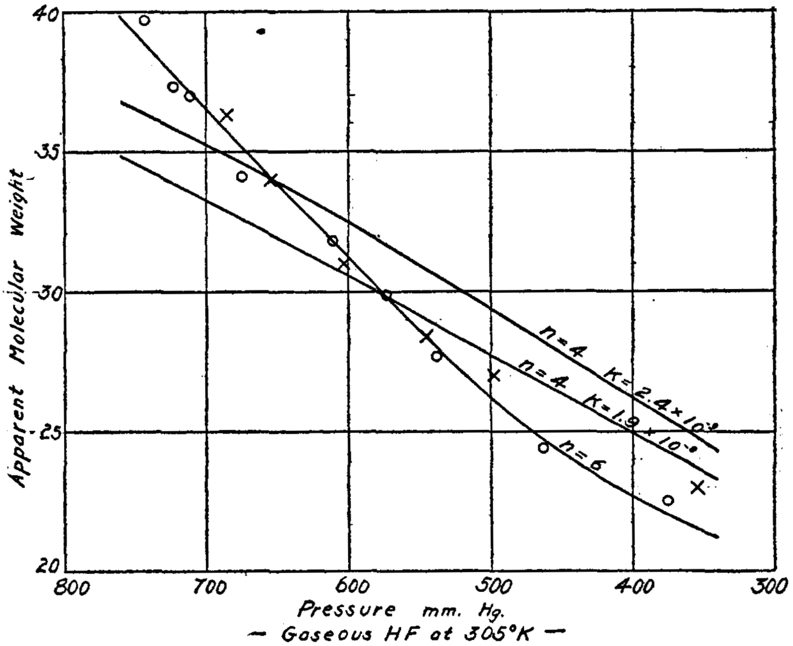

FIG. 2. VARIATION OF APPARENT MOLECULAR WEIGHT OF GASEOUS HYDROGEN FLUORIDE WITH PRESSURE

$$\log K = \frac{-\Delta H}{4.579\ T} + C.$$

When $\Delta H = -40{,}000$ calories and $C = -43{,}145$, the apparent molecular weight calculated from K in the above equation fits the experimentally determined values taken at constant pressure and varying temperature, as shown in figure 3 where the smooth curve represents the calculated values. Of course the test of this theory comes in comparing the calculated values with those obtained at low temperatures and at the saturation pressure. Figure 3 shows that this agreement is good.

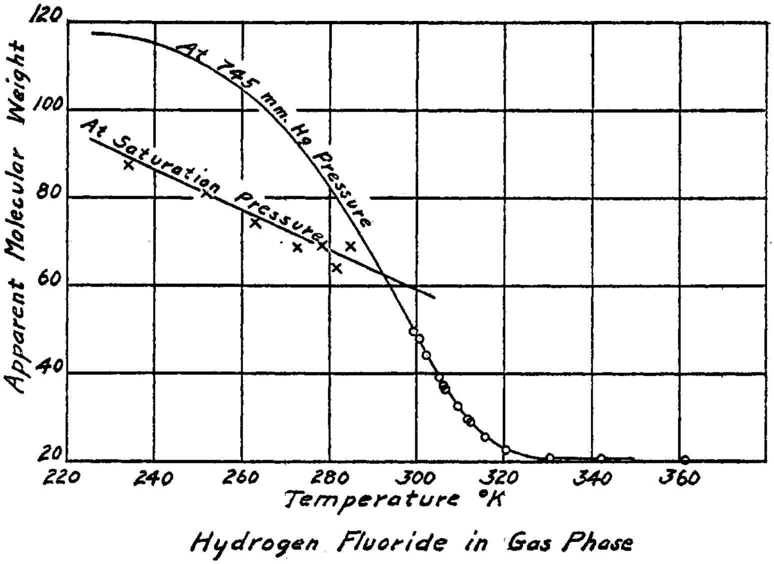

FIG. 3. VARIATION OF APPARENT MOLECULAR WEIGHT OF GASEOUS HYDROGEN FLUORIDE WITH TEMPERATURE

As the simple assumption of the equilibrium 6 HF = H_6F_6 agrees well with molecular weight determinations taken over a wide range of temperature and pressure, the evidence in favor of the molecular species H_6F_6 in the gas phase is very good. There is no indication of H_2F_2, and if it is present, it must be in very small concentration. The molecular structure of the liquid phase of hydrogen fluoride is not established; but it is interesting to note that the heat of association, $-40{,}000$ calories for six moles of HF or 6,670 calories per mole of HF, is close to its heat of vaporization.

SOLUBILITY OF SUBSTANCES IN ANHYDROUS LIQUID HYDROGEN FLUORIDE

Gore and Moissan were interested in solutions in liquid hydrogen fluoride, but neither of them made any systematic study of hydrogen fluoride as a solvent. In a footnote in one of his papers, Franklin (21) reports the qualitative solubility of a number of substances, chiefly inorganic salts, in liquid hydrogen fluoride. Fredenhagen has made a systematic study of the qualitative solubility of a large number of inorganic substances. Table 2 gives a summary of the solubilities of inorganic substances in liquid anhydrous hydrogen fluoride. In the table are given the quantitative solubilities, where they are known, in terms of grams of the solute in cubic centimeters of the solution. In cases where a reaction occurs and a gaseous product is formed, the formula of the gas is given in parentheses. The hydroxides and oxides that react produce water, which remains in the solution. It is interesting to note that the solubility of the fluorides of the alkali metals and also of the alkaline earth metals increases with the molecular weight. This is directly analogous to the solubilities of the hydroxides of the same elements in water.

Hydrogen fluoride is found to be a polar solvent very similar to water, as one would expect from the fact that its dielectric constant is near that of water. Some of this solubility data is contrary to what one might expect. An example of this is the insolubility of silicon tetrafluoride. It apparently does not combine with the solvent to form hydrofluosilicic acid. The insolubility of the other hydrogen halides does not follow the analogy with water. It is interesting to note that potassium cyanide evolves hydrogen cyanide, but that mercuric cyanide does not, and that mercuric cyanide is soluble, but that mercuric fluoride is not. The most surprising result is that hydrogen cyanide is not soluble, for hydrogen cyanide is a compound which appears to be very similar to hydrogen fluoride, having a high dielectric constant and a boiling point not greatly different. One would expect these liquids to be miscible.

TABLE 2

Solubility of inorganic substances in hydrogen fluoride

VERY SOLUBLE	SLIGHTLY SOLUBLE	NOT APPRECIABLY SOLUBLE	SOLUBLE WITH REACTION	REACT BUT PRODUCT INSOLUBLE	INSOLUBLE AND UNREACTIVE
H_2O	MgF_2	AlF_3	Alkali halides and alkaline earth halides dissolve to form hydrogen halides	$AlCl_3$ (HCl)	$ZnCl_2$
NH_4F	CaF_2	ZnF_2		$FeCl_2$ (HCl)	$SnCl_2$
LiF (2.6 per 100 at 18°)	SrF_2	FeF_3		$MnCl_2$ (HCl)	$NiCl_2$
NaF	↓ BaF_2	PbF_2		$CeCl_2$ (HCl)	$CdCl_2$
KF (36 per 100 at 0°)	$CaSO_4$	CuF_2	KCN(HCN)	MgO	$CuCl_2$
RbF	$KClO_4$	HgF_2	$NaN_3(HN_3)$	CaO	HgI_2
↓ CsF	H_2S	HCl	$K_2SiF_6(SiF_4)$	SrO	AgCl
TlF	CO	HBr	$KClO_3$ (ClO_2)	BaO	AgBr
AgF (33 per 100 at −15°)	CO_2	HI	$Ba(ClO_3)_2(ClO_2)$	PbO	AgI
		SiF_4	Hydroxides	BaO_2	HgO
$Hg(CN)_2$		$Cu(NO_3)_2$		Al_2O_3	PbO_2
KNO_3		$Bi(NO_3)_2$		CuO	MnO_2
$NaNO_3$		$Pb(NO_3)_2$			SnO_2
$AgNO_3$		$Co(NO_3)_2$			Cr_2O_3
K_2SO_4		$ZnSO_4$			WO_3
Na_2SO_4		$CdSO_4$			Mn_2O_3
		$CuSO_4$			
		Ag_2SO_4			

CONDUCTANCE OF SOLUTIONS IN ANHYDROUS HYDROGEN FLUORIDE

Gore found that water formed a conducting solution, when dissolved in hydrogen fluoride, and Moissan (7) found that potassium fluoride did likewise. It has remained for Fredenhagen and Cadenbach (12) to determine the equivalent conductivities of a number of solutes over a range of dilution. A summary of their measurements is given in table 3, and figure 4 shows these data graphically. Potassium fluoride and silver fluoride give very nearly the same conductivities, and they are apparently completely ionized in the more dilute solutions. The results for

TABLE 3

Conductivity of substances in solution in hydrogen fluoride

Normality	0.5	0.24	0.115	0.055	0.026	0.013
Dilution	2.0	4.2	8.7	18	38	79
	Equivalent conductivity at −15°					
H_2O	121	153	183	210	228	242
KF	172	203	225	241	251	255
AgF	174	201	222	238	247	255
KNO_3	360	429	482	558	610	622
$AgNO_3$	390	470				
H_2SO_4		151	184	209	232	245
$\frac{1}{2}K_2SO_4$	171	211	244	267	276	277
CH_3OH	139	164	200	225	243	251
C_2H_5OH	166	180	210	233	246	256
C_3H_7OH	142	163	196	215	231	236
$C_5H_{11}OH$	128	158	186	205	222	224
HCOOH	77	102	132	166	198	237
CH_3COOH	148	175	205	227	241	260
CCl_3COOH	9	11	11			
$\frac{1}{2}(COOH)_2$	94	117	137	161		
C_6H_5COOH	176	181	190	200	226	243
$(CH_3CO)_2O$	154	180	203	226	244	
CH_3COOK	325	367				
CH_3COCH_3	159	182	216	238	252	273
$(C_2H_5)_2O$	179	190	216	269	293	310
Glucose	114	165	208	247	279	310
C_6H_5OH	17	23	31	44	52	59
$C_6H_2(NO_2)_3OH$	only 0.2 per 100 soluble: conductivity less than for phenol					

potassium nitrate, silver nitrate, and potassium acetate are surprising, for these salts are binary electrolytes in aqueous solution, but in this solvent they apparently produce twice the number of ions that the binary salts potassium fluoride and silver fluoride produce. In order to account for this result, Fredenhagen and Cadenbach have first considered the ionization of water. The data show this as a binary electrolyte, the ionization of which could be represented as

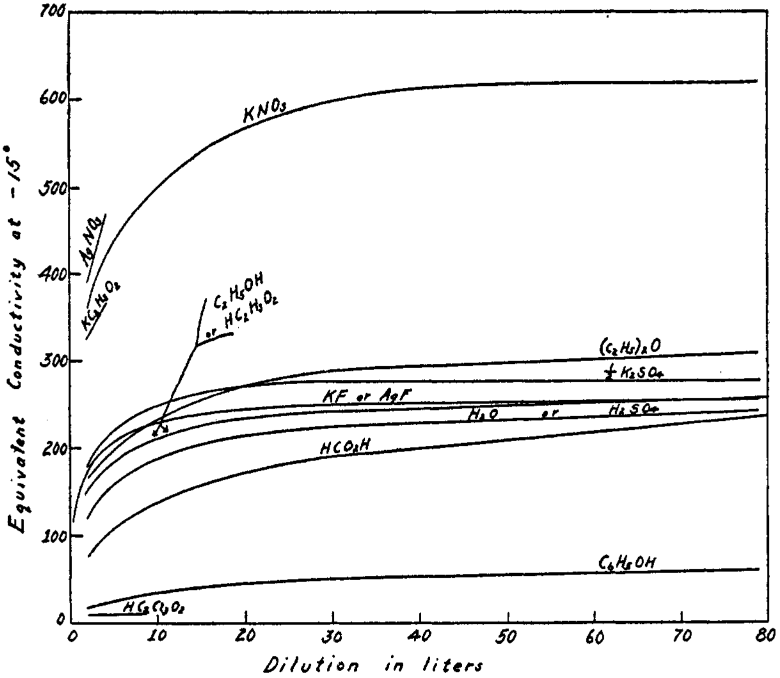

FIG. 4. CONDUCTIVITIES IN LIQUID ANHYDROUS HYDROGEN FLUORIDE

$$H_2O = H^+ + OH^-.$$

As hydrogen fluoride is an acid material, it may serve as donor of protons to the water according to the equation

$$H_2O + HF = H_3O^+ + F^-,$$

which would produce the same number of ions and so give a similar equivalent conductivity. In order to distinguish between these two possibilities, an equal molal mixture of water and potassium fluoride was dissolved in hydrogen fluoride and the conductivities determined. The results given in table 4 show that the conductivity of the mixture is approximately equal to the sum of the conductivities of the two solutes taken separately. This decides rather conclusively for the second mode of ionization of water for

TABLE 4

Conductivities of KF and H_2O singly and together in HF at −15°C.

CONCENTRATION	KF AND H_2O TOGETHER	KF	H_2O	SUM OF KF AND H_2O TAKEN SINGLY
moles per liter				
0.5	0.1126	0.0863	0.0606	0.1469
0.24	0.0685	0.0488	0.0367	0.0855
0.115	0.0396	0.0258	0.0214	0.0473
0.055	0.0224	0.0133	0.0115	0.0248
0.026	0.0124	0.00663	0.00600	0.0126
0.013	0.00620	0.00321	0.00305	0.00626

the following reason. The potassium fluoride ionizes according to the equation

$$KF = K^+ + F^-.$$

If the water ionizes to produce hydrogen ions, these would react to produce the unionized solvent with the fluoride ion

$$H^+ + F^- = HF,$$

and instead of four ions per mole each of water and potassium fluoride, there would result only two, as the following equations show:

$$KF + H_2O = K^+ + OH^- + HF$$
$$KF + H_2O + HF = K^+ + H_3O^+ + 2\,F^-.$$

The first equation is excluded on the basis of chemical knowledge, for potassium hydroxide reacts vigorously with anhydrous hydrogen fluoride to produce potassium fluoride and water, whereas the first equation shown immediately above represents the reverse of this reaction.

The high conductivity of potassium nitrate and silver nitrate is explained in a similar manner. The ionization of nitric acid in hydrogen fluoride is assumed to be according to the equation

$$HNO_3 + HF = H_2NO_3^+ + F^-,$$

and that of potassium nitrate

$$KNO_3 + 2HF = K^+ + H_2NO_3^+ + 2F^-.$$

This is, of course, equivalent to saying that nitric acid acts as an acceptor for protons from hydrogen fluoride or that it is basic in relation to it.

The conductivities of sulfuric acid are practically identical with those for water, and this is accounted for by a reaction to produce water.

$$H_2SO_4 + 2HF = HSO_3F + H_3O^+ + F^-$$

The analogous reaction for potassium sulfate is

$$K_2SO_4 + 3HF = KSO_3F + K^+ + H_3O^+ + 2F^-$$

However, a small ionization of KSO_3F must be assumed.

The conductivity of acetic acid could be accounted for in two ways. The first would be a reaction with hydrogen fluoride to form acetyl fluoride and water,

$$HC_2H_3O_2 + 2HF = CH_3COF + H_3O^+ + F^-,$$

and in the second, the acetic acid molecule would act as an acceptor for the proton from the hydrogen fluoride

$$HC_2H_3O_2 + HF = H_2C_2H_3O_2^+ + F^-.$$

In the first case, we should expect the conductivity to be exactly the same as for water, as was found for sulfuric acid. This is not true. We also know that acetyl fluoride does not ionize in this solution, because acetic anhydride gives conductivities practically identical with those of acetic acid. We know that acetic anhydride reacts to form acetyl fluoride and acetic acid according to the equation

$$(C_2H_3O)_2O + HF = CH_3COF + HC_2H_3O_2.$$

This permits us to explain the conductivity of potassium acetate by the reaction

$$KC_2H_3O_2 + 2HF = K^+ + H_2C_2H_3O_2^+ + 2F^-.$$

The acceptor theory to account for the conductivities of the organic acids allows us to explain the apparently low ionization of trichloroacetic acid. In aqueous solution, it is a stronger acid than acetic acid; this fact shows it to be a stronger donor and therefore a weaker acceptor. Being a weaker acceptor, it would have less tendency to take the proton from the hydrogen fluoride than acetic acid. The same reasoning accounts for the higher conductivity of benzoic acid as compared with acetic acid, for benzoic acid is a weaker acid in aqueous solution than acetic acid. Oxalic acid is a stronger acid in aqueous solution than acetic acid and in hydrogen fluoride shows a lower conductivity; this fact agrees with the theory, as oxalic acid would be a poorer acceptor than acetic acid. The same reasoning can be applied to formic acid.

The alcohols act as binary electrolytes in hydrogen fluoride solution. This may be accounted for in two ways: either they react to form a fluoride and water, or they act as acceptors for protons. The latter explanation seems to correspond more closely to the truth, as can be seen in the case of ethyl alcohol. If the former explanation held, we should expect the conductivity to be the same as that for water, whereas it is appreciably higher. In addition, ethyl alcohol has been shown not to react appreciably with hydrogen fluoride at room temperatures. Meslans and Girardet (22) found the reaction to begin only at 140°, and Fredenhagen (23) has been able to recover the alcohol from its solution in hydrogen fluoride without obtaining ethyl fluoride. Phenol is an alcohol which produces considerable hydrogen ions in aqueous solution. It is, therefore, a better donor of protons than ethyl alcohol and would be expected to be a poorer acceptor for them in hydrogen fluoride solution and so give a lower conductivity, which it does. Picric acid gives a lower conductivity than phenol, as we should expect from the fact that it is a stronger acid and therefore a weaker base.

The high conductivities of acetone and ethyl ether can also be accounted for on the basis that they act as acceptors for hydrogen ions in hydrogen fluoride. This agrees well with our knowledge of the structure and properties of these compounds. They seem to act as strong bases in these solutions, and if the conductivity measurements are significant, begin to accept the second proton at high dilution.

The insolubility of the other hydrogen halides can be well explained by this theory. They have much lower boiling points and low dielectric constants. Unless they ionized in the solution or reacted with the solvent, we should not expect them, on the basis of our ordinary laws of solubility, to be soluble. As they are themselves donors of protons, with little tendency to act as acceptors, they could not react with hydrogen fluoride, which cannot act as an acceptor. They apparently cannot ionize in the absence of an acceptor, for they do not ionize when in the pure liquid state.

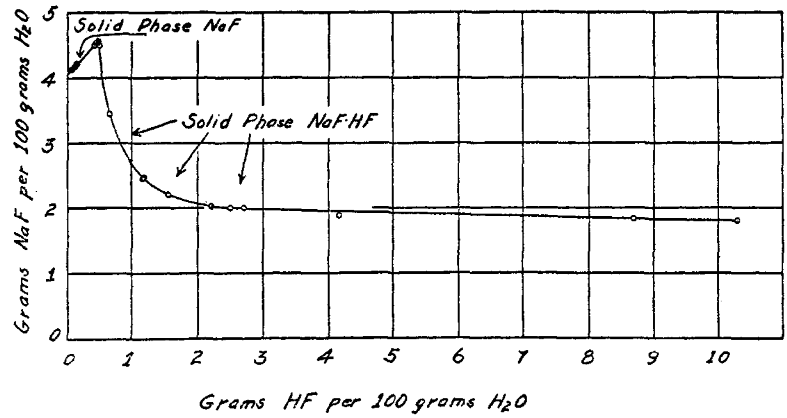

FIG. 5. SOLUBILITY OF SODIUM FLUORIDE IN AQUEOUS HYDROFLUORIC ACID

A comparison of the three liquids—ammonia, water, and hydrogen fluoride—shows that ammonia is more basic than water, and water more basic than hydrogen fluoride. Ammonia reacts with water in a manner similar to the reaction of water with hydrogen fluoride, namely

$$NH_3 + H_2O = NH_4^+ + OH^-.$$

Water acts as a donor to ammonia but as an acceptor to hydrogen fluoride. A strongly acid compound like hydrogen chloride acts as a donor to both ammonia and water but not to hydrogen fluoride, while a weaker acid compound like acetic acid acts as a donor to both ammonia and water but as an acceptor to hydrogen fluoride. The properties of a polar solvent are seen to depend not only upon the dielectric constant, but also upon the tendency to act as acceptor or donor of protons. Many of the properties of water are and have been explained by its ability to act in either capacity. Hydrogen fluoride apparently acts chiefly as a donor.

THE SYSTEM BENZENE—HYDROGEN FLUORIDE

The author (30) has made a study of the system benzene-hydrogen fluoride in the region of a very low proportion of hydrogen fluoride. The solubility of hydrogen fluoride in the gas phase was measured in benzene over a range of both temperature and partial pressure of hydrogen fluoride over the solution. Figure 5 shows the partial pressure of hydrogen fluoride in the gas phase plotted against its mole fraction in the solution. The straight lines in the graph represent the "ideal" solution, and so it is seen that the deviation from ideality is very great. This represents an unusual type of solution with a large positive deviation from Raoult's law at the higher concentrations and a negative deviation in the more dilute solution. The positive deviation is to be expected, because of the great difference between the dielectric constants of the two compounds, but the negative deviation is a surprising result.

A possible explanation of this phenomenon can be given by a consideration of the electric field surrounding the highly polar hydrogen fluoride molecule. When these molecules are in sufficient concentration to exert an influence upon one another, they will be mutually attracted and so tend to be removed from the solution. This explains the positive deviation from Raoult's law at high concentration. When the concentration is so low that the distances between the molecules of hydrogen fluoride are great enough to make the mutual attraction small, then the electric field around each hydrogen fluoride molecule will attract even the slightly polar benzene molecules and so cause the vapor pressure of hydrogen fluoride from the solution to be less than would be given by Raoult's law.

AQUEOUS SOLUTIONS OF HYDROGEN FLUORIDE

Aqueous solutions of hydrogen fluoride have been more extensively studied than has the pure liquid. After a number of authors had favored either HF or H_2F_2 as the formula for the undissociated molecules in aqueous solutions, Pick (24) suggested that the properties of hydrogen fluoride could be accounted for quantitatively as well as qualitatively by the assumption of the HF_2^- ion and the absence of the H_2F_2 molecules. He explained the conductivity of dilute hydrofluoric acid solutions very well by this means. In a series of papers by Hudleston and his coworkers, it has been shown that this assumption would account for the experimental data obtained in transference (25), hydrogen ion activity (26), and freezing point lowering experiments (27), and also the solubility of sodium fluoride (28) in dilute aqueous solutions with a varying concentration of hydrogen fluoride. By using the assumption of the two equilibria

$$\mathrm{HF} = \mathrm{H^+} + \mathrm{F^-} \qquad K_1 = \frac{[\mathrm{H^+}]\,[\mathrm{F^-}]}{[\mathrm{HF}]} = 7.4 \times 10^{-4}$$

and

$$\mathrm{HF} + \mathrm{F^-} = \mathrm{HF_2^-} \qquad K_2 = \frac{[\mathrm{HF_2^-}]}{[\mathrm{HF}]\,[\mathrm{F^-}]} = 4.7$$

they have been able to explain this entire mass of data. Their work on freezing point lowering in particular gives no indication of H_2F_2 but rather shows that, if it is present, it must be in extremely small concentration. Of course the existence of HF_2^- is no indication of H_2F_2 any more than the existence of NH_4^+ is an indication of N_2H_6.

The solubility of sodium fluoride in aqueous solution increases markedly as hydrogen fluoride is added to the solution, and then decreases as shown in figure 6. Jehu and Hudleston (28) have explained this with the above equilibria. As the hydrogen fluoride is added, it reacts with the fluoride ion and so increases the solubility of the sodium fluoride, the ionization of the hydrogen fluoride being small. When a sufficient concentration of HF_2^- is reached, the addition of more hydrogen fluoride increases it above the solubility product of $Na^+ + HF_2^-$, and so reduces the solubility of sodium fluoride in the solution.

Some unfinished experiments, which the author is conducting on the electrometric titration of aqueous solutions of hydrogen fluoride with solutions of potassium fluoride and ammonium fluoride, indicate that hydrofluoric acid is not a dibasic acid. This means that the ion HF_2^- does not ionize to produce hydrogen ion and the ion F_2^{--}. This may mean that in the ion HF_2^- the connection is not made through the two fluorine atoms, but through the hydrogen after the manner of the hydrogen bond of Lewis.

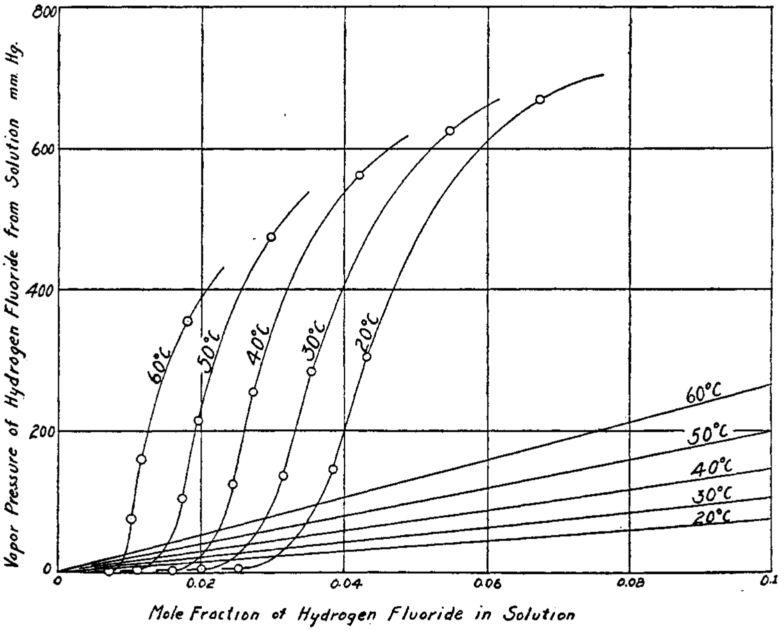

FIG. 6. HYDROGEN FLUORIDE SOLUTION IN BENZENE

The knowledge of the HF_2^- ion adds to our comparison of the three polar liquids—ammonia, water, and hydrogen fluoride. Comparing the other two in solution in water, we find that ammonia is basic and so adds the positive hydrogen ion

$$NH_3 + H^+ = NH_4^+.$$

Hydrogen fluoride, being acid, adds the negative fluoride ion,

$$HF + F^- = HF_2^-,$$

in an analogous reaction. It probably adds the fluoride ion in preference to the hydroxyl ion, as the fluoride ion is the more plentiful in aqueous hydrofluoric acid solutions. As the modern concept of a base is that it is not only a substance which will produce hydroxyl ions but also one that acts as an acceptor for hydrogen ions, so an acid can be considered not only as a substance which acts as a donor of hydrogen ions, but also as a substance which acts as an acceptor of its own negative ion. The strong tendency of hydrogen fluoride to act as an acid on this basis probably accounts for its being an apparently weak acid in aqueous solution. The fluoride ion in anhydrous hydrogen fluoride solutions is probably also solvated.

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