

$K_2Al_2O_4$  are very different from those of pure iron. The emissivity increases markedly with temperature as is the case for oxide coated filaments, indicating dissociation of the potassium oxide at elevated temperatures. The long wave length limit lies intermediate between that of iron and that of potassium, showing the surface to be sparsely covered with elemental potassium. The long wave length limits show clearly that the ratio of elemental potassium to the total potassium content is greatly reduced by the presence of aluminum oxide.

The photoelectric properties of the  $K_2Al_2O_4$  promoted catalyst appear to come from the  $K_2O$  which has failed to combine with the  $Al_2O_3$ . It is suggested that the poisoning action of  $K_2O$  alone is due to the ease with which it dissociates, and that it is the free potassium which is the actual poison.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## THE SOLUBILITY OF HYDROGEN FLUORIDE IN BENZENE AND IN OCTANE

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The study of the solubility of gaseous hydrogen fluoride in organic solvents was begun in an attempt to obtain more information about the polymer  $H_2F_6$  whose existence has been indicated by Simons and Hildebrand from considerations of the density of the gas.<sup>1</sup> While the results have not aided greatly in this connection, an example of an unusual type of solution has been found in the case of hydrogen fluoride dissolved in benzene.

**Apparatus.**—The apparatus, the design of which is shown in Fig. 1, was made entirely of copper with all permanent joints sealed together with silver solder. The three vessels of which the apparatus consisted were held together with screw connections. Two of the vessels were held in separate constant temperature baths; the one served as container for the liquid hydrogen fluoride and the other for the solution. The third vessel, which fastened on the bottom outlet of the solution container, was the constant volume sample tube. Copper is a suitable material for this apparatus, for hydrogen fluoride in the absence of an oxidizing agent, such as oxygen from the air, is without action on it, and oxygen was rigorously excluded.

**Materials Used.**—The anhydrous hydrogen fluoride was made in the manner described by Simons<sup>2</sup> and distilled directly into the apparatus, which had been carefully cleaned, dried and filled with dry nitrogen. The

<sup>1</sup> Simons and Hildebrand, *THIS JOURNAL*, **46**, 2183 (1924).

<sup>2</sup> Simons, *ibid.*, **46**, 2179 (1924).

benzene was pure thiophene-free material which was fractionated, dried with phosphorus pentoxide and with sodium, and finally distilled directly into the apparatus. The octane was prepared synthetically in this Laboratory and was carefully dried in the same manner as for the benzene. The nitrogen was the commercial gas from a cylinder from which the oxygen was removed by towers of cuprous ammonium chloride solution. It was dried with sulfuric acid and with phosphorus pentoxide.

**Method of Procedure.**—For the determinations made without the use of nitrogen, the vessel of hydrogen fluoride was allowed to warm up to the

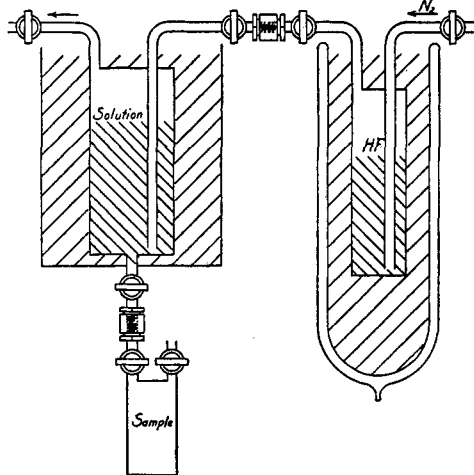


Fig. 1.—Solubility apparatus.

boiling point. The gas formed was passed slowly through the solvent, the solvent vessel being kept at a temperature sufficiently high so that liquid hydrogen fluoride would not condense in it. Equilibrium was considered established when samples of the solution taken over intervals of the passage of the gas gave check analyses. Raising the temperature of the solution vessel gave determinations at higher temperatures.

For the determinations made with a partial pressure of hydrogen fluoride less than that given

by boiling the liquid, nitrogen was passed through the vessel containing it while it was kept at a constant temperature. The sample for analysis was drawn off into the sample tube, which had a volume of about 20 cc. It was weighed, forced into an aqueous solution containing an excess of sodium hydroxide over that necessary to neutralize the hydrogen fluoride and the excess was titrated with a standard hydrochloric acid solution.

## Results

The results of these determinations are recorded in Table I and shown graphically in Fig. 2.

Several different lots of both benzene and hydrogen fluoride were used in these experiments, which extended over a considerable period of time. The agreement of the results indicates that they are free from large accidental errors.

The vapor pressure of hydrogen fluoride from the solution was plotted against its mole fraction at different temperatures as shown in Fig. 3.

It was calculated from the vapor pressure of liquid hydrogen fluoride at the temperature at which the pure liquid was held, the vapor pressure of benzene at the temperature of the solution, and the barometric pressure. Table II shows the data from which the curves were drawn. The mole fractions were taken from the smooth curves in Fig. 2. The straight lines represent the "ideal" vapor pressures of hydrogen fluoride from the solution as calculated from Raoult's law.

It is to be expected that hydrogen fluoride with its high dielectric constant would show a large positive deviation from Raoult's law in benzene solutions. This is found at the higher concentrations but at low concentrations a negative deviation is observed.

TABLE I  
SOLUBILITY OF HYDROGEN FLUORIDE IN BENZENE AND IN OCTANE

Hydrogen fluoride liquid at the boiling point		Solution in benzene						In octane HF liquid at the boiling point	
		HF liquid at 0°C.		HF liquid at -18°C.		HF liquid at -77°C.		Temp. of boiling point	
Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF	Temp. of soln., °C.	Mole fraction HF
23.1	0.0630	25.6	0.0384	23.0	0.0355	23.6	0.0227	25.1	0.00338
31.1	.0525	30.2	.0346	31.8	.0323	30.0	.0208	36.0	.00276
42.3	.0394	40.5	.0277	20.8	.0382	45.0	.0128	45.2	.00235
27.2	.0588	50.0	.0201	31.2	.0306	56.0	.00825	51.0	.00194
33.9	.0495	27.5	.0368	40.8	.0244	65.0	.00557	66.3	.00170
39.1	.0442	52.0	.0181	52.8	.0161	19.6	.0249		
39.4	.0427	56.3	.0150	58.1	.0117	38.3	.0163		
39.2	.0437	65.1	.0084	21.0	.0375	52.9	.0098		
25.8	.0596	21.0	.0425	20.9	.0381	60.8	.0067		
29.3	.0556	32.9	.0330	28.0	.0327				
29.4	.0548	61.2	.0108	38.0	.0258				
32.9	.0507			49.0	.0184				
44.8	.0365			60.6	.0098				
44.7	.0382								
54.1	.0243								
54.1	.0248								
21.5	.0653								
22.0	.0648								
21.6	.0650								
24.2	.0625								
24.2	.0620								
35.6	.0510								
36.7	.0468								
62.5	.0155								
62.4	.0150								
46.0	.0332								
51.0	.0280								
54.0	.0246								
61.0	.0167								
72.8	.00395								

NOTE.—The mole of hydrogen fluoride is taken as the formula weight of the molecular species, HF.

TABLE II  
EXPERIMENTAL DATA FOR CURVES

Temp. of soln., °C.	Mole fraction HF in solution Liquid hydrogen fluoride at				Vapor pressure HF	Vapor pressure C <sub>6</sub> H <sub>6</sub>	Partial pressure of HF over solution, mm.			
	-77°C.	-18°C.	0°C.	B. p.			-77°C.	-18°C.	0°C.	B. p.
20	0.0248	0.0385	0.0432	0.0673	768	75.6	4.5	147	203	669
30	.0203	.0315	.0355	.0548	1070	120.2	4.2	137	283	625
40	.0158	.0244	.0275	.0422	1470	183.6	3.8	123	254	561
50	.0112	.0173	.0196	.0298	1990	271.4	3.2	104	214	473.6
60	.0071	.0102	.0117	.0180	2630	390.1	2.4	77.5	160	354.9
Vapor pressure HF, mm.	5.1	166	342							
Average barometric pressure, mm.	750	740	742	745						

This is an example of an unusual type of solution. It is similar to the case of pyridine-water<sup>3</sup> in that both positive and negative deviations from Raoult's law are found in the same curve, but it is different in that pyridine has a negative deviation at very high concentration, but a positive deviation at moderate or low concentrations.

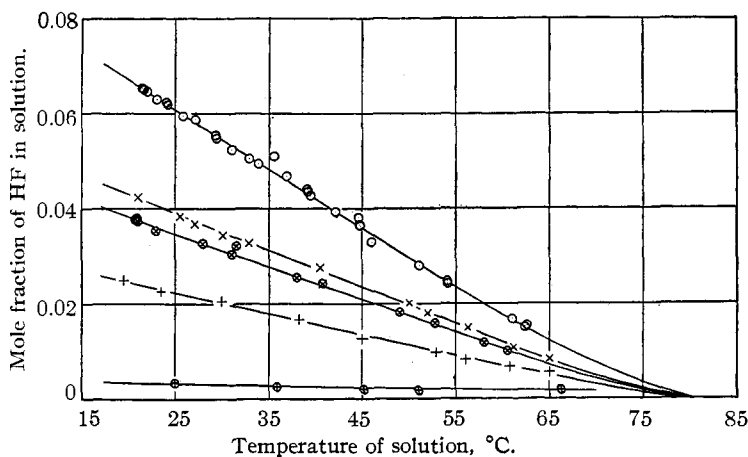


Fig. 2.—Solubility of hydrogen fluoride in benzene and in octane. O, Solubility in benzene with HF liquid at 19.5°; X, solubility in benzene with HF liquid at 0°; ⊙, solubility in benzene with HF liquid at -18°; +, solubility in benzene with HF liquid at -77°; ⊕, solubility in octane with HF liquid at 19.5°.

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

<sup>3</sup> J. H. Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924, p. 41.

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 distance between the molecules of hydrogen fluoride is great enough to make the mutual attraction small, then the electric field around each of the hydrogen fluoride molecules 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.

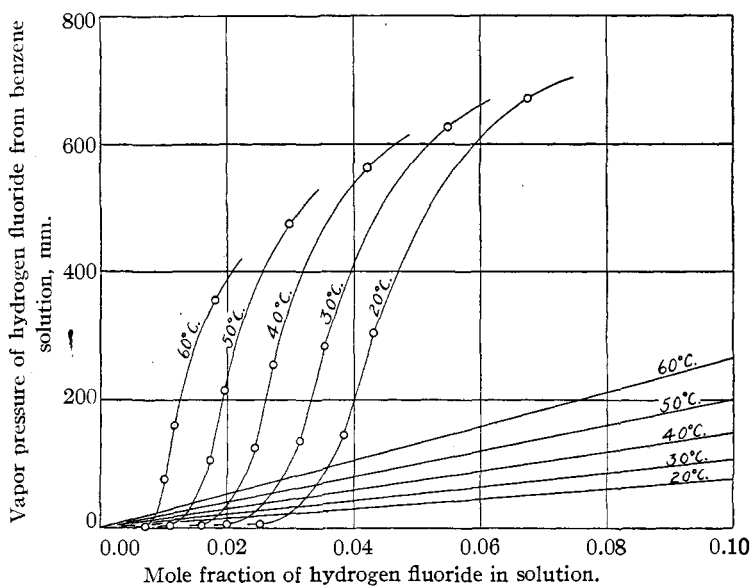


Fig. 3.—Hydrogen fluoride—benzene solution.

The author wishes to acknowledge the assistance of Mr. Eric E. Johnson in making the determinations.

### Summary

The solubility of hydrogen fluoride in octane has been measured.

The solubility of hydrogen fluoride in benzene has been measured over a range of temperature and partial pressure of hydrogen fluoride.

The vapor pressure of hydrogen fluoride from a benzene solution shows a negative deviation from Raoult's law at very low concentrations but a high positive deviation at higher concentrations.

A possible explanation of this phenomenon is given.

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