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Solubility of F_2, NF_3, and O_2 in Anhydrous Liquid HF

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The solubility of F_2, NF_3, and O_2 in anhydrous liquid HF was measured at several temperatures. The solubility of F_2 passes through a minimum between −0.21° and 19.8° C., but between −0.21° and −77.2° C. it can be computed to within 3% of the observed value. The heat of solution is −588 cal. $mole^{-1}$. The solubility of NF_3 was measured at three temperatures; it does not exhibit a solubility minumum similar to that of F_2. At −77.2° C. a curved plot of partial pressure *vs.* molality was observed at pressures exceeding 1 atm. The heat of solution is −1533 cal. $mole^{-1}$. The solubility of O_2, measured at −0.21° and 19.8° C., was similar to that of F_2. A heat of solution calculated from the solubility at these two temperatures is −352 cal. $mole^{-1}$. The solubility of O_2 in HF at 19.8° and −0.21° C. was larger by factors of 5 and 10, respectively, than the literature values for solubility in H_2O at the same temperatures.

The solubility of gases in liquids is of theoretical interest, and when measured with sufficient precision and sensitivity can be used along with other information such as conductivity to infer the presence or absence of interaction of the gas with the solvent. In our study of the chemistry of NF_3 and F_2 in liquid HF, it was of interest to determine their solubilities in this solvent. The solubility of O_2 in HF was also determined. These data permit comparison of the solubility of O_2 in HF and in H_2O. A similar comparison of the solubility of F_2 in the two solvents would have little value, because F_2 reacts with water.

EXPERIMENTAL

The method was similar to that of Kilpatrick and Luborsky (*2*), who with others (*1, 3*) have reported the solubility of BF_3 in liquid HF. In the present work, solubility measurements were made at several temperatures in a constant temperature bath. A Kontes K-87250 Model A thermoregulator provided room temperature regulation to ±0.2° C. The thermometer used for room temperature readings was calibrated against a platinum resistance thermometer. Slush baths were used to obtain temperatures lower than ambient. The temperature of the slush bath was determined with a $CFCl_3$ gas thermometer connected to a calibrated Wallace and Tiernan gage. A comparison of the pressure within the gas thermometer to that of the known vapor pressure curve for $CFCl_3$ gave the temperature of the slush bath. Thus, temperatures lower than ambient given in this paper are only as accurate as the Wallace and Tiernan gage and the known vapor pressure curve for $CFCl_3$.

The apparatus shown in Figure 1 was fabricated from Monel metal and assembled by brazing with silver solder.

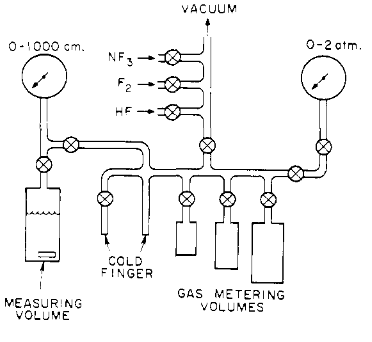


Figure 1. Solubility apparatus

All valves were Hoke 4552Q4M bellows valves. The volume of the measuring and metering vessels was determined from the weight and density of the distilled water that completely filled them. Volumes of the remainder of the system were calculated from PV changes of argon. Two Wallace and Tiernan pressure gages were used: a Model FA-145 or 0 to 1520-mm. gage and a dual-scale gage, Model FA-233, 0 to 200 p.s.i.a. and 0 to 1035 cm. of Hg. The high pressure gage used for the solubility measurements could be read to the nearest 0.2 cm. of Hg. The low pressure gage was calibrated at 1 atm. with a mercury manometer. Successive quantities of argon measured in the gas metering volumes with the calibrated low pressure gage were then condensed into the high pressure gage volume. Assumption of the perfect gas law permitted calculation of the pressures that should have resulted. The largest deviation of the pressures observed from those calculated was 0.7 cm. of Hg.

Before use, the solubility apparatus was thoroughly passivated with a high pressure of fluorine. The measuring volume was then treated with liquid HF to condition the vessel further. Because of the extremely corrosive nature of the chemicals involved, all work was performed in a hood behind Plexiglas doors. Fluorine and HF were slowly passed through a soda-lime trap preceding the vacuum pump which was vented into a H_2O trap beneath the sink, to prevent circulation of toxic vapors back into the laboratory.

Anhydrous hydrogen fluoride having a conductivity of 3×10^{-5} ohm^{-1} cm.$^{-1}$ was obtained from the Olin Corp. The HF was distilled into the 450-cc. measuring volume shown in Figure 1 and the vessel was weighed; 212.9 grams of anhydrous HF were initially present. Because only one charge of HF was made for all measurements, the liquid was purified between experiments by distillation. The measuring vessel was reweighed to determine the quantity of HF remaining. A net weight loss of 50 mg. of HF was observed for the entire solubility study.

Fluorine was obtained in 98% purity from the Allied Chemical Corp. For further purification, a known quantity of the gas was condensed into a trap packed with nickel spirals and cooled to −196° C. Gases volatile at −196° C. were then transferred to a receiver at about −210° C. The significant impurity remaining was approximately 1% air. To remove part of the nitrogen remaining, the vapor above the liquid fluorine was extracted into an evacuated vessel. The fluorine obtained in this manner was used without further purification or analysis and was stored in one of the gas-metering volumes shown in Figure 1.

Nitrogen trifluoride was obtained from the Air Products Co. in greater than 99% purity, the remainder being air. The liquid was pumped on at −196° C. until the literature value for the vapor pressure of NF_3 was observed. The purified sample was then stored in one of the gas metering volumes shown in Figure 1.

High purity oxygen was obtained from the General Dynamics Corp. and was not purified further.

The measurement of the solubility of fluorine in anhydrous liquid HF illustrates the general method used. The HF contained in the measuring volume was treated with 1 atm. of fluorine, thoroughly outgassed at −130° C., and then weighed. The measuring volume was then placed in a constant temperature bath and the HF vapor pressure was recorded. Successive quantities of purified fluorine were then measured in the appropriate gas-metering vessel with the low pressure Wallace and Tiernan gage and were condensed into the measuring vessel at about −210° C. Since fluorine has a vapor pressure of 22.5 mm. of Hg at −210° C., corrections were made for the amount of noncondensable fluorine. After the contents of the measuring vessel were allowed to equilibrate with stirring at the desired temperature for 2 hours, the valve between the vessel and the high pressure Wallace and Tiernan gage volume was opened. The system was again allowed to equilibrate for 6 to 48 hours with stirring before a final pressure measurement was taken. When a constant pressure was observed for at least 2 hours, it was assumed that equilibrium had been obtained.

The initial procedure of stirring the mixture in the measuring vessel and not in the gage line was found necessary to achieve the proper concentration of HF in the vapor phase. Because of the large differences in volatility between the gases studied and the HF solvent, the HF must diffuse through a very high pressure of the gas present, and without adequate mixing in a vessel of large cross section the HF mixture does not conform to Dalton's law. The observed pressures were first plotted against the pressure that the added gas should have exerted had there been no solvent present. Because these pressure measurements gave linear plots with an intercept at the known vapor pressure of HF, there was apparently no systematic error due to lack of mixing (*2*).

Whereas oxygen and fluorine, within small limits, behave as perfect gases from 1 to 13 atm. relative to their behavior at 1 atm., NF_3 does not. The deviations from ideal behavior of NF_3 above 1 atm. were determined and used to correct the observed pressures. Thus, the solubility reported for NF_3 includes this correction at each temperature.

RESULTS

From the knowledge of the free volume above the HF in the measuring vessel, it was possible to calculate the theoretical pressure that the added gas should exhibit if it were completely insoluble. The difference between the observed pressure above the mixture, corrected for the solvent's vapor pressure, and the theoretical pressure that the added gas should exhibit is the quantity of dissolved gas.

Data for the solubility of F_2, NF_3, and O_2 in anhydrous liquid HF are presented in Tables I, II, and III, respectively, and plotted in Figures 2, 3, and 4. The straight-line

Table I. Solubility of Fluorine in HF

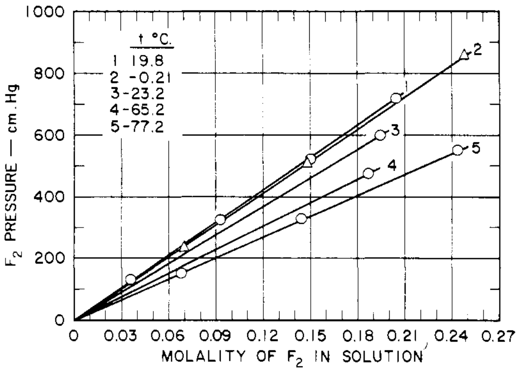
Run No.	F_2 Added, Cm. Hg	Observed Pressure		Moles F_2 Dissolved	Molality
		Cm. Hg	−V.P. HF		
			19.8° C.		
1	193	210	133	0.00759	0.0356
2	481	404	326	0.0197	0.00925
3	773	600	522	0.0319	0.150
4	1063	798	720	0.0435	0.204
5	1083	816	738	0.0438	0.206
			−0.21° C.		
1	341	273	237	0.0147	0.0690
2	347	278	242	0.0148	0.0697
3	733	547	511	0.0314	0.148
4	973	713	677	0.0418	0.196
5	1230	894	858	0.0527	0.247
			−23.2° C.		
1	856	612	599	0.0413	0.194
			−65.2° C.		
1	670	478	476	0.0398	0.187
			−77.2° C.		
1	217	153	152	0.0144	0.0675
2	221	157	156	0.0144	0.0678
3	468	330	329	0.0306	0.144
4	784	552	551	0.0517	0.243

Table II. Solubility of Nitrogen Trifluoride in HF

Run No.	NF_3 Added, Cm. Hg	Observed Pressure		NF_3 Deviation, Cm. Hg	Corrected NF_3 Pressure Observed, Cm. Hg	Moles NF_3 Dissolved	Molality
		Cm. Hg	-V.P. HF				
				19.8° C.			
1	96.0	127	48.9	0	48.9	0.00598	0.0281
2	388	278	200	1.8	202	0.0235	0.110
3	679	426	348	5.1	353	0.0413	0.194
4	971	574	496	10.6	506	0.0590	0.277
5	1261	719	641	18.0	659	0.0764	0.359
6	1552	864	786	27.8	814	0.0937	0.440
7	1841	1007	929	39.6	969	0.111	0.520
				-0.21° C.			
1	340	206	170	1.4	171	0.0238	0.112
2	848	458	422	7.6	430	0.0592	0.278
3	957	506	470	9.5	479	0.0674	0.317
4	1697	854	818	20.3	848	0.120	0.564
				-77.2° C			
1	217	71.0	70.3	0.6	70.9	0.0323	0.152
2	541	166	165	4.4	169	0.0823	0.387
3	610	186	186	5.4	191	0.0929	0.436
4	934	272	272	10.0	282	0.145	0.680
5	1082	311	310	12.6	322	0.168	0.791
6	1420	389	388	22.2	410	0.224	1.05

Table III. Solubility of Oxygen in HF

O_2 Added, Cm. Hg	Observed Pressure		Moles O_2 Dissolved	Molality
	Cm. Hg	-V.P. HF		
		19.8° C.		
824	633	556	0.0341	0.160
		-0.21° C.		
740	545	509	0.0327	0.153



CURVES 3 AND 4 ARE SINGLE POINT DETERMINATIONS EXTRAPOLATED TO THE ORIGIN.

Figure 2. Solubility of fluorine in HF at five temperatures

plots are given by a Henry's law expression, $p = km$, where the partial pressure of the gas in centimeters of mercury in the vapor phase equals a constant times the molality of the gas in solution. Values of k have the corresponding units (centimeters)(grams × 10^3)(mole^{-1}).

From a consideration of the standard deviation and readability of the high pressure Wallace and Tiernan gage, the difficulty in maintaining the temperature of a slush bath for extended periods of time, and the accuracy of the $CFCl_3$ gas thermometer, it was estimated that the k values presented in this work have an uncertainty of 2%, or less.

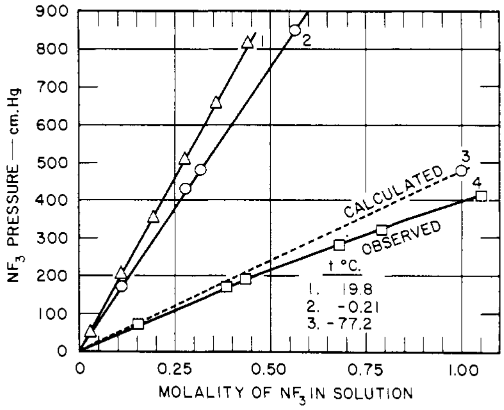
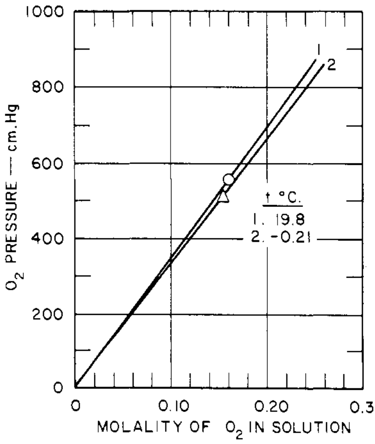


Figure 3. Solubility of nitrogen trifluoride in HF at three temperatures



CURVES 1 AND 2 ARE SINGLE POINT DETERMINATIONS EXTRAPOLATED TO THE ORIGIN.

Figure 4. Solubility of oxygen in HF at two temperatures

Heats of solution were calculated from the slopes of the solubility curves using the van't Hoff relationship, $dk/dt = \Delta H/RT^2$. From these data it was possible to calculate the solubility of the gas in HF at other temperatures.

The solubility of F_2 in HF at five temperatures is shown in Figure 2. The k values derived from the slopes of the curves shown in Figure 2 are given in Table IV.

It is apparent that the k values do not follow the van't Hoff expression between −0.21° and 19.8° C., which indicates that the solubility of fluorine between −0.21° and 19.8° C. goes through a minimum. However, between −0.21° and −77.2° C, it behaves linearly in terms of the van't Hoff equation and permits the heat of solution to be calculated as −588 cal. mole^{-1}. At −23.2° and −65.2° C., k values determined from the heat of solution agree within 3% with the values determined in single-point measurements at these temperatures. An error of unknown magnitude, which must be considered, results from the difficulty in maintaining constant temperature in a low temperature slush bath. The effect of less than 1% air impurity in the F_2 on the uncertainty in the values of k should be negligible, because N_2 and O_2, having boiling points similar to that of F_2, would be expected to exhibit similar solubilities. This proved to be the case for O_2 in HF, where the observed solubility was similar to that of F_2 at the same temperature.

The solubility of NF_3 in HF at three temperatures is shown in Figure 3; k values derived from the slopes of the curves shown in Figure 3 are presented in Table V.

At ice temperature and above, straight-line plots of partial pressure *vs.* molality were obtained. From these data it was possible to calculate the heat of solution of NF_3 in HF to be −1533 cal. mole^{-1}, nearly 2.5 times as exothermic as the heat of solution of F_2. At −77.2° C., a curved plot of partial pressure *vs.* molality was observed. Its limiting slope was very nearly equal to that predicted from the van't Hoff relationship from which the calculated curve was derived. It seems clear that NF_3 does not have a solubility minimum similar to that of F_2 in the temperature range studied. In addition, the nonlinearity of the solubility at −77.2° C. might be explained by effects such as hydrogen bonding between HF and NF_3 or, more likely, interaction of NF_3 with itself at a temperature below critical.

The solubility of O_2 in HF at two temperatures is shown in Figure 4. The Henry's law constants are $k = 3.47 \times 10^3$ at 19.8° C. and 3.32×10^3 at −0.21° C. for the expression $p = km$, where k has the units (centimeters)(grams × 10^3)(mole^{-1}). Using these data and the van't Hoff expression, the heat of solution of O_2 in HF is calculated as −352 cal. mole^{-1}.

The solubilities of O_2 and F_2 in HF are similar at −0.21° and 19.8° C. Because the solubility of O_2 was derived from single point determinations and not studied at other temperatures, no conclusions as to the existence of a solubility minimum similar to that observed for F_2 can be made. If a solubility minimum does occur in the temperature range studied, a serious error would be included in the heat of solution value reported above. It is therefore unlikely that oxygen solubility at other temperatures can be estimated reliably from the data presented in this work.

Table IV. Fluorine k Values

	t, ° C.	$k \times 10^{-4}$
1.	19.8	0.352
2.	−0.21	0.347
3.	−23.2	0.308
4.	−65.2	0.255
5.	−77.2	0.227

Table V. Nitrogen Trifluoride k Values

	t, ° C.	$k \times 10^{-4}$
1.	19.8	0.184
2.	−0.21	0.150
3.	−77.2	0.0477

A comparison of the solubility of O_2 in HF and H_2O (*2*) shows that O_2 is less soluble in H_2O by factors of 5 and 10 at 19.8° and −0.21° C., respectively.

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