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VAPOR PRESSURE STUDIES OF THE HYDROGEN FLUORIDE-ANTIMONY PENTAFLUORIDE SYSTEM

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SUMMARY

Vapor pressure data are reported for the hydrogen fluoride-antimony pentafluoride binary liquid system over the full compositional range (0 - 100 mole % SbF_5) and temperature range (233 - 293 K) commonly used in reaction chemistry of this superacid system.

INTRODUCTION

The enormous enhancement of hydrogen fluoride acidity when mixed with antimony pentafluoride has led to numerous studies with this superacid system [1-3]. Vapor pressure studies of pure SbF_5 [4,5] and pure HF [6-8] have been reported as have conductivity, Raman [9] and infrared [10] studies of SbF_5/HF solutions. However, reports of SbF_5/HF vapor pressure data and/or phase diagrams are fragmentary and limited in most cases to temperatures above ambient [11-13]. In this paper we report vapor pressure data over the full compositional range (0 - 100 mole % SbF_5) and the temperature range 233 - 293 K commonly used in reaction chemistry of this superacid system.

RESULTS AND DISCUSSION

Figure 1 presents the experimental vapor pressure data graphically. Because of the low vapor pressures at the lower temperatures, our data are most accurate above 230 K. Agreement is good between pure HF vapor pressure curves which we determined and similar data previously reported [4-8,12]. Extrapolation of the published SbF_5/HF solution data (10 mole % SbF_5, 313 - 353 K) to our temperature regime also gives satisfactory agreement [12,13]. Extrapolation of our data at various compositions thus might give reasonable vapor pressure values at temperatures modestly above ambient.

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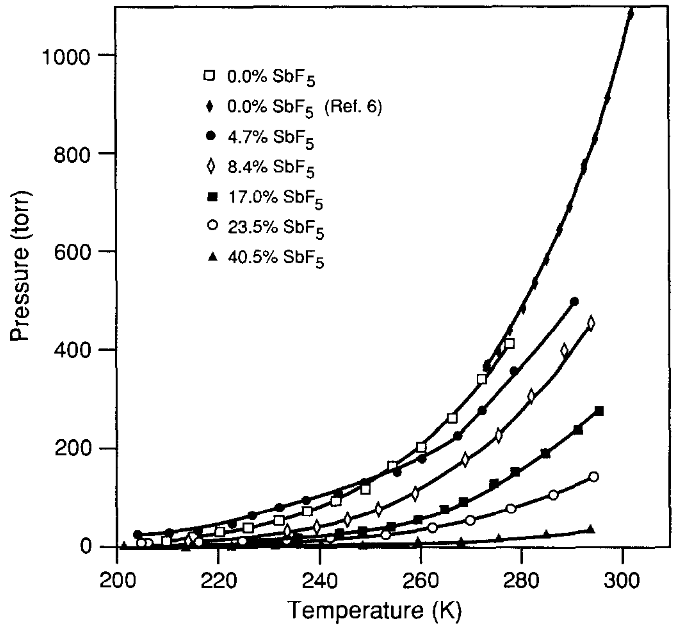

Fig. 1. Typical plots of vapor pressure *vs.*temperature and fitted polynomial curves for various SbF_5/HF compositions.

The experimentally derived data as well as the literature reports of pure HF and pure SbF_5 vapor pressures were fitted to third-order polynomial equations (Table 1, Figure 1). Since the pure HF data could not be fitted satisfactorily with a single third-order polynomial over the entire vapor pressure range, separate fits were performed for experimental data above ambient temperature [6] and below ambient temperature. Reference 7 gives an exponential expression for the vapor pressure of pure HF. A curve was generated from this equation and fits well with a third-order polynomial over the temperature range 233 - 293 K. The fits are within experimental error. The difficulty in fitting the pure HF experimental curves over the full range of temperatures with a single polynomial is due to inherent difficulties in using such a simple mathematical model over the wide pressure range and to the highly nonideal gas phase behavior of HF at moderate and high pressures.

As is well known, SbF_5/HF solutions exhibit behavior far from ideal due to formation of complex fluoroantimonate anions [1-3]. Based upon the derived polynomial expressions, it is possible to calculate vapor pressures for specific concentrations at various temperatures (Table 2, Figure 2) and to fit each curve to simple mathematical expressions. Both polynomial and exponential fits were carried out, but more satisfactory results were obtained with the latter (Table 3). As can be seen there is some scatter for the calculated points primarily due to sizable percentage errors at low vapor pressures but fits of experimental data to the calculated curves are reasonable.

TABLE 1

Coefficients from third order polynomial fits to experimental vapor pressure - temperature plots at various SbF_5/HF compositions. P(torr) = $a + bT + cT^2 + dT^3$ (T in degrees Kelvin)

Mole % SbF_5	a	b	c	d x 10^4
0.0§	-54170.	629.1440	-2.4679	32.781
0.0*	-14069.	192.5677	-0.8842	13.641
0.0**	-12818.	174.8008	-0.8009	12.351
4.7	-8464.62	114.4805	-0.5210	8.023
8.4	-7302.97	101.7167	-0.4746	7.429
17.0	-2104.39	34.9204	-0.1853	3.191
23.5	-2862.05	39.1901	-0.1791	2.737
40.5	-1020.62	13.7744	-0.0618	0.924
100.0‡	-768.60	9.0552	-0.035517	0.46428

§ Experimental data from Reference 6. Applicable to temperatures above ambient.

* Not plotted in Figure 1. Vapor pressure curve calculated from the functional relation given in Reference 7.

** Applicable to temperatures below ambient.

‡ Data from Reference 4.

TABLE 2

Vapor pressures (torr) calculated from the derived polynomial fits (Table 1) at selected temperatures as a function of mole % SbF_5

Mole % SbF_5	293 K	273 K	253 K	233 K
0.0§	758.98	353.78	——	——
0.0*	756.89	356.99	145.07	50.90
0.0	709.34	342.20	143.35	53.54
4.7	531.70	282.88	142.93	73.33
8.4	442.81	209.58	83.41	28.65
17.0	246.03	111.20	37.20	8.72
23.5	129.68	57.52	21.41	8.21
40.5	34.02	13.91	4.90	2.55
100.0‡	3.31	1.07	0.83	0.36

§ Experimental data from Reference 6.

* Pressures calculated from exponential functions given in Reference 7.

‡ Experimental data from Reference 4.

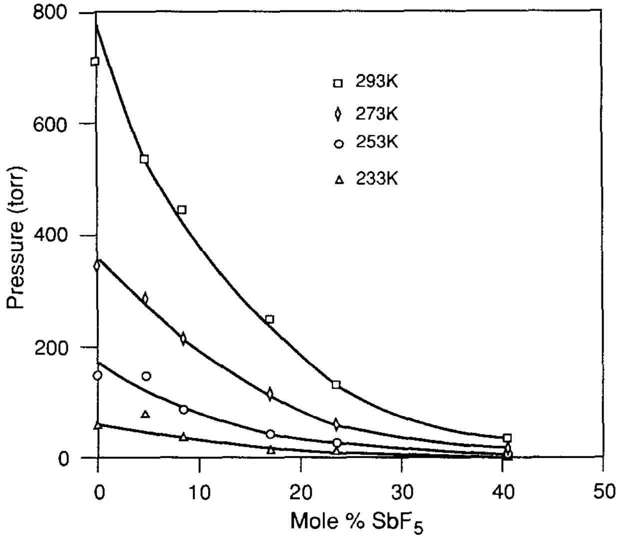

Fig. 2. Plots of vapor pressure *vs* SbF_5/HF composition at various temperatures from calculated data in Table 2 fitted with exponential curves.

TABLE 3

Coefficients from exponential fits of data in Table 2. P(torr) = $a \cdot 10^{(b \cdot x)}$ (x in mole % SbF_5)

Temperature (K)	a	b x 100
293	783.52	- 3.3004
273	394.66	- 3.5295
253	171.94	- 3.8135
233	60.89	- 3.5996

EXPERIMENTAL

Vacuum manipulations employed a Monel/stainless steel and FEP™/PFA™ fluoropolymer vacuum manifold operating at a nominal vacuum of less than ten mtorr. Antimony pentafluoride (Allied Chemicals Corp.) was purified by vacuum distillation. Hydrogen fluoride was dried by prolonged exposure to elemental fluorine and K_2NiF_6, followed by vacuum distillation. Because of the extreme corrosiveness of SbF_5/HF solutions to common metals of construction, transfers

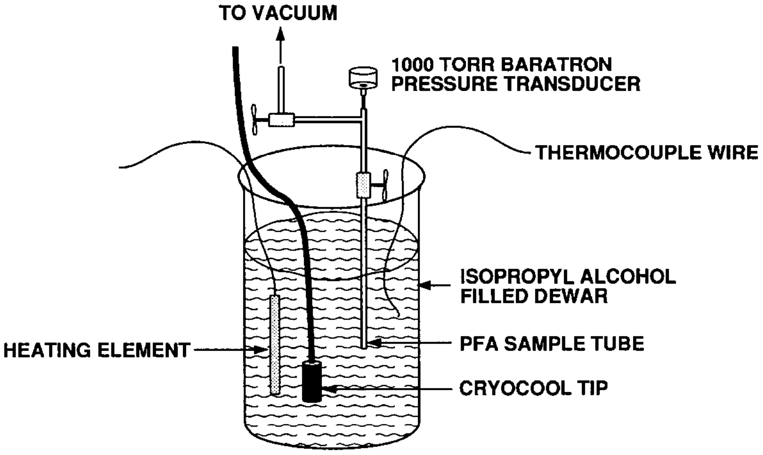

Fig. 3. Schematic of apparatus used for SbF_5/HF vapor pressure measurements.

were made so that contact of liquids with metallic portions of the vacuum system were avoided. Likewise the vapor pressure measurement system (Figure 3) was constructed so that liquid-metal contact did not occur.

The liquid sample tube itself consisted of 3/8" PFA tubing which had been heat sealed at one end. Pressures were measured with MKS Baratron™ pressure transducers that were attached to the uppermost portion of the pressure measurement apparatus and which could be isolated by a valve from the bulk of the system when desired. The precision of the pressure measurements was estimated to be ± 0.2 torr at relatively low pressures (less than 10 torr) and ± 0.5 torr at high pressures (up to 800 torr). The temperature of the liquid SbF_5/HF sample was controlled by immersion of the PFA sample tube in an isopropyl alcohol bath with the temperature controlled by a Neslab Cryocool immersion cooler equipped with a Neslab Exatrol temperature controller. Solutions of desired composition were prepared in the valved PFA sample tube by consecutive vacuum transfers of SbF_5 and HF, with detachment and weighing of the tube between transfers. The tube was attached to the vapor pressure measurement system and cooled to the desired temperature after connecting linkages were evacuated. The apparatus was then closed off to the vacuum and the valve connecting the pressure transducer to the SbF_5/HF solution was opened. Temperature and pressure readings were made at intervals of 3 - 5 minutes until the system stabilized. The temperature was raised in 5 - 10 K increments and new readings were taken until the entire temperature range had been covered. Duplicate runs and cooling cycles were also used to ensure that equilibrium had been achieved and to check reproducibility. At the end of a run with a particular composition, the tube was disconnected, emptied and cleaned, and reloaded with a new SbF_5/HF composition. The vapor pressure measurements were then repeated as described above.

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