Proceedings of the Indiana Academy of Science
(1987) Volume 97 p. 219-222.

Evolution of Water Vapor from Complex Solutions of Concentrated Acids

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Introduction

In the commercial production of phosphoric acid from phosphate ore and sulfuric acid, various silico-fluorides are produced (1,3,7). Vapor phase recovery of the volatile silico-flourides presents an opportunity to obtain several compounds of significant commercial value, including high purity silicon, silicon tetrafluoride and hydroflouric acid (4,6,8). At present, the only one of these potential by-products recovered commercially is fluosilicic acid (2). A question central to the development of recovery processes, for other by-products, is the equilibrium of the vapor phase composition above process streams of interest. These have not been previously reported.

A major difficulty in the investigation of these systems is the highly corrosive nature of the liquid and the gas phases. Fourier transform infrared spectroscopy (FTIR) was used to follow the vapor pressure of the key species of interest over a liquid which simulated a commercial process stream. FTIR provides a convenient, non-invasive means of investigating the vapor phase composition.

Among the key species of interest is water vapor. Dühring's Rule, an empirical method to reduce the number of measurements needed to determine the temperature dependence of vapor pressure, was reported over a century ago (5). However, it does not apply to systems with more than one volatile species and there is no evidence that it can be relied upon to describe the system of mixed acids of interest. Accordingly, it was necessary to determine the vapor pressure of water as a function of temperature for the single solution composition targeted for the recovery process and to use these data to test the applicability of Dühring's Rule for our system.

Materials and Methods

A specially designed gas-tight cell was constructed to contain both the liquid and the gas phase. All portions of the cell contacting either phase were constructed of polytetrafluoro ethylene (PTFE). The cell was fitted with an external heater controlled by a Digitech 2770A controller with the control thermocouple along the exterior of the cell. The temperature of the gas phase was measured by a PTFE coated thermocouple placed in the cell head space. The basic cell construction is shown in Figure 1.

The bottom one third of the cell windows was obscured with PTFE tape to prevent the spectrometer beam from encountering the liquid phase in the cell and to protect the windows from contact with the liquid phase. The cell windows used were zinc selenide. Sodium chloride windows can also be used but they must be kept at or above the cell temperature to prevent condensation and resulting erosion of the windows.

The simulated process stream mixture was made from ACS reagent grade phosphoric acid, sulfuric acid, hydrofluoric acid, high purity precipitated silica, and deionized water. To prevent the loss of volatile species during mixing after addition of sulfuric acid, and during storage, the mixture was cooled below O °C whenever not in a closed container.

Each experiment began with the cell at ambient temperature. The cell was purged with ultra-high purity helium while monitoring the water and carbon dioxide peaks until they stabilized. At that point the background spectrum was taken and the cell was charged with 2 ml of the simulated process mixture. FTIR spectra were collected at about 2 minute

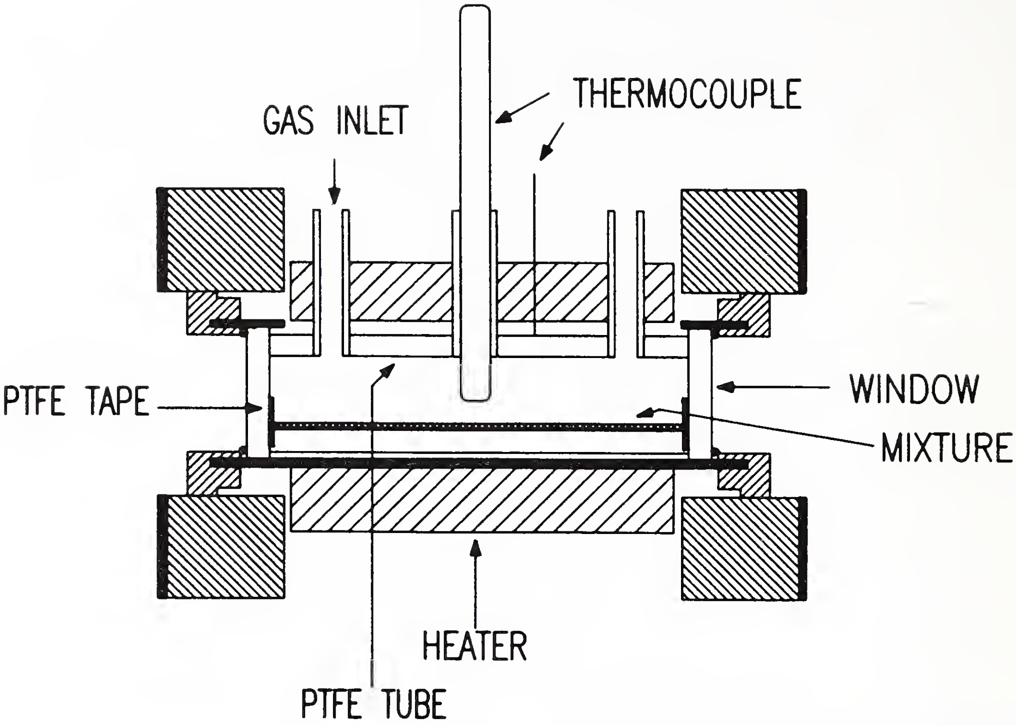

FIGURE 1. Heated FTIR sample cell in cross section. The optical path is in the plane of the drawing from right to left.

intervals while the temperature of the cell was increased to 100 °C at 0.5 °C per minute. The temperature differential between the exterior cell wall and the vapor phase was about 2 °C during the heating cycle.

FTIR spectra were collected using a Nicolet 170SX spectrometer at 4 cm^{-1} resolution. The spectra from sample measurements were ratioed to a spectrum taken through the empty cell, thus effecting an optical null. The integrated area of the spectral region from 1850 to 1240 cm^{-1} was used to measure the water vapor concentration of the vapor phase.

Results

The cell constant for water vapor concentration was determined using deionized water over the temperature range from 32 °C to 100 °C. The constant, 1.17, was determined by plotting the log of the integrated absorbance versus the log of published vapor pressure data. This calibration was checked using a mixture of 75.5% sulfuric acid in water. Figure 2 shows good agreement between measured and published values (9).

The vapor pressure of water above a simulated process stream containing 42% H_2SO_4, 16% H_3PO_4, 1% HF, and 0.5% SiO_2 is shown on a Dühring plot in Figure 3. In this representation of the data, the abcissa is the temperature of the mixture and the ordinate is the temperature at which a reference liquid (water in this instance) has the same vapor pressure as the mixture. If the mixture follows Dühring's Rule, the vapor pressure as a function of temperature may be determined from a plot of two measurements made at different temperatures and the points will fall on a straight line. Figure 3 shows that Dühring's Rule applies with reasonable precision to the water vapor pressure above the mixed acid system. The infrared spectrum of the process stream clearly displays volatile

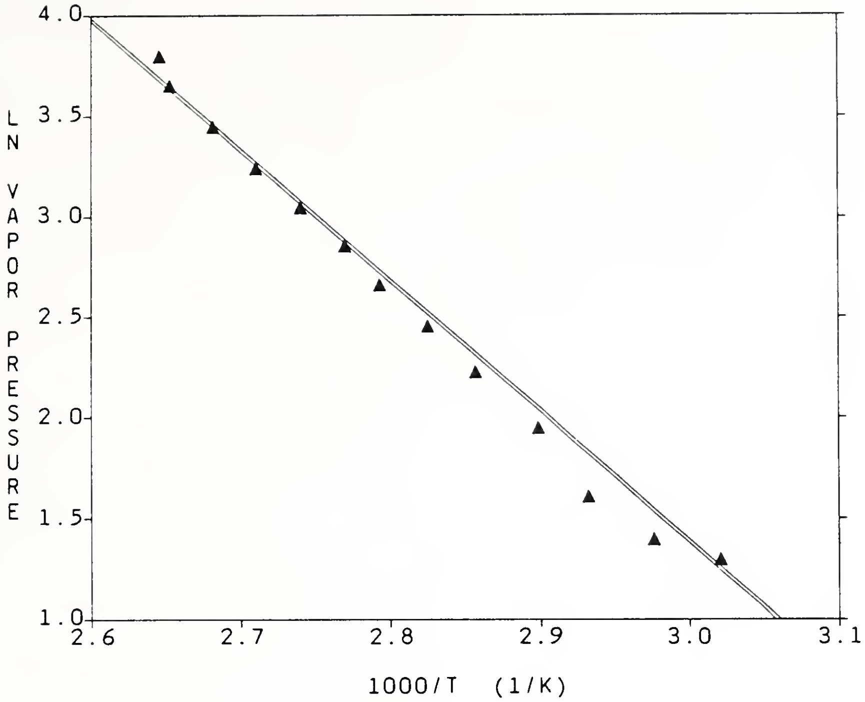

FIGURE 2. Water vapor pressure above a 75.5 percent solution of sulfuric acid: points represent measured values, the line represents published values (9).

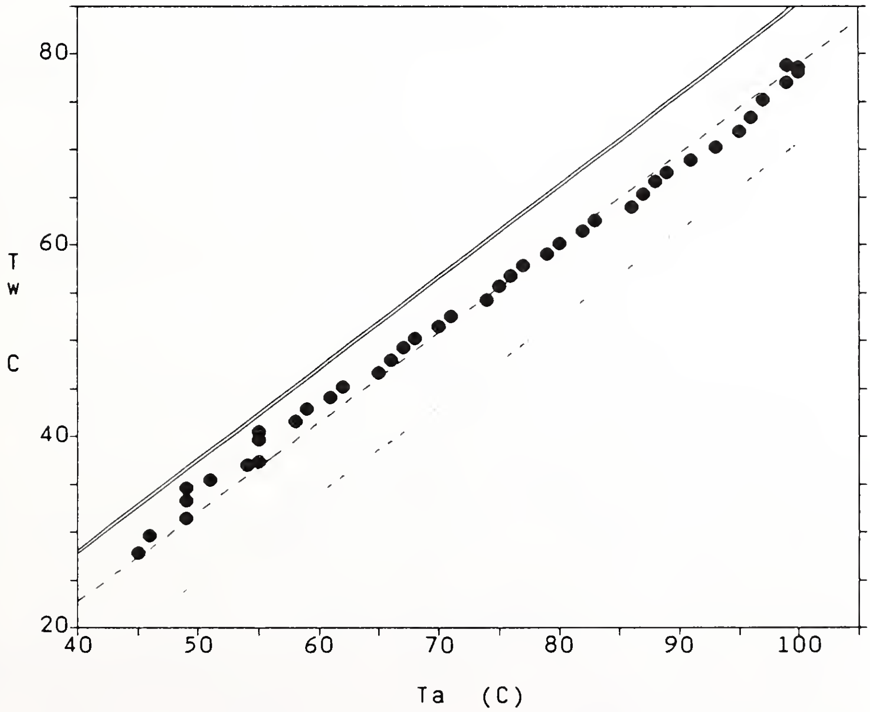

FIGURE 3. Dühring plot of the vapor pressure of water above an aqueous mixture containing 42% sulfuric acid, 16% phosphoric acid, 1% silicon dioxide, and 0.5% hydrogen fluoride: solid line—published values for 42% sulfuric acid, dotted line—published values for 56% sulfuric acid, dashed line—published values for 49% sulfuric acid (9).

species in addition to water. There is a large peak due to SiF_4 and a small peak which has not been identified but is consistent with HF.

For practical purposes, it would be convenient to be able to estimate the vapor pressure of mixtures having compositions similar to the one tested. The lines in Figure 3 represent published data for the vapor pressure of aqueous sulfuric acid solutions. The upper line is for sulfuric acid at the same concentration as the synthetic mixture. The lower line is equal in concentration to the sum of sulfuric and phosphoric acids. An effective sulfuric acid concentration of the mix may be determined by recalculating the sulfuric acid normalized by ignoring the phosphoric acid. The center line is calculated using the effective sulfuric acid concentration. The free energy, enthalpy, and entropy of evaporation are all the same as those of pure water, within experimental error (5%).

Discussion

The heated PTFE cell provides a satisfactory means of measuring the vapor pressure of water over highly corrosive liquids. These data are sufficient to permit systematic design of processes for recovering high-purity silico-fluorides from the production of phosphoric acid. The mixed acid system studied obeys Dühring's rule. Thus, simplifying the determination of water vapor pressure above the condensed phase as a function of temperature. For the mixed acid system, with about 40% sulfuric acid and less than about 20% phosphoric acid, the vapor pressure can be described by the published data for the effective sulfuric acid concentration, normalized by ignoring the phosphoric acid. Energy requirements for water evaporation in the recovery of fluoro-silicates can be calculated from data for pure water. Additional work which would assist development of recovery processes includes; measurement of the vapor pressure of actual process streams, identification of other volatile species, and quantitation of silicon and fluorine containing species.

Acknowledgment

Jerome L. Martin contributed to analysis of experimental results and suggested application of Dühring's Rule.

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