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Laboratory Studies of $\text{HNO}_3/\text{H}_2\text{O}$ Mixtures at Low Temperatures

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The possibility of stratospheric HNO_3 condensing out of the gas-phase at low temperatures has become important in the chemical explanations of the rapid loss of antarctic ozone in spring. Consequently, knowledge about the behavior of the vapor pressures of H_2O and HNO_3 over $\text{HNO}_3/\text{H}_2\text{O}$ mixtures at stratospheric temperatures is needed to determine if HNO_3 could condense, and by how much the HNO_3 vapor pressure could be depressed.

This paper describes laboratory investigations of vapor pressures above $\text{HNO}_3/\text{H}_2\text{O}$ mixtures. Vapor pressures were initially measured over liquid and frozen bulk mixtures contained in a glass still which was attached to a stainless steel vacuum chamber. The total pressure in the chamber was monitored with a precision pressure sensor, and the vapor pressures of HNO_3 , H_2O and impurities were analyzed with a mass spectrometer-beam system (1).

In a second set of experiments vapor deposits were made to produce ice and the mono- and trihydrate of HNO_3 .

Temperatures of liquid and frozen $\text{HNO}_3/\text{H}_2\text{O}$ bulk mixtures were varied from 200 to 260 K. The measured vapor pressures of HNO_3 and H_2O are in fairly good agreement with Clavelin and Mirabel's vapor pressure data (2) when extrapolated toward lower temperatures. For partially frozen bulk mixtures, the three phase equilibria solid/liquid/vapor and for frozen mixture trihydrate/monohydrate/vapor and trihydrate/ice/vapor were also investigated. These all resulted in one vapor pressure curve for both H_2O

and HNO_3 as expected from binary mixtures. The measured pressures for the freezing envelope (solid/liquid/vapor) were in close agreement with data obtained from freezing temperatures (3) and Clavelin and Mirabel's data (2).

Vapor deposits to form the trihydrate are initially made by establishing a 3-to-1 $\text{H}_2\text{O}/\text{HNO}_3$ gas mixtures in the vacuum chamber and rapidly cooling the glass still. Initially a thin, amorphous film over the whole glass surface is formed, which then changes to small crystalline structures. HNO_3 and H_2O vapor pressures have been determined for temperatures between 190 and 205 K. In addition, studies of the relevant solid/solid/vapor three-phase equilibria were again performed using vapor deposition to form the condensed phases. The ice/trihydrate/vapor equilibrium pressures were measured up to the eutectic temperatures of 230 K and a better determination of the HNO_3 pressure has been made. The H_2O pressure was essentially that of ice which was also found during bulk measurements. The trihydrate/monohydrate/vapor equilibrium was studied from 190 to 200 K and the vapor pressures were in general agreement with those measured over frozen bulk mixtures. As expected, the vapor pressures over the trihydrate lay in the region between these two three-phase equilibria and the H_2O and HNO_3 pressures over the trihydrate were seen to be well correlated.

From these data it can be concluded that the lower stratosphere becomes saturated with respect to the trihydrate about 5 K above the ice-saturation point. A strong temperature-dependence of the HNO_3 pressure over the trihydrate can also be demonstrated. As the temperature is lowered by 3 degrees and the H_2O pressure is kept constant, the equilibrium HNO_3 pressure over the trihydrate is lowered by a factor between 5 and 9. For comparison,

the HNO_3 pressure over the ice/trihydrate/vapor equilibrium is lowered by a factor of approximately 2 after a 3 degree cooling. This temperature dependence could lead to a wide variation in the local HNO_3 pressure and consequently to localized ozone destruction.

References

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