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An Implication of a Model of Ammonia-Sulfur Dioxide Reactions to the Atmosphere

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A laboratory study of gas phase reactions between ammonia and sulfur dioxide, reported by Scott *et al.* (1969), suggested that the resulting solid products may be stable under conditions that prevail in the lower stratosphere and, thereby, that such reactions may be of importance to the formation of the stratospheric aerosol layer. The stability of the products was determined by measuring their equilibrium vapor pressures. These pressures were found to be dependent on the composition of the products and to form a family of curves when plotted against temperature. To explain this result, a thermodynamic model was developed by Scott and Lamb (1970) which fits the vapor pressure data and gives further insight into the nature of the chemical interactions. The assumptions of the model are that compounds which have $\text{NH}_3\text{-SO}_2$ stoichiometric ratios of only 1:1 and 2:1 are formed reversibly from the component vapors at temperatures $< 10\text{C}$ and that the two condensed compounds form an ideal solution. The first assumption is consistent with results reported by others (see, for example, Badar-ud-Din and Aslam, 1953).

The model clearly shows that the enthalpies of formation of the two compounds cannot be identified simply with the slopes of the vapor pressure curves plotted on a van't Hoff plot. Hence, the enthalpies reported by Scott *et al.* (1969) are incorrect. The theoretical analysis (Scott and Lamb, 1970) indicates that the enthalpies of formation should be 62.2 and

32.2 kcal mole⁻¹ for the 2:1 and 1:1 compounds, respectively.

Under the experimental conditions of Scott *et al.* the solid product resulting from a particular experiment was of particular composition; that is, the relative amount of each compound in the product was constant throughout the run. In the atmosphere, on the other hand, it is a better approximation to assume that the mole fraction y of NH_3 in the vapor phase is constant. The thermodynamic model then predicts a family of curves which forms a trough when y is taken parametrically as the third dimension. Representations in which the composition of the solid and the composition of the vapor are independently constant are depicted in Scott and Lamb.

Considering now constant *temperature* sections of the trough formed by the constant y curves, one obtains the family of curves shown in Fig. 1. Each of the three curves represents the total equilibrium vapor pressure over the reaction products assumed to obey the thermodynamic model at the given constant temperature. The numbers shown along the sides of the curves give the values of y which apply at the extremes of the curves. This way of viewing the predicted dependence of the vapor pressure on the mole fraction of NH_3 in the vapor phase and temperature emphasizes the existence of a broad trough. It can be seen that the presence of a great excess of either reactant in the vapor phase, NH_3 or SO_2 , results in a high vapor pressure and a high

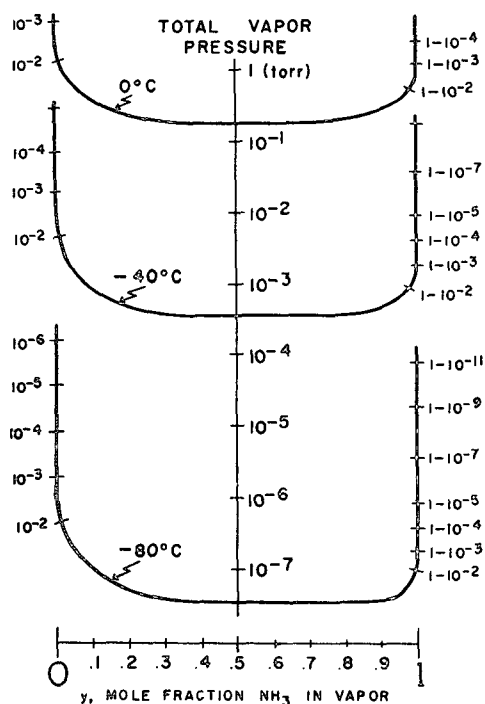


FIG. 1. The total equilibrium vapor pressure above solid products of $\text{NH}_3\text{-SO}_2$ reactions as a function of vapor composition y (calculated from the model of Scott and Lamb, 1970).

probability of evaporation. This very effect may, in fact, have been observed by Bricard *et al.* (1969) when they noted that the concentration of aerosol in their chamber decreased with the addition of NH_3 . In the atmosphere, however, it is likely that the mole fractions of NH_3 and SO_2 are comparable in magnitude and, as a result, that the vapor pressure over the products of reaction will be minimal. The mole fraction of NH_3 in the vapor phase can vary widely and still enable compounds with reasonable thermodynamic stability to form.

From this model one sees that total vapor pressures on the order of 10^{-7} torr are to be expected at the -70 to -80°C temperatures generally found in the lower stratosphere. This corresponds to a mixing ratio with air of roughly 10^{-9} . Although no direct measurements of NH_3 or SO_2 concentrations have yet been made in the lower stratosphere, such concentrations are close to values expected on the basis of measurements made in the troposphere, for instance, by Georgii and Jost (1964). Thus, given the proper atmospheric conditions of low temperature and comparably high concentrations of NH_3 and SO_2 , the reaction products may condense onto suitable nuclei in a process analogous to ordinary cloud formation. Since a temperature minimum is often found at or just above the tropopause, it is possible that direct reactions between NH_3 and SO_2 may be important to the formation of the sulfate layer.

The extension of these thermodynamic results to the formation of aerosols in the atmosphere is not likely to be so straightforward, however, since the experiments of Scott *et al.* (1969) and the model of Scott and Lamb (1970) were concerned with a relatively pure system and since little is known of the reaction kinetics. The real atmosphere contains many substances, of course, which may well interact with the $\text{NH}_3\text{-SO}_2$ reactions. Two constituents of particular interest in this respect are water vapor and atomic oxygen. Water vapor has been shown to enhance the rate of reaction, at least near room temperature where the anhydrous reactions proceed only slowly, if at all (see Divers and Ogawa, 1900), and ground state atomic oxygen seems to react readily with SO_2 , particularly in the stratosphere where the concentration of atomic oxygen is high (Cadle and Powers, 1966). The main effect of $\text{SO}_2\text{-O}$ reactions acting simultaneously in the lower stratosphere would be to deplete the supply of SO_2 available to the $\text{NH}_3\text{-SO}_2$ reaction. Without some measurements of at least the rate of reaction between NH_3 and SO_2 , however, little more can be said on the relative effectiveness of these two reactions. Nevertheless, the direct reaction of NH_3 with SO_2 should be considered as a potentially important reaction in view of the relatively high abundance of these two trace gases in the atmosphere.

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