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Freezing points of H_2SO_4 aqueous solutions and formation of stratospheric ice clouds

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ABSTRACT

The freezing temperature of H_2SO_4 aqueous solutions as a function of concentration was experimentally measured in an investigation of the ice nucleation of natural H_2SO_4 mixed aerosols. Based on these measurements, it is suggested that the formation of ice crystals in cirrus and polar stratospheric clouds is the result of the condensation of water vapor and subsequent freezing of natural H_2SO_4 aerosols.

1. Introduction

Sulfuric acid aqueous solutions are currently receiving much attention because they have a profound effect on the formation of polar stratospheric clouds, which are important in the ozone depletion cycle. Since sulfuric acid particles are strongly hygroscopic, they can act as condensation nuclei for cloud droplets (Ohtake, 1983; Shaw, 1989) and as subsequent freezing nuclei for atmospheric ice crystals (Ohtake, 1984). Because of the great importance of these processes in atmospheric physics, we made measurements to determine the freezing points of sulfuric acid solutions. Previous tabulations of the freezing temperatures of H_2SO_4 given in the Chemical Engineers' Handbook (Perry, 1963) seemed to be at variance with our observations; for instance, it was claimed (with no reference given) that the freezing point of an H_2SO_4 solution at 100% concentration was 10°C while we never observed such solutions to freeze.

Gable et al. (1950) have reported measurements of phase equilibrium points of H_2SO_4. These phase equilibria are often assumed to represent both freezing and melting points for common substances. Since Gable's experiments were so carefully controlled, no later measurements have been reported. However, we found Gable's phase equilibrium points to be melting points for H_2SO_4 and unlikely to be applicable to nucleation temperatures of natural H_2SO_4 droplets. In this paper, we report new preliminary measurements on the freezing points of bulk aqueous solutions of H_2SO_4 and discuss the significance of these results with respect to the nucleation processes in polar stratospheric clouds.

2. Measurements of freezing temperatures of H_2SO_4 aqueous solutions

Sulfuric acid solutions were prepared by diluting 98% reagent grade H_2SO_4 with distilled water utilizing a Brinkmann macro-transferpettor, which was accurately calibrated prior to preparation of the solutions. Samples of approximately 10 ml of solution were placed in test tubes 16 mm in diameter and 15 cm long. The tubes were sealed with polyethylene stoppers to minimize any further dilution of the acid concentration by water absorbed from the room air. The measurements were made in a room at normal temperature and standard atmospheric pressure. The tubes containing the test acid solutions were immersed into a low-temperature methanol or ethanol bath which was usually controlled to about 5°C lower than the expected freezing point. The cooling rate was nominally 1°C/min. Temperatures were monitored with a thermocouple dipped into the solutions, following the procedure of Gable et al. (1950).

The solution was agitated before each measure-

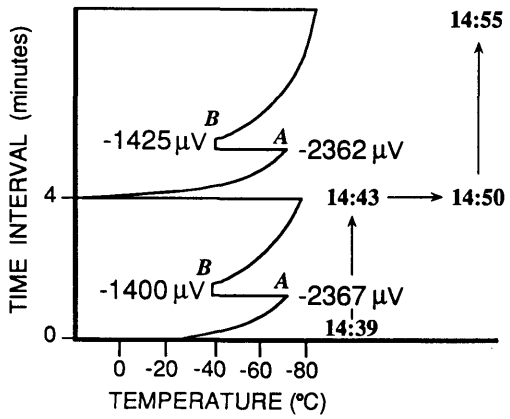

Fig. 1. A mode of temperature change with time of H_2SO_4 solution with concentration of 60% by weight. The freezing points are indicated A and the melting points are indicated B. The record shows 3 repeated trials for the sample.

ment of the freezing point. Since frost on the tube walls tended to seed premature freezing of the solution, the tube was kept still except when checked for the occurrence of freezing. The undisturbed condition of the solution in the tube was also a simulation of the process occurring in natural cloud drops. "Freezing point" in this experiment refers to the temperature of the solution when freezing of any part of the mixture was noticed. The visible sign of freezing was usually a white embryo in the solution. A typical record of temperature measurements in continuous cooling is shown in Fig. 1. The figure, which indicates temperature change with time, shows that once freezing started in this sample, the temperature rose rapidly to the melting point and remained there until the sample froze completely. Cooling then resumed and the temperature continued to drop.

Early measurements experienced problems with erroneous high freezing point readings. These may have been due to solution contamination. In our later measurements, precautions were taken to eliminate contamination.

3. Results of measurements

The results of the freezing point measurements are shown in Fig. 2. The measured freezing points depart substantially from the Gable melting point data for concentrations of H_2SO_4 greater than about 37.5% by weight. Although this finding was unexpected, we believe it to be valid; repeating the measurement of freezing points of H_2SO_4 aqueous solutions produced consistent results.

The modes of temperature change and shape of the frozen part of the solution varied with acid concentration. Solutions of less than 15% concentration froze quickly and completely after reaching the temperature indicated in Fig. 2. The shape of the forming crystal could not be distinguished because of the rapidity of the freezing.

Solutions of H_2SO_4 concentration between 30% and 40% by weight started to freeze in the shape of hexagonal solid thick plates. The crystals grew slowly, thereby making it difficult to determine the freezing point very accurately. An example of a nucleated-out freezing crystal is shown in Fig. 3. The changes of freezing shape with concentration of H_2SO_4 are similar to those of snow crystals changing with air temperature and moisture supply (Magono and Lee, 1966). The temperature did not rise sharply, which meant the difference between the melting points and the freezing points were not very distinguishable. In this concentration range, our measured freezing points nearly agreed with the melting points reported by Gable et al. (1950).

The solutions with concentrations between 40% and 52.5% by weight started freezing most frequently at the tip of the thermocouple, and always developed 3-dimensional white clusters with nearly sharp hexagonal ends, similar to the shape of a sea urchin. An example is shown in Fig. 4. In this concentration range, once the freezing had started, the temperature rose quickly up to the melting point and stayed there for a short time. The crystal grew rapidly. The temperature then dropped to that of the surrounding coolant which was colder than the freezing point of the solution. The measured freezing temperatures of solutions above 37.5% depart significantly from Gable's phase equilibrium points, as can be seen in Fig. 2.

The solutions between about 50% and 62.5% started freezing at the thermocouple weld point in either a planar crystal shape or distorted cubic to rhombic shape block, and grew to structures that resemble the shape of sea urchins.

All solutions with concentrations higher than 65% remained clear and unfrozen, but became

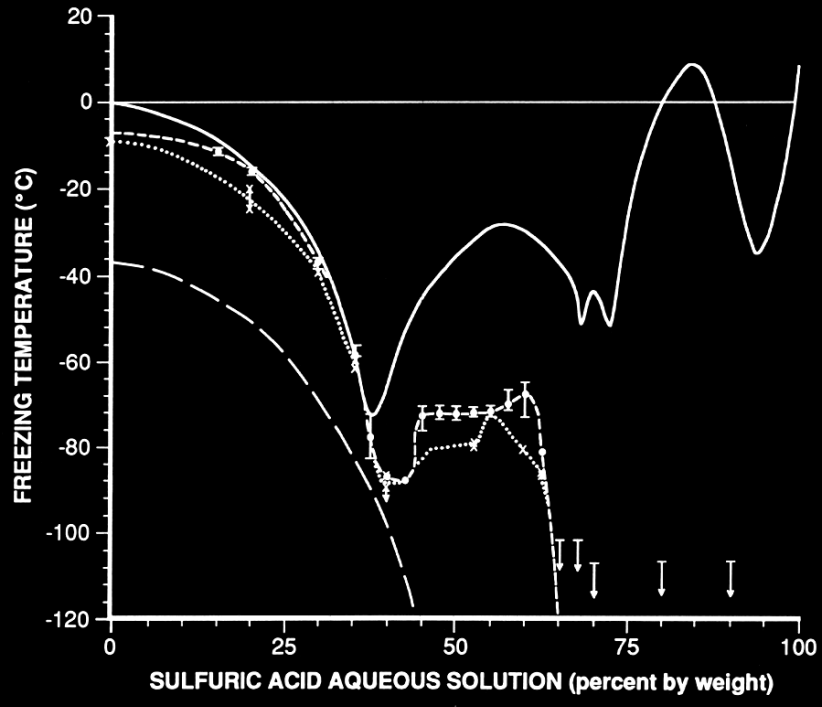

Fig. 2. Freezing points of H_2SO_4 aqueous solutions; solid line indicates the phase equilibrium points given by Gable et al. (1950), vertical bars or dots connecting dashed line indicate present measurements, and dotted line and × marks are the freezing points of H_2SO_4 solutions without immersion of thermocouple. Broken line indicates estimated freezing points of 10 μm diameter H_2SO_4 droplets.

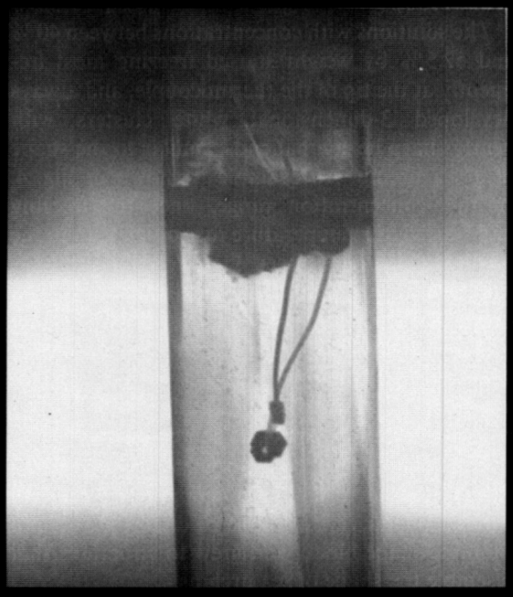

Fig. 3. Frozen crystal appeared in H_2SO_4 35.0% by weight solution.

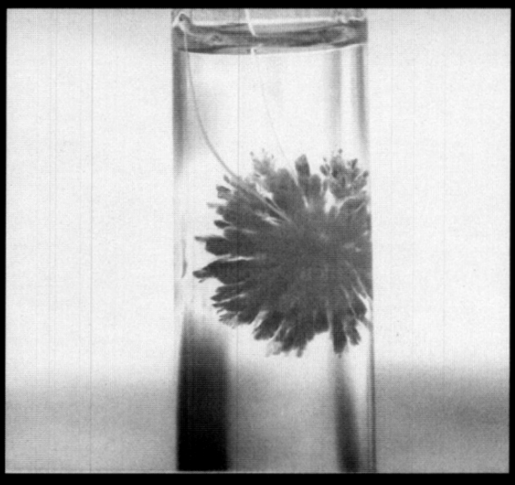

Fig. 4. A sea-urchin shaped crystal in 47.5% H_2SO_4 solution, oriented from the tip of the immersed thermocouple.

viscous by temperatures of $-104°C$ which is the lowest temperature the apparatus could reach. Solutions of 80% and 90% H_2SO_4 also were so viscous that removal of the thermocouple was difficult. The surface of the solution took on an inverse conical shape as shown in Fig. 5.

Although the transformation and characteristics of the test solutions during freezing were not fully investigated, they seemed to depend on the ratio in which the H_2SO_4 and H_2O combined.

Several complications were encountered during this experiment. Immersion of the thermocouple into the solutions affected the freezing points. Additional experiments have been conducted for solutions without immersion of the thermocouple. The thermocouple was attached outside in contact with the test tube. The coolant in the bath was stirred well and the temperature close to the expected freezing points to minimize the rate of cooling and the temperature difference with the sample solution.

The freezing of 0% H_2SO_4 solution (distilled water) occurred instantly at temperatures between $-7.5°C$ and $-7.9°C$. The solution with 20% H_2SO_4 froze at temperatures between $-20.1°C$ and $-25.0°C$. The sample with 30% concentration of H_2SO_4 froze at $-38.5°C$, slightly lower than the freezing temperature with the thermocouple dipped in the solution, but it started to freeze from small hexagonal thin plate dendritic crystals at the middle of the tube and drastically produced a number of small crystals with fine dendritic structure. The 35% solution froze at a temperature between $-59.1°C$ and $-60.9°C$. It started to freeze from a few hexagonal plane dendrites in the middle of the solution, which grew to thick hexagonal plates at the top while the bottom of the solution remained clear and unfrozen. The solution of 40% by weight H_2SO_4 became viscous and started to freeze into a thick cubic crystal at the top of the solution at $-83.8°C$. The crystal grew larger to solidify the solution at the surface, but the solution remained clear at the bottom at $-89.0°C$ when the tube broke with a small audible noise. The other tests for 40% concentration did not freeze even at $-89.0°C$, which was the lowest temperature the apparatus could reach.

The solution of 52.5% by weight H_2SO_4 without the immersed thermocouple started to freeze in a cubic- or rhombic-shaped block at the bottom of the tube at $-78.0°C$ and grew to large assembled narrow parallel planes, which were essentially the same as the "sea urchin" mentioned previously, as shown in Fig. 6. The test sample of 55% H_2SO_4 solution froze at temperatures

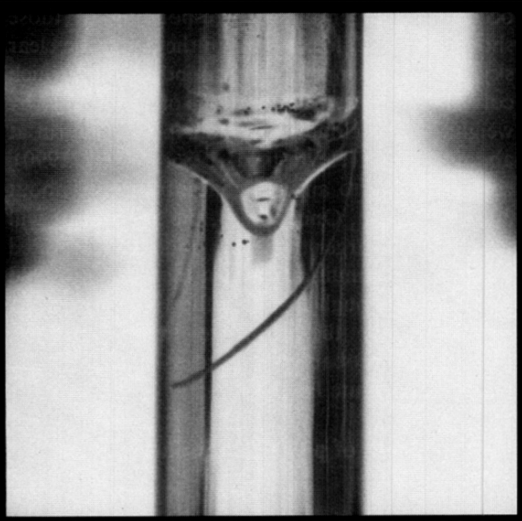

Fig. 5. H_2SO_4 90% solution at $-106.9°C$.

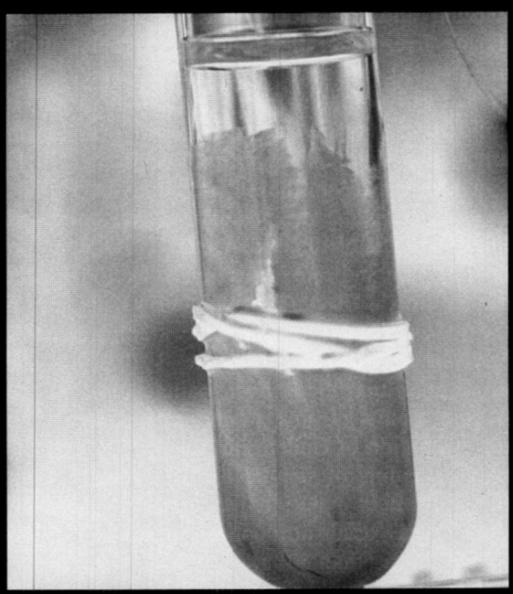

Fig. 6. A sea-urchin shaped crystal in 52.5% H_2SO_4 solution without the immersed thermocouple, oriented from distorted cubic or rhombic block at $-78.0°C$.

between −71.9°C and −72.9°C, which are nearly the same as those with the immersed thermocouple. However, the freezing temperature without thermocouple for 60% H_2SO_4 was −79.4°C, which was about 11°C lower than the freezing points with the thermocouple in the solution; before freezing, the solution became viscous. Similarly, the 62.5% solution froze at −85.2°C to −86.0°C after the solution became very viscous. This temperature with the thermocouple outside the tube was about 8°C lower than temperatures attained by the solution with the immersed thermocouple.

In conclusion, the immersion of the thermocouple in H_2SO_4 solutions was raising the freezing temperatures by 6°C to 11°C. Therefore, our measured freezing temperatures of H_2SO_4 solution using a thermocouple may be somewhat higher than those that would occur in nature as indicated in Fig. 2. The variance of measured points may be due to the probability of freezing H_2O molecules or to some erroneous readings. These freezing points of H_2SO_4 solutions without immersion of a thermocouple are shown in Fig. 2. The freezing habits did not change very much either in crystal shape or temperature history.

The shape of the crystal at the beginning of freezing and the mode of temperature change during freezing of the solutions were not fully investigated. Although this paper is presented only as a report of preliminary measurements, it is anticipated that the major results will not alter in any substantial manner with further work.

A size effect on the supercooling of H_2SO_4 solution droplets was postulated. The estimated freezing points of 10 μm diameter H_2SO_4 solution droplets are indicated tentatively by the longer dashed line in Fig. 2. This estimate was based on the freezing temperature of pure water fog droplets in clean air in ice fog (Ohtake, 1970), with the assumption that the curve remains parallel to the freezing points of bulk solutions and referred to the estimation of Hallett and Lewis (1967). If the freezing points of smaller drops are lower than those of bulk solutions, nucleation at about −80°C may occur at a concentration of 35% by weight, rather than 50%.

The phase equilibria of the SO_3-water system given by Gable et al. (1950) appear to differ substantially from the freezing points of natural H_2SO_4 droplets, which should be applicable to the nucleation temperature in the formation of ice crystals in the free atmosphere.

There is not yet evidence that frozen sulfuric acid droplets can grow to ice crystals in the atmosphere. In order to nucleate H_2SO_4 to a frozen solution, the temperature of the solution should be even slightly lower than the presently measured freezing points. Note that this temperature is neither the equilibrium point nor melting point.

4. Implication of the measurements of the freezing points of H_2SO_4

Sulfuric acid aerosols are always present any place on the earth from the surface up to the stratosphere (Bigg, 1975). At the South Pole, most of the aerosols were identified as pure H_2SO_4 (Ohtake, 1985).

An important conclusion of the present experimental result is that atmospheric ice crystal precipitations, like the diamond dust frequently observed in the Antarctic clear sky (Hogan, 1975; Ohtake, 1975) and cirrus clouds, may result from the freezing of the aerosols. The aqueous H_2SO_4 droplets or some aerosols covered with a film of H_2SO_4 can grow larger and become more dilute by absorbing moisture, even at humidities slightly below ice saturation. As H_2SO_4 solution droplets reach dilution to a certain concentration, according to our measurements, freezing may occur. The freezing of the H_2SO_4 solution droplets occurs at temperatures corresponding to those shown in Fig. 2. Ice crystals in the Antarctic clear sky appear at temperatures around −22°C, which corresponds to H_2SO_4 dilutions of about 20% by weight. Cirrus cloud ice crystals possibly form at about −40°C (Heymsfield, 1986; Sassen, 1990), corresponding to an acid concentration of about 30% by weight. Once frozen, the ice crystals will rapidly grow larger thereafter under ice-saturated water vapor conditions. When the air is not cold and humid enough to dilute the H_2SO_4 solution sufficiently for the drops to freeze, insoluble aerosols are probably involved as nuclei in crystallizing the dilute H_2SO_4.

5. Formation of polar stratospheric cloud particles

Polar stratospheric clouds (PSCs) are known to appear at about 25 km altitude when the air

temperature falls to approximately $-80°C$; temperature is the primary factor in PSC formation (McCormick et al., 1982). They have been found to play an important role in the Cl-catalyzed destruction of the stratospheric ozone layer (Solomon et al., 1986). It has been proposed that PSCs are composed of ice combined with nitric acid trihydrate $HNO_3 \cdot 3H_2O$ (NAT) or HNO_3 particles depending on whether nucleation is homogeneous or heterogeneous, respectively (Steel et al., 1983; Toon et al., 1986).

At 25 km altitude, even though the saturation vapor pressures of H_2O and HNO_3 drop with decreasing air temperature, the vapor pressures of these gases may not be high enough to condense into solid PSC particles without the presence of nuclei, unless the environment is strongly supersaturated. However, the few existing H_2SO_4 droplets at about $-80°C$ will be diluted through the absorption of water vapor as the saturation water vapor pressure decreases. They will grow larger into dilute H_2SO_4 droplets, then freeze, forming H_2SO_4-ice particles. Typically, when the concentration of the H_2SO_4 droplets becomes about 60% by weight, the solution should freeze to form H_2SO_4-ice particles at a temperature between $-75°C$ and $-82°C$ as can be seen in Fig. 2. Since the air temperature stays higher than $-104°C$ throughout the air column aloft, the 65% H_2SO_4 solution will never freeze in the atmosphere. Pueschel et al. (1986) suggested through their Antarctic Ozone Experiment that H_2SO_4 may remain supercooled liquid at around $-80°C$.

Since the surface of the H_2SO_4-ice particles is maintained near ice-saturation by the growth process, water vapor in the surrounding chilled air will readily diffuse onto the ice particle surfaces, where the local vapor density is lower. Nitric acid vapor in the stratosphere may uptake preferably on frozen sulfuric acid solution (Manion and Tolbert, 1991), to grow to the larger cloud particles forming PSCs. On the other hand, pure HNO_3 solution droplets, which freeze at temperatures higher than does H_2SO_4 solution, do not exist at 25 km altitude, and are not very hygroscopic. Therefore, all H_2SO_4 particles will eventually freeze after the air temperature falls sufficiently; then with a sufficient number of frozen ice-H_2SO_4 particles acting as nuclei, there will be strong deposition of water vapor and NAT or HNO_3 gases to form cloud particles. Since most of the H_2SO_4 particles are smaller than 0.1 μm diameter, the final PSC particles may contain an undetectable small fraction of H_2SO_4 compared to its major components of H_2O and HNO_3. It is hypothesized that this leads to the formation of PSCs.

Note added in proof

Since this paper was first submitted for publication, Jensen et al. (1991) published a theoretical determination of freezing temperatures of H_2SO_4 solutions relevant to PSC particle nucleation. As requested by one of the referees, we reviewed this paper and compared it to this one. Their theoretical work had results more realistic to PSC nucleation but they have drawn essentially the same conclusions as in the present paper. Their conclusion that there is no size effect on freezing temperatures of H_2SO_4, however, is not necessarily in agreement with the present paper.

6. Acknowledgements

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