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Deliquescence Properties and Particle Size Change of Hygroscopic Aerosols*

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DISCLAIMER

Abstract

Ambient aerosols frequently contain large proportions of hygroscopic inorganic salts such as sulfates and nitrates, which may induce adverse health effects upon inhalation. The inhaled salt particles are invariably exposed to a humid environment; their deposition along the respiratory tract will necessarily depend upon the size change resulting from water vapor condensation. This paper discusses the deliquescent properties of pure and mixed salt aerosols and the particle size change as a function of relative humidity. Experimental results are presented for the growth of mixed chlorides (NaCl-KCl), mixed sulfates (H_2SO_4-$(NH_4)_2SO_4$), and mixed $(NH_4)_2SO_4$-NH_4NO_3 aerosol systems. It is shown that the behavior of the mixed salt aerosols in a moist atmosphere can be predicted from phase diagrams and pertinent thermodynamic properties of the bulk solutions. The evaporation of a saline droplet in an atmosphere of decreasing humidities is also investigated experimentally. For each deliquescent salt aerosol, there is a threshold humidity below which the solution droplets will quickly evaporate to become crystalline particles. The information is useful in the selection of a suitable humidification procedure to generate test aerosols for exposure studies.

INTRODUCTION

Ambient aerosols frequently contain large proportions of hygroscopic inorganic salts such as chlorides, sulfates, and nitrates, which may induce adverse health effects when inhaled. Thus, in exposure studies employing animal or human subjects, test aerosols are routinely generated from saline solutions of known composition and the observed physiological effects are often correlated not only with the chemical nature, the dosage, but with the particle size[1,2] of the test aerosol as well. Since in most cases the nebulized test aerosol is mixed with a carrier gas before entering the test chamber where the relative humidity may or may not be regulated, the particle size is subject to change as a result of water vapor condensation or evaporation. A knowledge of the hygroscopic properties of salt aerosols, therefore, is essential in estimating particle size variations under either dry or humid conditions.

More important, however, is the fact that inhaled salt particles are always exposed to an environment of high humidity in the respiratory tract, where the particles often deposit. Milburn, et al.[3] have considered the effect of particle rehydration on the retention of hygroscopic dusts in the human lungs. They concluded that, for NaCl particles of initial dry diameter less than 2 μm, rehydration would be most likely to occur in the lungs, resulting in a significant increase in retention.

This paper discusses the deliquescence properties of pure and mixed salt aerosols and the particle size change as a function of relative humidity. Experimental results of the particle growth characteristics are presented for some mixed-salt aerosols of chlorides, sulfates, and nitrates, which are of physiological or environmental importance.

THERMODYNAMIC CONSIDERATIONS

Deliquescence Properties

Most of the inorganic salts exhibit the properties of deliquescence upon exposure to moisture. The phase transition from a solid particle to a saline droplet occurs rather suddenly when the relative humidity reaches a specific value corresponding to the water activity of the saturated solution. Water activity data[4] necessary for determining aerosol deliquescence properties are usually available in the literature for aqueous solutions of single electrolytes. The theory of droplet growth for single-component salt aerosols[5,6,7,8] has been well established on the basis of thermodynamics. It is relatively simple, therefore, to calculate the size of a saline droplet in equilibrium with the water vapor of the surrounding air. The calculation, however, requires extensive thermodynamic properties such as water vapor activity, solution density, and surface tension as a function of droplet composition and temperature. Such information is usually available only for dilute electrolyte solutions.[4,9]

On the other hand, the growth of a mixed-salt aerosol is complicated by the fact that, dependent upon its initial composition, a salt particle may pass through several regions of multi-phase equilibria before its complete dissolution to form a homogeneous solution droplet. Recent thermodynamic considerations[10] have shown that the phase transformation and droplet growth of a mixed-salt aerosol in a moist atmosphere can be understood with reference to the phase diagram of the multicomponent system of interest. Stage-wise phase transformation during growth is often expected and the deliquescence humidity can be predicted from the thermodynamic properties in the solid-liquid coexistence regions.

Consider, for example, the growth characteristics of letovicite aerosols.

Letovicite, $(NH_4)_3H(SO_4)_2$, is a mixed salt composed of 0.75 mole fraction of ammonium sulfate and 0.25 mole fraction of sulfuric acid. Its presence in atmospheric particulates has occasionally been observed and identified by Brosset et al.[11] using x-ray diffraction techniques. Referring to the solubility diagram shown in Fig. 1 for the H_2O-$(NH_4)_2SO_4$-H_2SO_4 system, letovicite in its crystalline state has chemical composition represented by point B on the diagonal line.

Upon exposure to an increasing relative humidity, a solid letovicite particle would take up water with its composition changing along the Line BO. However, since the particle must first pass through the three-phase coexistence region indicated by A+B+ℓ, in which only one degree of freedom is allowed by the phase rule, nothing will then happen until the relative humidity reaches a value of 69.3% corresponding to the water activity of the eutonic point E_1 as shown in the diagram. This is the first deliquescence point for letovicite and all other mixed $(NH_4)_2SO_4$-H_2SO_4 aerosols having initial composition between pure ammonium sulfate and letovicite as represented by the line segment AB. At this deliquescence humidity, the dry salt particle suddently transforms into a partially dissolved solution droplet, thus marking the onset of growth. A second marked growth will occur at 72% r.h. when the line BO crosses the solubility line EE_1, and all of the remaining solid dissolves in the solution at this time.

Figure 2 shows the growth curves calculated for sulfate aerosols $(NH_4)_2SO_4$ NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, and H_2SO_4 at 25°C. While the H_2SO_4 aerosol grows continuously and smoothly with increasing humidity, the $(NH_4)_2SO_4$ aerosol displays the deliquescence property at 79.5% r.h. with a distinct onset of growth. The $(NH_4)_3H(SO_4)_2$ aerosol shows a two-stage growth as dictated by the phase diagram.

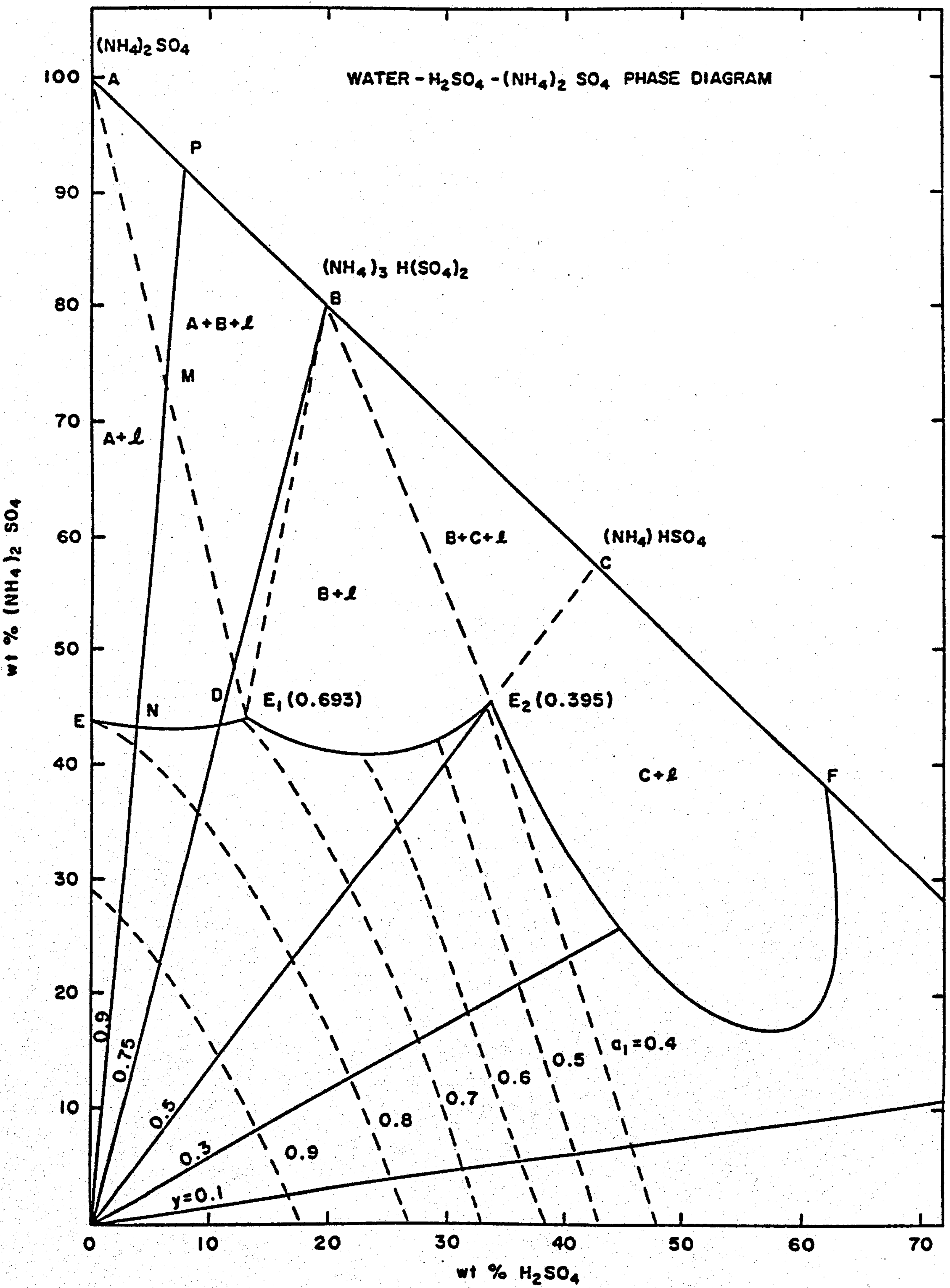

Fig. 1 Solubility Diagram for the $H_2O-(NH_4)_2SO_4-H_2SO_4$ System at 30°C

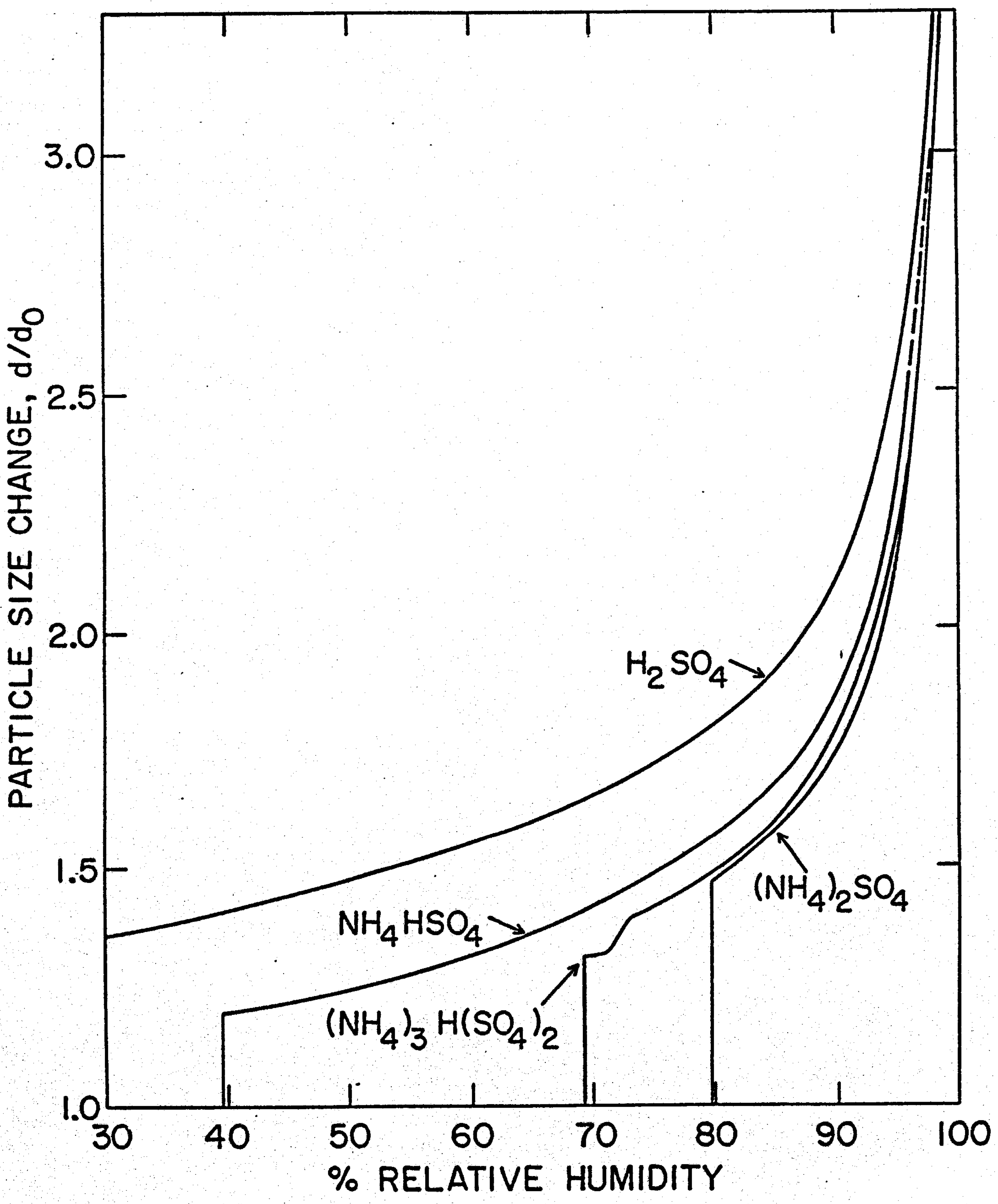

Fig. 2 Growth Curves for Sulfate Aerosols at 25°C

The NH_4HSO_4 aerosol, although being a mixed salt, is expected to behave like a single-component salt aerosol since its growth path goes through the second eutonic point E_2 as shown in the phase diagram in Fig. 1. The growth curve for the NH_4HSO_4 has been verified experimentally.[12] The deliquescence properties for the mixed sulfate aerosols have been determined.[13]

Equilibrium Size of Saline Droplets

It has been shown[11] that for a solution droplet containing nonvolatile multicomponent electrolytes, the equation

$$\ln \frac{p_1}{p_1^o} = \ln \gamma_1 \chi_1 + \frac{2\bar{v}_1 \sigma}{RTr_e} \qquad (1)$$

is quite general and applies to both single and multicomponent systems as long as the solution properties are determined for the system. Equation (1) relates the equilibrium radius r_e of a droplet of composition χ_1 (mole fraction) to the relative humidity, $H = p_1/p_1^o$, and the solution properties such as the activity coefficient γ_1, partial molar volume $\bar{v}_1$, and surface tension σ. Here the subscript 1 refers to the solvent, i.e., water in the present case. For droplets of radius larger than ~ 0.05 µm, the contribution of the second term on the right-hand side of Equation (1) is small and one may relate the composition of the droplet directly to that of a bulk solution in equilibrium with its water vapor pressure at temperature T. The calculation, however, requires vapor pressure data for the entire concentration range extending from the solid-liquid coexistence regions to infinite dilution. Such information is usually not available in the literature for multicomponent electrolyte solutions.

The change in particle size at a given relative humidity can readily be deduced from a material balance on salt content before and after droplet growth to its equilibrium size. The following equation is obtained:

$$\frac{d}{d_o} = \left(\frac{100\,\rho_o}{W_2\,\rho}\right)^{1/3} . \qquad (2)$$

Here, d and ρ are, respectively, the diameter and density of a droplet containing W_2% by wt of salt, and d_o and ρ_o are, respectively, the diameter and density of the dry salt particle. The calculation, of course, requires density data as a function of composition. The following relationship[14] may be used to estimate the density of a solution droplet at composition W_2:

$$\rho = \rho_1 + \left(1-\frac{\rho_1}{\rho_2}\right)\rho\, W_2 \quad , \tag{3}$$

where ρ_1 is the density of pure water and ρ_2 is the hypothetical density of of the solutes. The factor $(1-\rho_1/\rho_2)$ may be evaluated from the known density and composition of the saturated solution and taken to be independent of composition. Such a procedure has been demonstrated[12] to be quite adequate for practical droplet growth calcuations.

In the case of a multicomponent salt particle which is only partially dissolved under certain humidity conditions, the fraction of undissolved salt may be estimated from the solubility diagram. Referring again to Fig. 1 for the $H_2O-(NH_4)_2SO_4-H_2SO_4$ system, one observes that a mixed-sulfate particle having initial composition denoted by point P will deliquesce at 69.3% r.h., at which time the particle becomes partially dissolved and the fraction of undissolved solid is given by the ratio of the line segment ME_1 to AE_1. The liquid phase should have a composition denoted by the eutonic point E_1, and the solid phase is pure $(NH_4)_2SO_4$ as dictated by the two-phase coexistence $A + \ell$. The solid-to-liquid ratio should be taken into consideration when making growth calculations.

EXPERIMENTAL PROCEDURE

The deliquescence properties of mixed-salt aerosols and subsequent droplet growth by water vapor condensation were investigated in a continuous-flow apparatus at 25°C as a function of relative humidity. The design, construction, and characterization of the apparatus have been described in detail elsewhere.[15] Briefly, salt aerosols were generated by bubbling nitrogen gas through a coarse glass frit immersed in an aqueous solution of known composition. The aerosol stream was dried and passed through an electrostatic separator where charged particles were sorted according to their electrical mobility. A distinct size fraction, usually exhibiting a lognormal particle-size distribution with a geometric standard deviation ranging from 1.07 to 1.14 was selected and extracted from the separator.

Figure 3 shows the electron micrograph of a size-selected letovicite aerosol sample collected on a 0.4 μm Fluropore filter. The size distribution shown with the electron micrograph was obtained with a Carl Zeiss Particle Size Analyzer. Since the particle concentration was typically about 10 particles/cm^3 in the growth chamber, a long sampling time was required to collect enough particles on the filter for electron microscopic examination. In this particular case, a six-hour sampling time was used, during which period some fluctuation of the operating conditions for the aerosol generation system was unavoidable. This might have contributed to the fact that the collected aerosol sample showed a rather large σg (1.14). Under normal experimental conditions, the extracted aerosol is quite monodisperse with good size resolution.

The size-selected aerosol stream was mixed in a thermostated growth chamber with N_2 carrier gas containing a measured amount of moisture. The particle-size distribution after equilibration at each given relative humidity was continuously monitored with an optical particle counter. The output signal of the particle counter was preamplified, shaped, and sorted in a 100 Mhz pulse-height analyzer and subsequently stored in a 1024 multichannel analyzer. The data was displayed on the screen of an oscilloscope and later retrieved by a high-speed printer for processing.

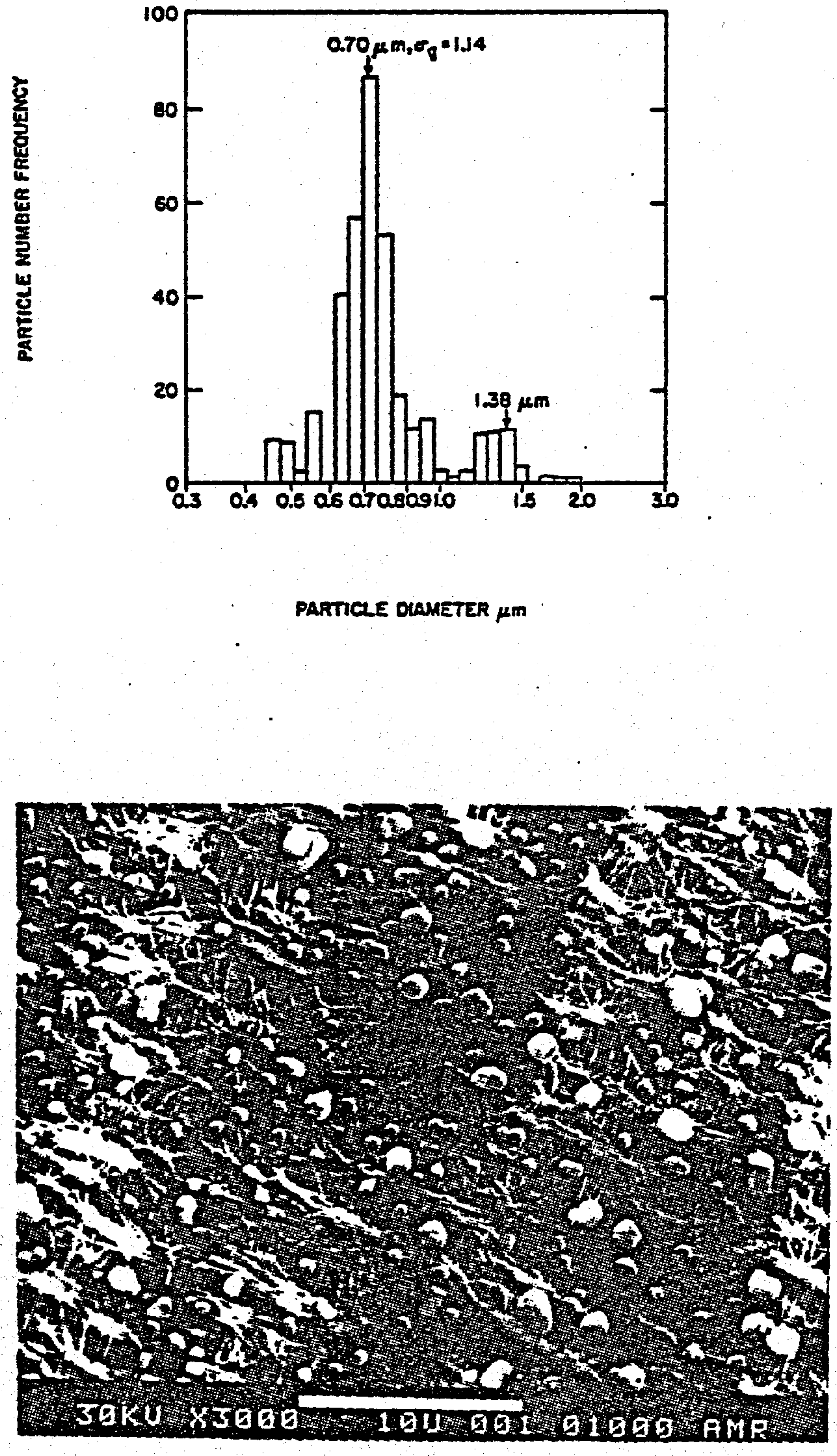

Fig. 3 Electron Micrograph and Particle-Size Distribution of a Letovicite Aerosol

A composite of three oscilloscope tracings for a letovicite aerosol grown at different humidities is shown in Fig. 4. The dry salt aerosol has a median diameter of 0.67 µm. As the humidity was gradually raised to the deliquescence point of 69.3% r.h., there was a sudden shift of the peak position from channel No. 100 to 137 with only a small increment of relative humidity, thus marking the onset of particle growth. From the particle size change before and after exposure to moisture, aerosol growth by water vapor condensation was obtained as a function of relative humidity.

RESULTS AND DISCUSSION

Deliquescence Properties and Droplet Growth

Inorganic salt aerosols composed of either single component or combinations of NaCl, KCl, $(NH_4)_2SO_4$, H_2SO_4, and NH_4NO_3 were investigated at 25°C in the continuous-flow apparatus. The size of the initial dry aerosols used in the investigation ranged from 0.4 to 0.9 µm in median diameter. The relative humidity at which phase transformation took place was determined for each aerosol, and the subsequent droplet growth was measured as a function of relative humidity. In the case of mixed-sulfate aerosols, the observed deliquescence properties were further substantiated by vapor pressure measurements made in a separate study.[16]

The growth curves for two mixed-sulfate aerosols showing the typical stagewise growth characteristics predicted from thermodynamic considerations are given in Fig. 5. The observed deliquescence point at 69.0 ± 0.5% r.h. is in good agreement with the water activity at the eutonic composition.

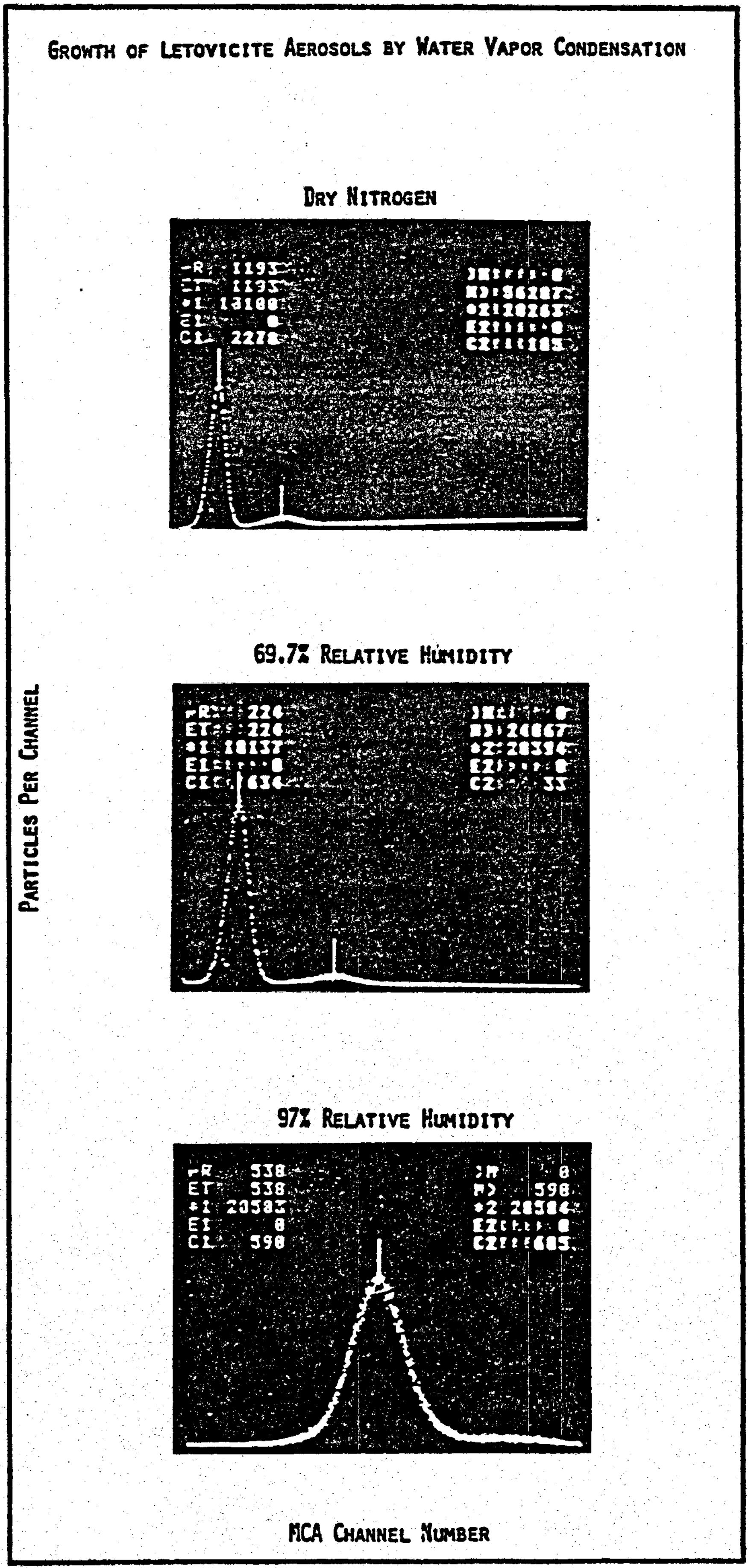

Fig. 4 Oscilloscope Tracings Showing the Growth of a Letovicite Aerosol as Monitored with the Optical Particle Counter

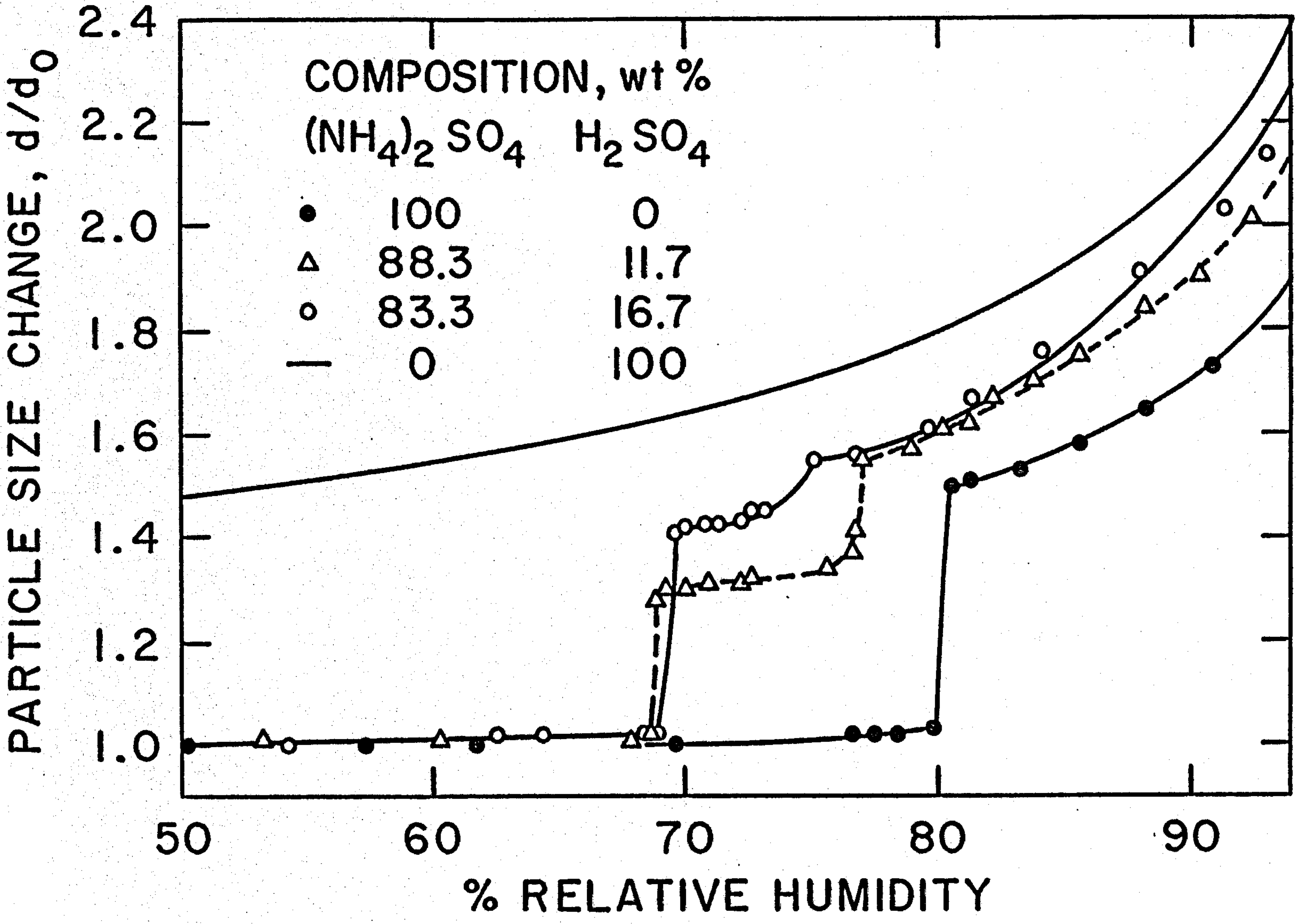

Fig. 5 Growth of Sulfate Aerosols as a Function of Relative Humidity

Table I. Deliquescence Properties of Some Salt Aerosols at 25°C

Aerosol Composition	Deliquescence Humidity
NaCl	75.7
KCl	84.3
NaCl-KCl	73.8
$(NH_4)_2SO_4$	79.5
$(NH_4)_3H(SO_4)_2$	69.0
NH_4HSO_4	39.0
$2NH_4NO_3 \cdot (NH_4)_2SO_4$	56.4

The deliquescence humidities of some environmentally important aerosols investigated in our laboratory are given in Table I. The growth of the NH_4NO_3 aerosol was also investigated, however, no deliquescence point was experimentally established for this salt aerosol. As indicated by the data shown in Fig. 6, the NH_4NO_3 aerosol already became quite hygroscopic at ∿ 30% r.h., and the phase transition at the predicted deliquescence point of 62% r.h. was not observed with certainty. In contrast, a definite phase transition was observed to occur at 56.4% r.h. for a mixed salt aerosol containing 45% by wt NH_4NO_3 and 55% by wt $(NH_4)_2SO_4$, in agreement with the behavior predicted from the phase diagram of the system. The measured droplet growth for the NH_4NO_3 aerosol, as shown in Fig. 6, follows the theoretical curve rather closely at relative humidities greater than the expected deliquescence point.

Droplet Evaporation and Crystallization

Evaporation of solvent water will take place when a wet saline aerosol is mixed with dry carrier gas, a situation often encountered with in many exposure

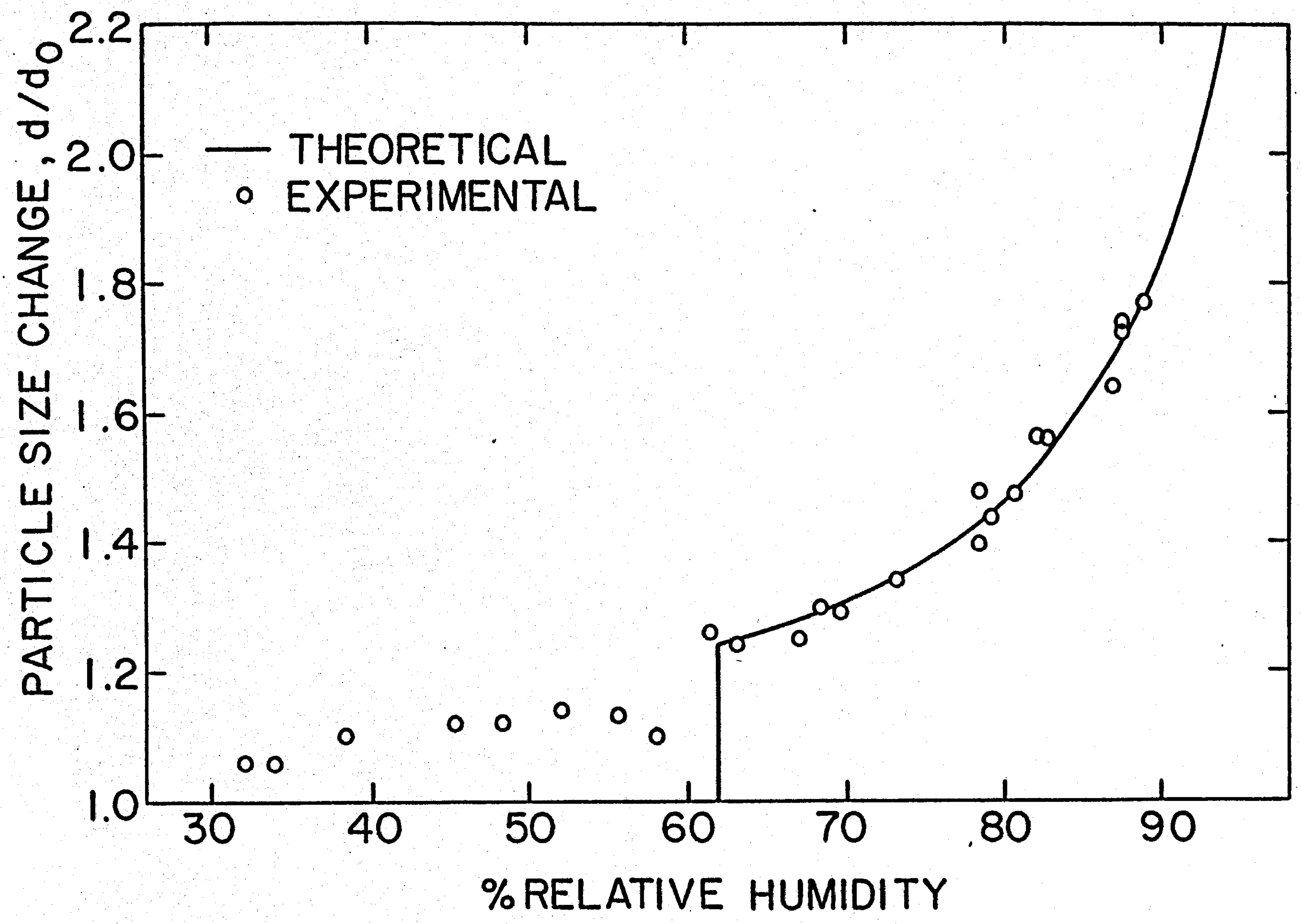

Fig. 6 Growth of NH_4NO_3 Aerosols in a Moist Atmosphere at 25°C

facilities. The particle-size distribution of the nebulized aerosol will depend upon the transit time and the relative humidity finally reached in the mixing process. Equations (1) and (2) are equally applicable to the case of decreasing relative humidity for calculating the ultimate size of a saline droplet, provided that equilibrium prevails at the final relative humidity. In reality, however, it is very common for a saline aerosol to exhibit the so-called "hysteresis" phenomenon, which is typically illustrated by the $(NH_4)_2SO_4$ aerosol as shown in Fig. 7.

The measured growth of $(NH_4)_2SO_4$ aerosols with increasing relative humidity is shown by the filled points in Fig. 7. The deliquescence properties at 79.5% r.h. and subsequent droplet growth are seen to agree with theoretical predictions. The open circles represent experimentally determined size changes when the relative humidity was gradually decreased. The droplet size follows the growth curve very closely until the deliquescence point is reached. A further decrease in humidity does not usually result in an abrupt reduction in particle size by crystallization of the salt content as might be expected. Instead, a continuous and gradual reduction in size takes place as a result of the droplet becoming supersaturated. These "hysteresis" phenomena are well known for many inorganic salt solutions and have been observed by other investigators.[6,17] In fact, "hysteresis" is responsible for the often noted lingering of smogs[18] below the humidities at which they first appeared.

When crystallization does occur, it will occur spontaneously and the particle size will suddenly shift to its initial dry size. Although the lingering time, in general, depends upon the extent of humidity lowering, there appears for each saline aerosol a specific humidity below which the lingering time is order-of-magnitude shorter than at slightly higher humidities. To demonstrate this fact

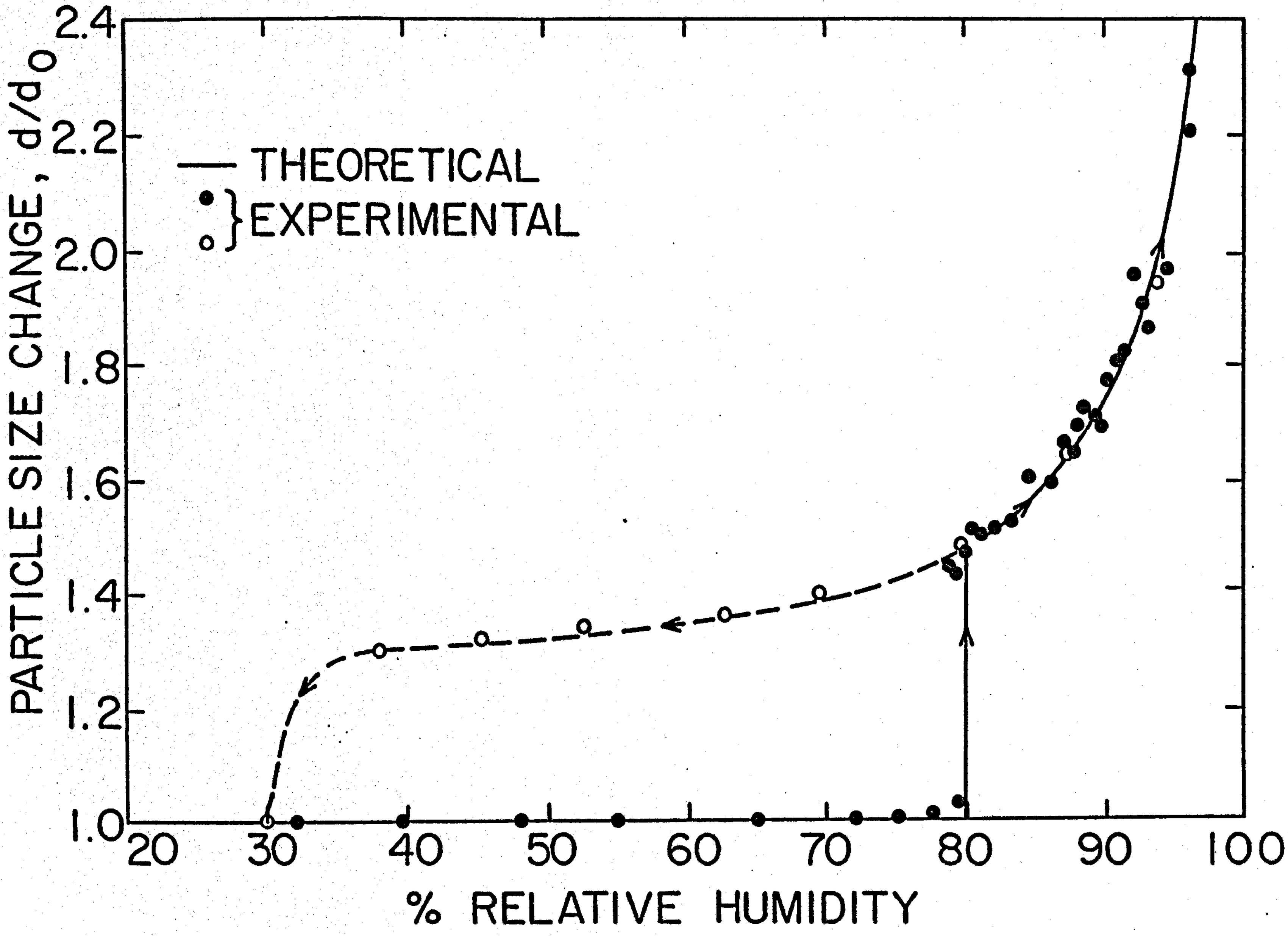

Fig. 7 Condensational Growth and Evaporation of $(NH_4)_2SO_4$ Aerosols in a Moist Atmosphere at 25°C

with NaCl, KCl, and mixed NaCl-KCl aerosols the reciprocal of lingering time, called transition rate, is plotted in Fig. 8 vs the relative humidity at which the crystallization occurs. In each case, a sharp rise in transition rate is noted to occur about a specific humidity. These crystallization humidities are quite reproducible in our experiments and compare fairly well with the observations by Orr et al.[6], who employed salt aerosols in the size range of 0.01 to 0.1 μm in radius. Table II gives the crystallization humidities for a few salt aerosols.

Table II. Crystallization Humidities of Salt Aerosols

Aerosol Composition	This Work	Reference 6
NaCl	43	42
KCl	53	48
NaCl-KCl	38	-
$(NH_4)_2SO_4$	∿ 36	40

CONCLUSION

Theoretical and experimental results are presented to show that the growth of a mixed-salt aerosol by water vapor condensation may go through several stages of multiphase equilibria before its complete dissolution to form a homogeneous solution droplet. The deliquescence properties are predictable from the phase diagram of the system of interest. The size of a saline droplet in equilibrium with the relative humidity in the surrounding air may be calculated from the thermodynamic properties of the bulk solutions. The increase in particle size as a result of rehydration and condensational growth may significantly affect the retention of inhaled particulates in the respiratory tract.

Experiments with $(NH_4)_2SO_4$ and chlorides show that for each deliquescent

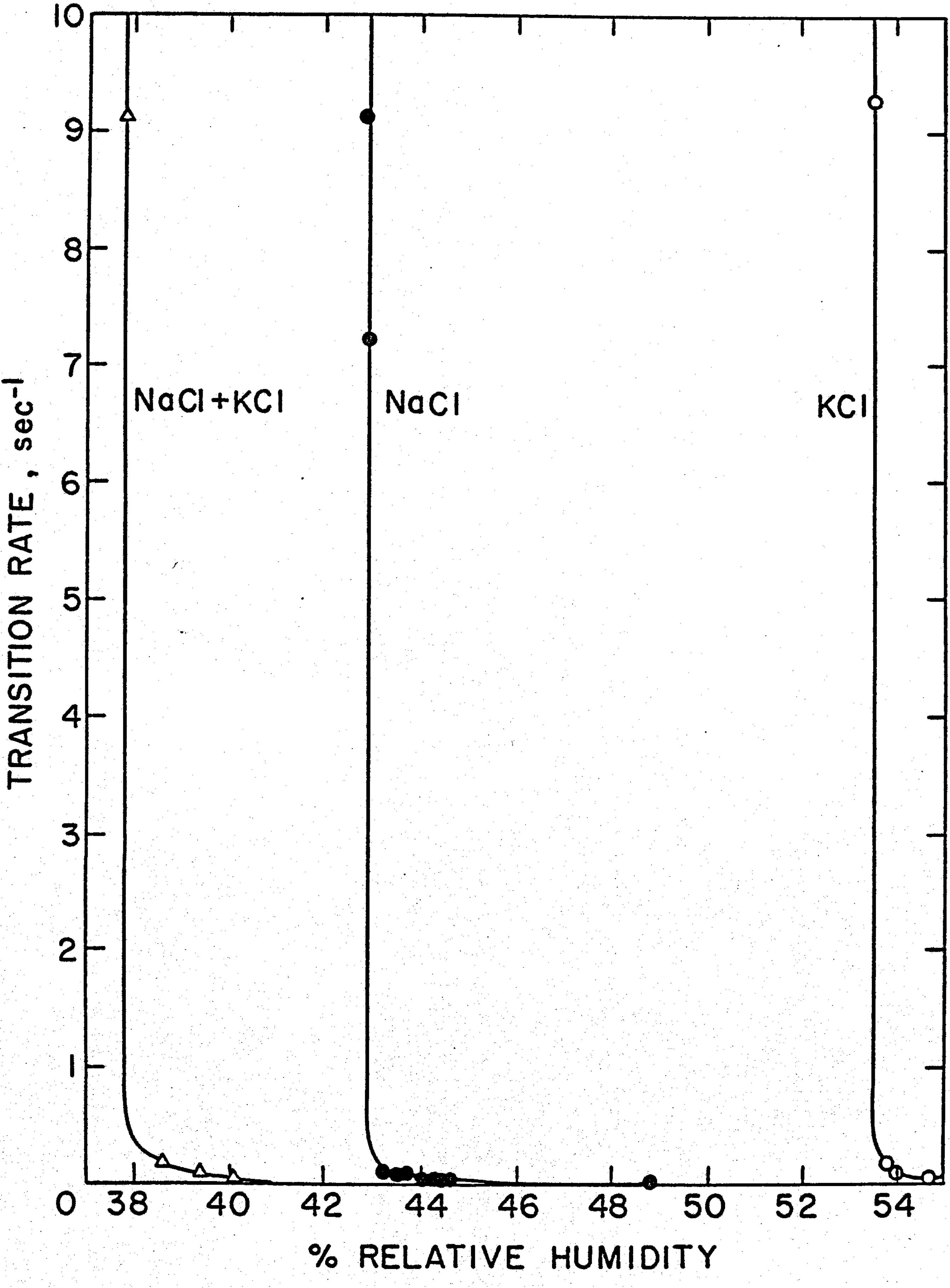

Fig. 8 Crystallization of Salt Aerosols

salt aerosol there is a threshold humidity below which the solution droplets will quickly evaporate to become crystalline particles. The threshold crystallization humidity is generally much lower than the deliquescence humidity of the given salt aerosol. The information should provide a basis for selecting a suitable humidification procedure to generate test aerosols for exposure studies.

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REFERENCES

1. Frank, R. "Sulfur Oxides and Particles: Effects on Pulmonary Physiology in Man and Animals," in Conf. on Health Effects of Atm. Salts and Gases of Sulfur and Nitrogen in Assoc. with Photochem. Oxidant, Newport Beach, Calif. January 7-8, 1974.
2. Crocker, T. T. "Effects of Sulfur Oxides in Animal and Man," ibid, 1974.
3. Milburn, R. H., Crider, W. L., and Morton, S. D. "The Retention of Hygroscopic Dusts in the Human Lungs," AMA Arch. Ind. Health 15, 59-62 (1957).
4. Robinson, R. A. and Stokes, R. H. Electrolyte Solutions, 2nd, rev. ed., Butterworths, London (1970).
5. Kohler, H. "The Nucleus in and the Growth of Hygroscopic Droplets," Trans. Faraday Soc. 32, 1152-1161 (1936).
6. Orr, C. Jr., Hurd, F. K., and Corbett, W. J. "Aerosol Size and Relative Humidity," J. Colloid Sci. 13, 472-482 (1958).
7. Dufour, L. and Defay, R. Thermodynamics of Clouds, Ch. VIII, Academic, New York, 1963.
8. Sedunov, Yu. S. Physics of Drop Formation in the Atmosphere, Ch. 2, Wiley & Sons, New York, 1974.
9. West, C. J. and Hull, C. International Critical Tables, McGraw-Hill, 1933.
10. Tang, I. N. "Phase Transformation and Growth of Aerosol Particles Composed of Mixed Salts," J. Aerosol Sci. 8, 361-371 (1976).
11. Brosset, C., Andreasson, K., and Ferm, M. "The Nature and Possible Origin of Acid Particles Observed at the Swedish West Coast," Atm. Environ. 9, 631-642 (1975).

12. Tang, I. N. and Munkelwitz, H. R. "Aerosol Growth Studies - III. Ammonium Bisulfate Aerosols in a Moist Atmosphere," J. Aerosol Sci. 8, 321-330 (1977).

13. Tang, I. N., Munkelwitz, H. R., and Davis, J. G. "Aerosol Growth Studies - IV. Phase Transformation of Mixed Salt Aerosols in a Moist Atmosphere," J. Aerosol Sci. 9, 505-511 (1978).

14. Moelwyn-Hughes, E. A. Physical Chemistry, 2nd. ed. p. 808, Pergamon Press, Oxford, 1961.

15. Tang, I. N., Munkelwitz, H. R., and Davis, J. G. "Aerosol Growth Studies - II. Preparation and Growth Measurements of Monodisperse Salt Aerosols," J. Aerosol Sci. 8, 149-159 (1977).

16. Tang, I. N. and Munkelwitz, H. R. "The Optical and Thermodynamic Properties of $(NH_4)_3H(SO_4)_2$ (Letovicite) Aerosols, presented at the May 1978 Industrial Hygiene Conf., Los Angeles.

17. Winkler, P. and Junge, C. "The Growth of Atomospheric Aerosol Particles as a Function of the Relative Humidity," J. Rech. Atm. 4, 617-638 (1972).

18. La Mer, V. K. and Cotson, S. "The Growth and Shrinkage of Aerosols," Science 118, 516-7 (1953).