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CLOUD STUDIES SEEN FROM A PHYSICAL CHEMIST'S PERSPECTIVE

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SUMMARY

Substantial advances have been made in recent years in describing the rates of chemical reactions in clouds. Inputs to these calculations are concentrations of reagent species, solubilities of reactive gases, rate expressions for interphase mass transport, rate expressions for aqueous-phase reaction of the dissolved species, the liquid-water content of the cloud and its drop-size spectrum, and the composition of the cloudwater (especially pH) as it affects solubility and reaction rates. Armed with this information one can calculate the rates of reactions of interest. The question still remains as to the accuracy of such calculations. To answer this we need field measurements, of cloud properties and the concentrations of reagents--to permit evaluation of reaction rates--and of differences in composition that may be attributed to chemical reaction. However determination of rates and extents of in-cloud reactions presents a major challenge because of uncertainties associated with measurements of concentration changes. Even attribution of a measured composition change to a specific reaction is difficult. Another challenge to the field measurement community is determining the size dependence of cloudwater composition (especially pH) and the resultant difference between reaction rates based on bulk composition and actual reaction rates integrated over the cloud droplet spectrum. This paper reviews these issues and offers suggestions for field measurements to confirm model based-understanding of these processes.

1. INTRODUCTION

The physical and chemical properties and processes of clouds continue to be of keen interest from a variety of practical perspectives: acid deposition, oxidant chemistry, short- and longwave radiative transfer, visibility, and the like. Considerable advances have been made in recent years in understanding the physico-chemical processes governing cloud properties pertinent to these issues, but many issues remain. This article examines several key issues:

- Description of aqueous- phase chemical kinetics in clouds.
- Evaluations of rates in-cloud reactions of SO_2 oxidation with O_3 and H_2O_2.
- Dependence of the rate of aqueous-phase reaction on drop size and implications for field measurements.
- Requirements of field measurements of extent and rate of in-cloud reaction.

2. MASS TRANSPORT AND CHEMICAL KINETICS IN CLOUDS

The coupling of mass transport of trace gases between aqueous drops in clouds and the surrounding air in conjunction with aqueous-phase reaction has been previously described *(6. 15. 16. 19. 21)*. For cloud droplets (diameter ~ 10 μm) mass transport in the gas-phase in the vicinity of the drop and within the drop is governed by molecular diffusion. Mass transport across the interface occurs only by molecular collisions; the rate of this transfer is given as the molecular collision rate (as given by the kinetic theory of gases) times the mass accommodation coefficient (the fraction of collisions leading to transfer of material across the interface). These processes can be considered schematically as reactions occurring in series:

$$\begin{array}{c}\text{Soluble}\\\text{reactive}\\\text{trace gas}\end{array} \overset{\textit{Mass Transport}}{\rightleftharpoons} \begin{array}{c}\text{Dissolved}\\\text{reagent}\\\text{gas}\end{array} \xrightarrow{\textit{Chemical Reaction}} \text{Product}$$

The rate of change of the partial pressure of gas-phase reagent in the bulk gas phase and of the concentration of the dissolved aqueous phase reagent gas due to these processes is described by a set of coupled differential equations:

$$\frac{dp}{dt} = -p\int k_{mt}(a)\left(\frac{dL}{da}\right)da + \frac{1}{H}\int \frac{k_{mt}(a)}{Q(a)}\,\overline{C(a)}\left(\frac{dL}{da}\right)da \qquad (1)$$

$$\frac{d\overline{C(a_i)}}{dt} = \frac{k_{mt}(a_i)}{R\ T}p - \frac{k_{mt}(a_i)}{H\ R\ T\ Q(a_i)}\,\overline{C(a_i)} - \overline{R(a_i)} \qquad (2)$$

Equation (2) pertains to each of n droplet radius classes a_i; thus there are $n + 1$ coupled equations. In these equations the following symbols are employed:

p is the partial pressure of the reagent gas, atm;

$k_{mt}(a)$ is the rate coefficient describing gas-phase and interfacial mass transport, s^{-1};

a is the drop radius, cm;

H is the Henry's law coefficient or effective Henry's law coefficient of the reagent gas, M atm^{-1};

$\overline{C(a)}$ is the mean aqueous concentration of the dissolved reagent gas in the drop, M;

$Q(a)$ is the ratio of mean to surface concentration of the dissolved reagent gas in the drop;

$\overline{R(a)}$ is the mean aqueous-phase reaction rate in the drop, M s^{-1};

R is the universal gas constant, atm M^{-1} K^{-1};

T is the absolute temperature, K, and

$\frac{dL}{da}$, volume size distribution of cloudwater such that $L = \int\left(\frac{dL}{da}\right)da$, where

L is the liquid-water volume fraction in the cloud (dimensionless).

For a reagent gas that reacts according to a first-order or pseudo-first-order rate law, the aqueous-phase mass-transport limitation is given by the factor Q(a),

$$Q(a) = \frac{\overline{C(a)}}{C_a(a)} = 3\left(\frac{\coth q}{q} - \frac{1}{q^2}\right) \le 1 \qquad (3)$$

where $q = a\left(k^{(1)}/D_{aq}\right)^{1/2}$;

D_{aq} is the aqueous-phase diffusion coefficient of the dissolved reagent gas, and

$k^{(1)}$ is the effective first order reaction rate coefficient, s^{-1}, such that the local reaction rate is $R = k^{(1)}C$.

The gas-phase and interfacial mass-transport rate coefficient is

$$k_{\mathrm{mt}} = \left(\frac{a^2}{3D_g} + \frac{4a}{3\bar{v}\alpha}\right)^{-1} \qquad (4)$$

where D_g is the gas-phase diffusion coefficient of the reagent gas,

α is the mass accommodation coefficient of the gas on aqueous solution, and

$\bar{v}$ is the mean molecular speed = $(8kT/\pi m)^{1/2}$;

k is the Boltzmann constant, and m is the molecular mass of the reagent gas.

If phase equilibrium is established rapidly relative to the rate of depletion of the gas-phase reagent by aqueous reaction (this is generally the case), the concentration of the dissolved reagent gas may be treated in steady state, and the rate of aqueous-phase reaction in each size cut can be expressed in terms of the partial pressure of the reagent gas as

$$\overline{R(a_i)} = \frac{Hk^{(1)}p}{1 + \frac{H\ R\ T\ Q(a_i)}{k_{mt}(a_i)}} \qquad (5)$$

The rate of reaction integrated over the drop size distribution and expressed as a rate of change in gas-phase partial pressure is

$$R^{(g)} = pR\,T \int \frac{Hk^{(1)}}{1 + \dfrac{H\,R\,T\,Q(a_i)}{k_{mt}(a_i)}} \left(\frac{dL}{da} \right) da \tag{6}$$

Criteria have been adduced and graphical methods developed to determine whether the rate of a given chemical reaction in a cloud drop is or is not limited by mass-transport rates in the gas-phase, at the interface, or in the aqueous phase *(16, 19, 21)*. In the absence of mass-transport limitation equations (5) and (6) simplify to

$$\overline{R(a_i)} = Hk^{(1)} p \tag{5a}$$

and

$$R_g = pR\,T \int Hk^{(1)} \left(\frac{dL}{da} \right) da \tag{6a}$$

Finally, if the composition of the cloudwater is uniform so that H and $k^{(1)}$ are independent of drop size, equation (6) further simplifies to

$$R_g = Hk^{(1)} pLR\,T \tag{6b}$$

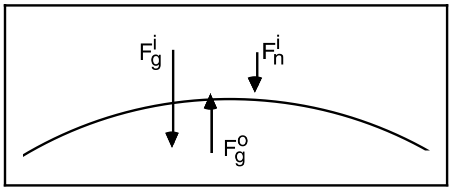


Figure 1. Schematic representation of fluxes into and out of drop.

The mass accommodation coefficient α must be defined with some care, as various investigators have used different definitions and terminologies for this quantity, and this has led to some confusion. Figure 1 indicates schematically the exchange of a gaseous species between the gas phase and aqueous solution. Here F_g^i is the gross flux of gas into the drop, F_g^o is the gross flux out of the drop, and $F_n^i = F_g^i - F_g^o$ is the net flux into the drop. The mass accommodation coefficient is the ratio of the gross flux into the drop to the gas kinetic collision rate:

$$\alpha = \frac{\text{gross flux in}}{\text{gas - kinetic collision rate}} = \frac{F_g^i}{C\bar{v}/4} \tag{7}$$

where C is the concentration of the gas just outside the drop. Part of the confusion in definitions arises from the fact that the gross flux into the drop cannot be measured. Only the net flux can be measured. To avoid confusion it is recommended that the ratio of the net flux into the drop to the gas kinetic collision rate be denoted the "uptake coefficient" and that the symbol γ be employed for this quantity:

$$\gamma = \frac{\text{net flux in}}{\text{gas - kinetic collision rate}} = \frac{F_n^i}{C\bar{v}/4} \tag{8}$$

Clearly α ≥ γ. They are equal when there is no return flux. The challenge to the experimentalist is to achieve this, either by measuring the uptake flux immediately following contact of the liquid to the gas containing the species of interest, or by measuring a steady state flux under conditions where the dissolved gas reacts sufficiently rapidly that the return flux is small compared to the inward flux. Figure 2 shows the dependence of k_{mt} on drop radius and α. For drop sizes in the range of cloud drops (D ~ 10 μm), k_{mt} is relatively insensitive to α, for α ≳ 0.1.

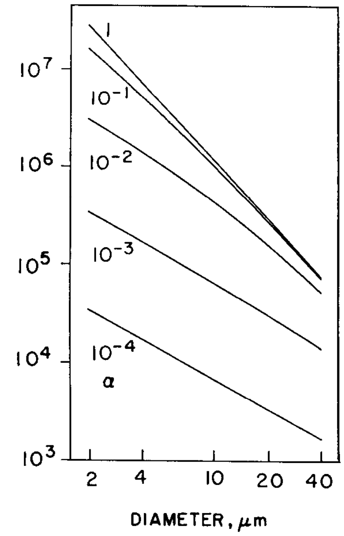


Figure 2. Dependence of mass-transfer rate coefficient k_{mt}, representing combined influence of gas-phase and interfacial mass transport, on drop diameter and mass accommodation coefficient α.

Just a few years ago little was known about values of the mass accommodation coefficients on water of trace gases of interest to the tropospheric chemistry of atmospheric pollutants. However because of the importance of these coefficients they have been the subject of measurements by a number of groups *(8, 12, 22, 24)*, which have found that these coefficients are of order 0.1 for a variety of gases. Based on these recent measurements of mass-accommodation coefficients of SO_2, H_2O_2, and O_3, it appears that the important in-cloud oxidation of SO_2 by these oxidants is not appreciably limited by mass transport *(17)*.

3. OXIDATION OF SULFUR DIOXIDE BY HYDROGEN PEROXIDE AND OZONE

It has been recognized for some time that SO_2 can be rapidly oxidized in cloudwater by the strong oxidants H_2O_2 and O_3 *(14)*. Evaluation of the rates of these reactions requires knowledge of the solubilities of the several reagents and of the reaction rate constants. The effective Henry's law coefficient of SO_2 increases with increasing pH because of acid dissociation equilibria to form bisulfite and sulfite ions [collectively, S(IV)], and the second order rate constants of both reactions are also strongly pH dependent, so it is necessary to consider these quantities as a function of pH, Figures 3 to 5.

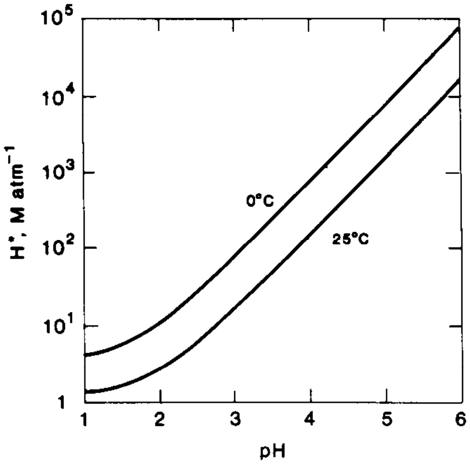


Figure 3. Effective Henry's law coefficient of S(IV) as a function of solution pH, evaluated from data of Goldberg and Parker *(4)*.

The resultant oxidation rates, evaluated by equations 5b and 6c are shown in Figure 6. Because of a cancellation of the pH dependences of S(IV) solubility and the acid catalyzed rate coefficient, the H_2O_2 rate is nearly independent of pH. The oxidation is quite rapid, about 100% hr^{-1} for the indicated H_2O_2 concentration and liquid water content. This reaction dominates SO_2 oxidation if H_2O_2 is present. The reaction is expected to rapidly proceed to completion, thereby exhausting the reagent that is present in lower concentration (the limiting reagent). This expectation is borne out in measurements of SO_2 and H_2O_2 in non-precipitating liquid-water stratiform clouds *(1, 2)*. Studies of the reaction rate in fresh precipitation samples show that the rate is comparable to the rate in purified water *(10)*, supporting the applicability of this rate expression to reaction in cloudwater.

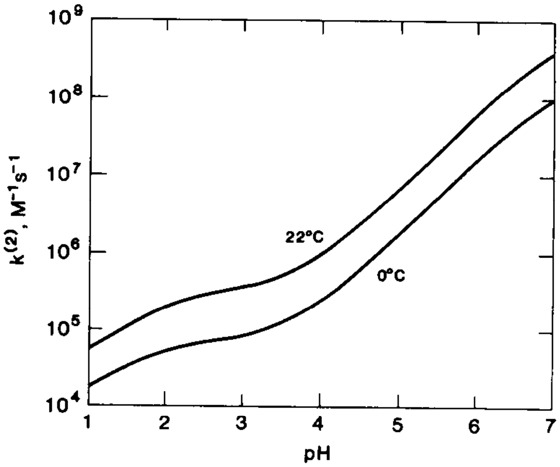


Figure 4. Effective second-order rate coefficient for aqueous-phase reaction of S(IV) with O_3 as a function of pH, evaluated from rate coefficients of Hoigné et al., *(5)* with, for 0°C, temperature adjustment according to Erickson et al. *(3)*.

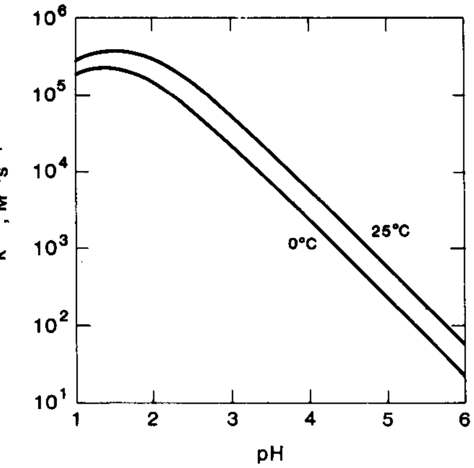


Figure 5. Effective second-order rate coefficient for aqueous-phase reaction of S(IV) with H_2O_2 as a function of pH, evaluated from rate expression of Overton *(13)*.

In contrast to the H_2O_2 reaction, the ozone reaction, although rapid at high pH, decreases strongly with decreasing pH. Consequently the reaction is self limiting; as acid is produced in the reaction the rate of further reaction decreases. Consequences of this pH dependence are illustrated in Figures 7 and 8. It is seen in Figure 7 that for initial strong acid concentrations less than about 10 μM, the acid concentration reached after a reaction time of, say, 2 hours, is roughly independent of initial concentration. However for initial acid concentration of 20 μM, the concentrations will effectively never converge. Figure 8 shows another way of looking at this. The ozone oxidation rapidly produces a strong acid concentration of 10 μM (0.2 hours) but requires 10 hours to get to 50 μM. Implications of this on the drop size dependence of cloudwater composition are explored below.

It is essential that the rate of SO_2 oxidation by other reactions, e.g., metal-catalyzed O_2 oxidation, be compared to these rates also as a function of pH *(11, 18)*.

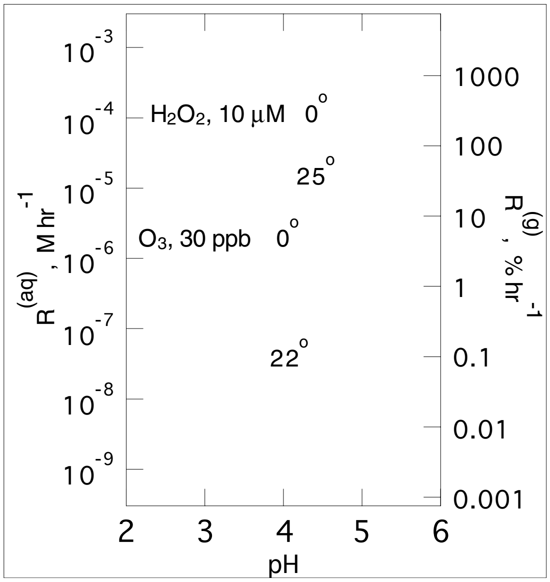


Figure 6. Instantaneous rate of aqueous-phase oxidation of S(IV) by H_2O_2 and O_3, evaluated as a function of pH for representative non-urban reagent concentrations. The rates scale approximately linearly with reagent concentrations. The right hand ordinate gives the oxidation rate of SO_2 referred to the gas-phase partial pressure and expressed as percent per hour for a liquid water content L = 1 x 10^{-6} (1 cm^3 m^{-3}); the rate scales approximately linearly with L.

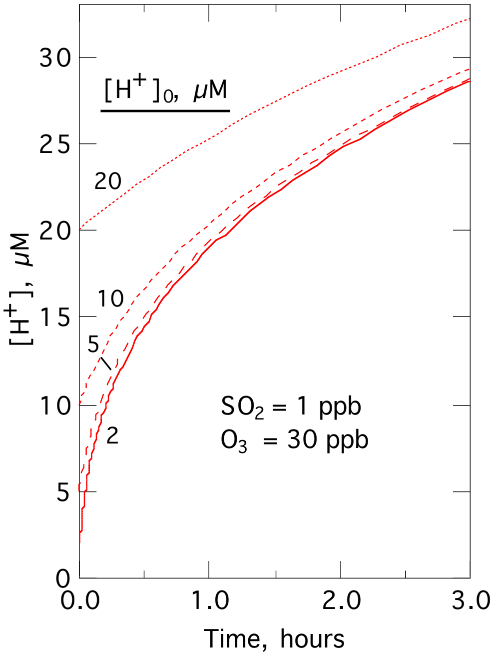


Figure 7. Strong acid concentration as a function of reaction time for the O_3 - SO_2 reaction, showing decrease in reaction rate as acid concentration increases.

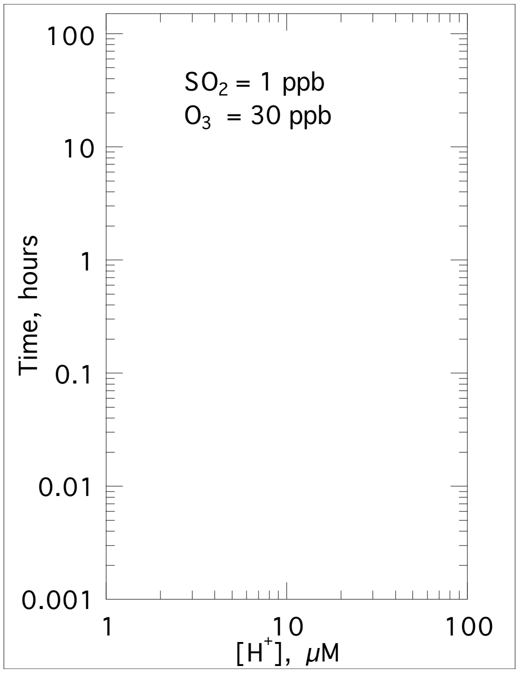
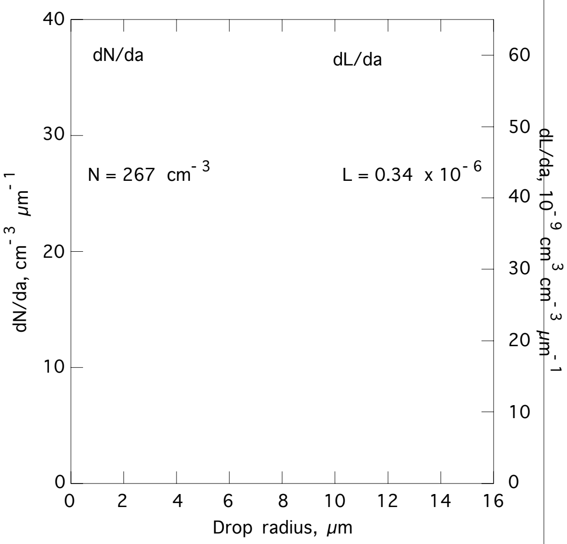


Figure 8. Time required to reach a specified strong acid concentration by the O_3 - SO_2 reaction.

4. DROP-SIZE DEPENDENCE OF REACTION RATES AND COMPOSITION

In view of the strong drop-size dependence of the mass-transport rate coefficient k_{mt} indicated in Figure 2, it might be anticipated that there would be a resultant influence on reaction rates and cloudwater composition that might be discernible in field measurements, thereby lending confirmation to the modeling approach. I explore this here for the uptake of



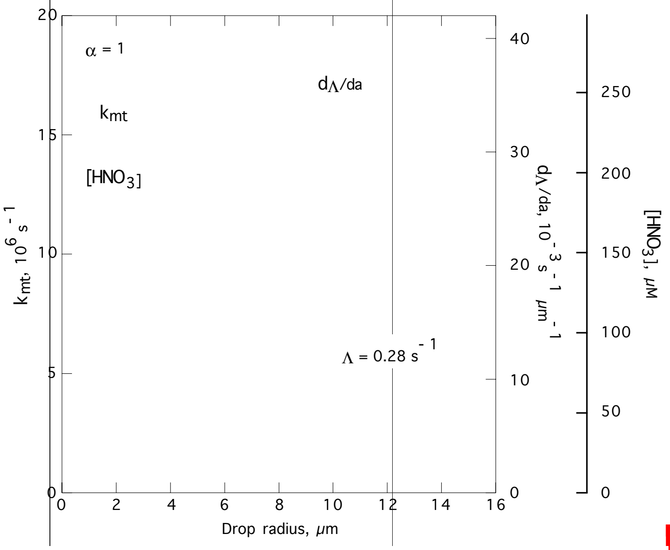


Figure 9: Number (dN/da) and volume (dL/da) distributions of cloudwater used in mass transfer and chemical calculations. Data for aged stratus cloud from Knollenberg *(9)*.

Figure 10. Spectrum of mass-transport rate coefficient k_{mt} and of partial contributions to uptake rate for various size cuts of drop size spectrum shown in Figure 9, evaluated for HNO_3 with mass accommodation coefficient $\alpha = 1$. HNO_3 concentration spectrum, for initial gas-phase partial pressure 1×10^{-10} atm, can be read on auxiliary scale at right.

nitric acid vapor, which is controlled entirely by mass transport, and which leads to a composition spectrum where the acid concentration increases strongly with decreasing drop size. This uptake is essentially complete within a few tens of seconds. I then proceed to examine the influence of this initial acidity on the rate of the ozone-S(IV) reaction occurring subsequently over a time scale of about an hour.

For the drop size distribution I take a representative "aged stratus" distribution shown in Figure 9, for which the droplet concentration is 267 cm^{-3} and the liquid water volume fraction is 0.34 cm^3 m^{-3}. Figure 10 shows the drop-size dependence of the mass-transport rate coefficient k_{mt} and of the contribution to the uptake rate Λ; because of the high solubility of HNO_3, the uptake is essentially irreversible, so the second term on the right hand side of equations (1) and (2) vanishes, and

$$\Lambda \equiv -d\ln p/dt = -\int k_{mt}(a)\left(\frac{dL}{da}\right)da \qquad (9)$$

As indicated also in Figure 2, k_{mt} decreases strongly with drop size. The contributions to Λ are weighted by the volume distribution in Figure 9, so that $d\Lambda/da$ is much less dominated by small drops than is k_{mt}. The overall scavenging rate of HNO_3 is 0.28 s^{-1}; that is, the characteristic time of scrubbing HNO_3 from the gas phase to the aqueous phase is about 4 s.

The concentration of HNO_3 in cloudwater is proportional to k_{mt} and falls off sharply with increasing drop radius. The amount of HNO_3 in each size cut (HNO_3 mass spectrum) is proportional to $d\Lambda/da$. Figure 11 shows the mass spectrum of HNO_3 for various values of α and also, for comparison, the liquid water spectrum.

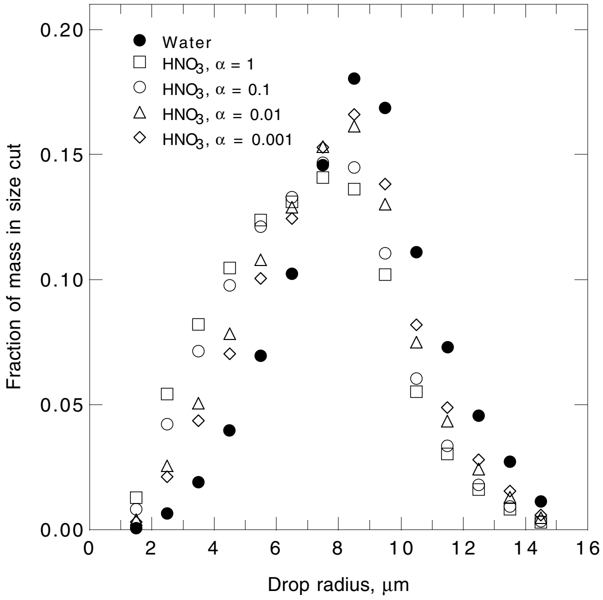


Figure 11. Relative amount HNO_3 in each 1 µm size cut for aged stratus cloud, evaluated for indicated values of α ranging from 0.001 to 1. Liquid water spectrum is shown for comparison.

Despite the strong peaking of k_{mt} at low radii, all of the spectra, including the water spectrum, tend to peak at about the same radius, 8 μm. The similarity of these spectra would make them difficult to distinguish by field measurements.

We consider now the drop-size dependence of the rate of SO_2 oxidation by ozone. Because of the high initial acid concentration in the small drops, the rate will be lower in these drops. Such a drop-size dependent reaction rate has been suggested previously *(20, 23)*. Figure 12 shows the drop-size dependence of the rate of SO_2 oxidation by O_3 in an aged stratus cloud having the drop-size distribution given in Figure 9 and the initial HNO_3 concentration given in Figure 10, corresponding to a pre-cloud HNO_3 mixing ratio of 0.1 ppb. The SO_2 and O_3 mixing ratios are 1 ppb and 30 ppb, respectively, as in Figure 6. Initially (t = 0) the oxidation rate is rather high in the larger drops, which contain a lower HNO_3 concentration, but with increasing time the rate decreases and the spectrum flattens, reflecting the convergence of oxidation rates indicated in Figure 7. By 1 hour the oxidation rate averaged over the drop size distribution is indistinguishable from that which would obtain for a solution having initial HNO_3 concentration equal to the initial HNO_3 concentration averaged over the cloud. Despite this convergence of rates a considerable dispersion of sulfate concentration persists, Figure 13, the large drops exhibiting substantially greater concentration than the small drops. Note also the great difference in the drop-size dependence of concentration compared to HNO_3, Figure, 10. However, as was the case for HNO_3, the spectrum of sulfate mass, Figure 14, remains

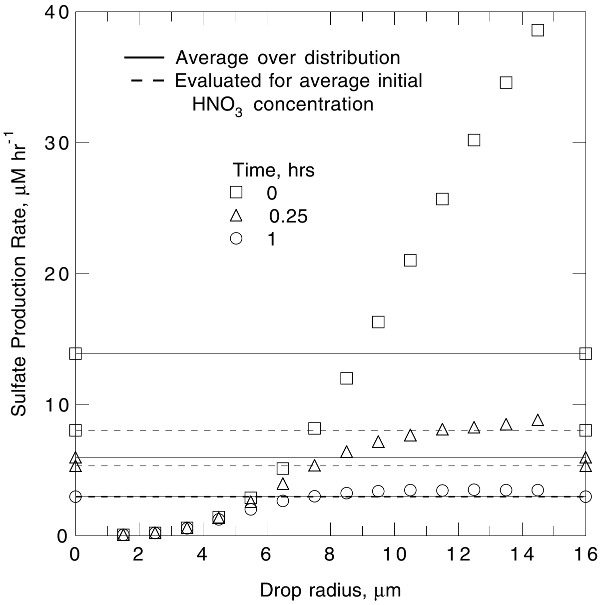


Figure 12. Sulfate production rate as a function of time and drop size for aged stratus cloud (Fig. 9) having initial HNO_3 concentration spectrum of Fig. 10. Solid line represents oxidation rate averaged over drop-size distribution; dashed line represents rate calculated for average initial HNO_3 concentration. SO_2, 1 ppb; O_3, 30 ppb.

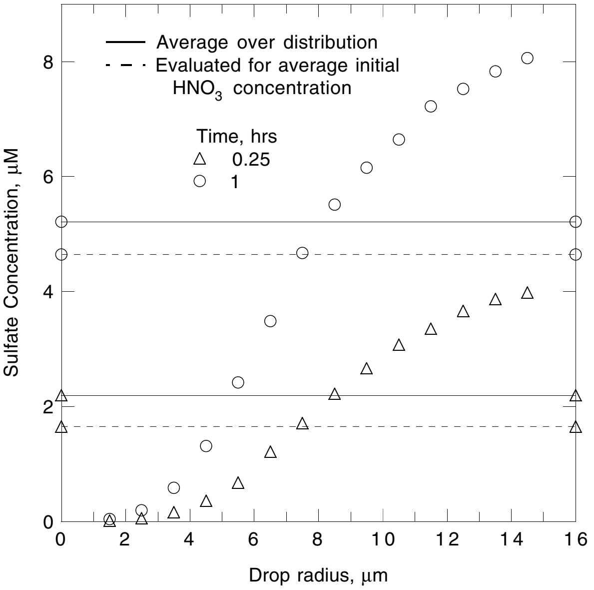


Figure 13. Sulfate concentration as a function of time and drop size for aged stratus cloud, as in Figure 10.

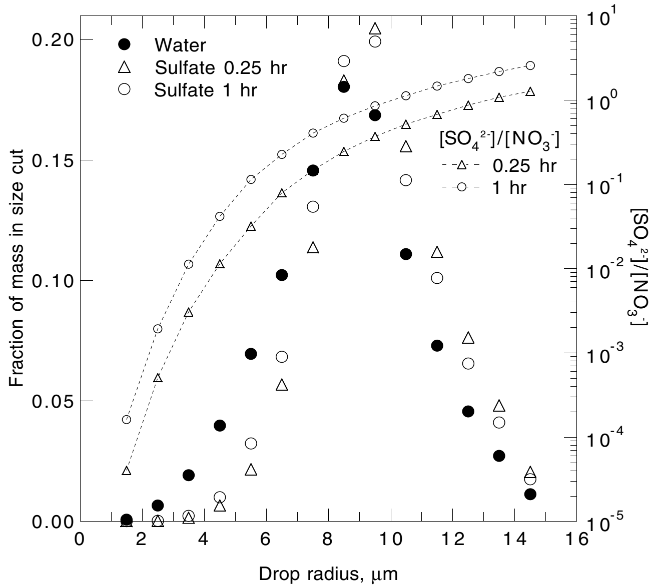


Figure 14. Relative amount sulfate in each 1 μm size cut for aged stratus cloud, corresponding to concentrations in Figure 13. Liquid water spectrum is shown for comparison. Right-hand scale shows ratio of sulfate to nitrate concentrations.

dominated by the influence of the liquid water distribution, peaking at about 9 μm radius, Consequently the similarity of these spectra to the HNO_3 spectra, Figure 11, or to the spectrum of water itself would make them difficult to distinguish by field measurements. In contrast the ratio of sulfate to nitrate concentration or mass varies by four orders of magnitude over the drop-size range, suggesting that this ratio may be a sensitive index in field studies to test model predictions such as these.

5. FIELD MEASUREMENT OF IN-CLOUD CHEMICAL REACTIONS

It is tempting to directly measure chemical reactions in clouds. Possible objectives of such studies might be to empirically determine the extent of reaction under specific conditions and thereby determine the reaction stoichiometry and rate, and the rate expression that gives the dependence of the rate on reagent concentrations, on other chemical variables such as pH, and on physical variables such as liquid-water content, drop-size distribution, temperature, and light intensity. Comparison of measured and modeled quantities would confirm or refute the applicability of models based on laboratory-determined solubility, mass-transport, and kinetic properties, as outlined above.

Here it is useful to consider the analogy to laboratory measurements of chemical reactions. Such studies initially entail determination of reaction stoichiometry, by comparison of changes in concentrations of reagents and products. Reaction rates are determined from the change of concentration with time either directly, or, in a flow tube, as a function of distance with Δ time determined from the flow speed. Both approaches find analogy in field studies. The direct approach is analogous to the Lagrangian approach, in which change in composition of a parcel is examined as a function of time by following the parcel as it is advected in the atmosphere. The flow tube approach is analogous to the steady-state approach in which a composition difference between inflow and outflow of, say, a cap cloud is ascribed to reaction in the cloud.

As with laboratory measurements, the ability to determine the extent or rate of reaction depends on the ability to sensitively measure the composition difference. This in turn depends on the extent of reaction in comparison to measurement uncertainties and, in the case of field measurements, fluctuations in concentrations due to time and space variability of atmospheric composition. Such comparisons were carried out by Kelly et al. *(7)*, who found that oxidation of SO_2 by the H_2O_2 reaction would be sufficiently fast for representative conditions that its extent might be expected to be measurable by field measurements, whereas the extent of the O_3 reaction would not be expected to be measurable.

In addition to measurability of the extent of reaction, there are further issues that must be dealt with in field measurements of in-cloud reactions:

- Changes in composition due to phenomena other than reaction. Apparent concentration changes may occur because of entrainment of air of different composition within the parcel or because of inaccuracy in following the parcel. Both of these would masquerade as a composition change due to reaction and lead to a false measure of the extent of reaction.

- Ascription of composition changes to a specific reaction. Unlike the situation in the laboratory, concentration changes may occur because of multiple reactions occurring in parallel.

- Determining stoichiometry of reaction. Determination of reaction stoichiometry requires measurement of corresponding changes in concentrations of reagents and products. Such measurements are often precluded in the atmosphere because of analytical limitations, e.g., a given change in SO_2 concentration corresponding to a small relative change in O_3 concentration. In contrast to the laboratory situation, initial concentrations cannot be adjusted to make such measurements more feasible.

- Influence of variables that influence reaction rates. Both chemical quantities such as pH, and physical quantities such as liquid-water content, drop-size distribution, temperature, and light intensity may be unknown and/or variable in the clouds under examination. The influence of these variables could be mis-ascribed to other variables in attempts to adduce rate laws from field measurements. Also the limited range of natural variability and the inability to systematically change one variable at a time limits the ability to adduce these dependencies from field measurements.

In view of these considerations, ascribing changes in composition to a given reaction, determining reaction extents or rates, and deducing rate laws from field measurements must be viewed as a not inconsiderable challenge to the field measurement community.

6. CONCLUSIONS

1. Methods exist for readily calculating rates of gas-aqueous reactions in clouds using rate expressions and solubilities derived from laboratory measurements.
2. A substantial body of evidence supports the occurrence of the $SO_2 + H_2O_2$ reaction in clouds at rapid rates consistent with model evaluations.
3. The $SO_2 + O_3$ reaction can be rapid in clouds at $pH > 5$, but is self limiting because of the production of acid.
4. The rate of the $SO_2 + O_3$ reaction may exhibit considerable drop-size dependence, but this dependence will be self-limiting and difficult to discern in spectral studies of cloudwater composition.
5. Determination by field measurements of the extent, stoichiometry, rate, and rate expression of in-cloud reactions must be viewed as a substantial challenge.

Acknowledgment.

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REFERENCES

(1) Daum, P.H. (1988). Processes determining cloudwater composition: Inferences from field measurements. In *Acid Deposition at High Elevation Sites*. Edited by M.H. Unsworth and D. Fowler, pp. 139-153. Kluwer, Dordrecht.

(2) Daum, P.H., Kelly, T.J., Schwartz, S.E., and Newman, L. (1984). Measurements of the chemical composition of stratiform clouds. Atmos. Environ. 18:2671-2684.

(3) Erickson, R.E., Yates, L.M., Clark, R.L., and MacEwen, D. (1977). The reaction of sulfur dioxide with ozone in water and its possible atmospheric significance. Atmos. Environ. 11:813-817.

(4) Goldberg, R.N. and Parker, V.B. (1985). Thermodynamics of solution of $SO_2(g)$ in water and of aqueous sulfur dioxide solutions. J. Res. Natl. Bur. Stand. 90:341-358.

(5) Hoigné, J., Bader, H., Haag, W.R., and Staehlin, J. (1985). Rate constants of reactions of ozone with organic and inorganic compounds in water--III. Water Res. 19:993-1004.

(6) Jacob, D.J. (1986). Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate. J. Geophys. Res. 91:9807-9826.

(7) Kelly, T.J., Schwartz, S.E., and Daum, P.H. (1989). Detectability of acid producing reactions in natural clouds. Atmos. Environ. 23:569-583.

(8) Kirchner, W., Welter, F., Bongartz, A., Kames, J., Schweighoefer, S., and Schurath, U. (1990). Trace gas exchange at the air/water interface: Measurements of mass accommodation coefficients. J. Atmos. Chem. 10:427-449.

(9) Knollenberg, R.G. (1981). Techniques for probing cloud microstructure. In *Clouds--Their Formation, Optical Properties, and Effects*. Edited by P.V. Hobbs and A. Deepak, pp. 15-91. Academic Press, NY.

(10) Lee, Y.-N., Shen, J., Klotz, P.J., Schwartz, S.E., and Newman, L. (1986). Kinetics of the hydrogen peroxide-sulfur(IV) reaction in rainwater collected at a northeastern U.S. site. J. Geophys. Res. 91:13264-13274.

(11) Martin, L.R. (1984). In *SO_2, NO and NO_2 Oxidation Mechanisms: Atmospheric Considerations*. Edited by J.G. Calvert, pp. 63-100. Butterworth, Boston.

(12) Mozurkewich, M., McMurry, P.H., Gupta, A., and Calvert, J.G. (1987). Mass accommodation coefficient for HO_2 radicals on aqueous particles. J. Geophys. Res. 92:4163-4170.

(13) Overton, J.H., Jr. (1985). Validation of the Hoffmann and Edwards' S(IV)--H_2O_2 mechanism. Atmos. Environ. 19:687-690.

(14) Penkett, S.A., Jones, B.M.R., Brice, K.A., and Eggleton, A.E.J. (1979). The importance of atmospheric ozone and hydrogen peroxide in oxidising sulphur dioxide in cloud and rainwater. Atmos. Environ. 13:123.

(15) Schwartz, S.E. (1984). Gas-aqueous reactions of sulfur and nitrogen oxides in liquid-water clouds. In *SO_2, NO and NO_2 Oxidation Mechanisms: Atmospheric Considerations*. Edited by J. G. Calvert, pp. 173-208. Butterworth, Boston.

(16) Schwartz, S. E. (1986). Mass-transport considerations pertinent to aqueous-phase reactions of gases in liquid-water clouds. In *Chemistry of Multiphase Atmospheric Systems*. Edited by W. Jaeschke, pp. 415-471. Springer, Heidelberg.

(17) Schwartz, S.E. (1988). Mass-transport limitation to the rate of in-cloud oxidation of SO_2: Reexamination in the light of new data. Atmos. Environ. 22:2491-2499.

(18) Schwartz, S.E. (1990). Aqueous Phase Reactions. In *Atmospheric processes research and process model development*. State of Science and State of Technology Report No. 2, Vol. 1, National Acid Precipitation Assessment Program, pp. 2-93 to 2-104. Government Printing Office, Washington.

(19) Schwartz, S.E. and Freiberg, J.E. (1981). Mass-transport limitation to the rate of reaction of gases in liquid droplets: Application to oxidation of SO_2 in aqueous solutions. Atmos. Environ. 15:1129-1144.

(20) Seidl, W. (1989). Ionic concentrations and initial S(IV)-oxidation rates in droplets during the condensational stage of cloud. Tellus 41B:32-50.

(21) Shi, B. and Seinfeld, J.H. (1991). On mass transport limitation to the rate of reaction of gases in liquid droplets. Atmos. Environ. 25A:2371-2383.

(22) Tang, I.N. and Lee, J.H. (1987). Accommodation coefficients of ozone and sulfur dioxide: Their implications on SO_2 oxidation in cloud water. In *The Chemistry of Acid Rain: Sources and Atmospheric Processes*. Edited by R.W. Johnson and G.E. Gordon, pp. 109-117, American Chemical Society Symposium Series. Washington, DC.

(23) Twohy, C. H., Austin, P. H., and Charlson, R. J. (1989). Chemical consequences of the initial diffusional growth of cloud droplets: a clean marine case. Tellus 41B:51-60.

(24) Worsnop, D.R., Zahniser, M.S., Kolb, C.E., Gardner, J.A., Watson, L.R., Van Doren, J.M., Jayne, J.T., and Davidovits, P. (1989). Temperature dependence of mass accommodation of SO_2 and H_2O_2 on aqueous surfaces. J. Phys. Chem. 93:1159-1172.