Both Sides Now

The Chemistry of Clouds[a]

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INTRODUCTION

The past several years have seen considerable research effort directed toward examination of the chemistry of clouds. Much of the motivation for undertaking such studies has arisen from concern over the so-called "acid rain" phenomenon and the desire to understand the role of clouds in the transport, transformation, and delivery to the earth's surface of pollutants involved in acid deposition. Cloud chemistry is thus of interest in this context not only because clouds are the source of precipitation, but also because of the possibility that clouds may represent an important medium for chemical reaction in the atmosphere.

This article is an account of research on cloud chemistry that has been conducted over the past several years, with examples taken principally from work carried out by myself and my colleagues at Brookhaven National Laboratory. In carrying out this research, we have followed a two-sided approach:

(1) Laboratory studies of the thermodynamics and kinetics of processes involved in cloudwater acidification, and

(2) Field measurements directed to determination of cloud composition and elucidation of the mechanisms by which this composition is established. The title of this article refers to the two "sides" of our approach to the study of this chemistry and is taken from the popular song, "Both Sides Now" by Joni Mitchell[1] whose refrain begins "I've looked at clouds from both sides now."

BACKGROUND

Since the impetus for research into cloud chemistry is the presumed role of clouds in the acid deposition process, it seems worthwhile briefly to review

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this process in order to place the cloud chemistry research in a context. Much more exhaustive accounts of the present understanding of the acid deposition process have been given in the report of a National Academy of Sciences panel chaired by Calvert,[2] in a compilation of review papers edited by Altshuller,[3] and in the report of the U.S.-Canada Work Group on Transboundary Air Pollution.[4] For a historical account of acid precipitation studies see Cowling.[5] A brief but insightful description of the overall process of acid deposition and the implications of acid deposition research on control strategies has been given by Gordon.[6]

A schematic representation of the subprocesses involved in the overall acid deposition process is shown in FIGURE 1. In brief these subprocesses are:

- Emission of acid precursors, mostly SO_2 and NO, into the atmosphere. These species are emitted largely as byproducts of combustion reactions: SO_2 from oxidation of sulfur in fuel; NO from oxidation of nitrogen in fuel or from partial oxidation of atmospheric N_2. Noncombustion emissions of SO_2 (e.g., from metal smelting) are also substantial in some regions. Natural emissions of SO_2 and NO_x (NO_x refers to the sum of NO plus NO_2) are substantially less than anthropogenic emissions, except in regions of very low industrial activity.[7]
- Transport of acidic and related pollutants in the atmosphere. Transport processes include motion with the mean wind, vertical motion, motion brought about by clear-air convective processes or associated with storms, and mixing processes.
- Transformations – processes altering the chemical or physical state of acidic pollutants and related substances. These processes include both chemical reactions (e.g., oxidation of SO_2 and nitrogen oxides to higher oxidation state acids) and physical processes (e.g., aerosol formation, dissolution of gaseous species by atmospheric liquid water, and coagulation of aerosol particles on cloud droplets).
- Deposition – the delivery of acidic pollutant to the earth's surface. This deposition is conveniently distinguished into two categories: wet deposition, the delivery of dissolved materials in precipitation, principally rain and snow; and dry deposition, the loss of gaseous or aerosol materials to the surface of the earth in the absence of precipitation. For gases the dry deposition process consists of turbulent transport followed by molecular diffusion across a laminar sublayer. For materials present in aerosol particles dry deposition processes include inertial impact and gravitational settling in addition to Brownian diffusion. It might be observed that the distinction between wet and dry deposition is somewhat arbitrary; Lovett *et al.*[8] have noted that impaction of cloud droplets to mountainous terrain represents a major fraction of both the water budget and pollutant deposition at such sites.

The foregoing subprocesses represent the phenomena that must be included in the description of the overall acid deposition process. It is toward elucidation of these phenomena that much of the current research into acid deposition is directed, the overall objective being an improved description of the relation between emissions of these materials and the location and amount of deposition attributable to these sources.

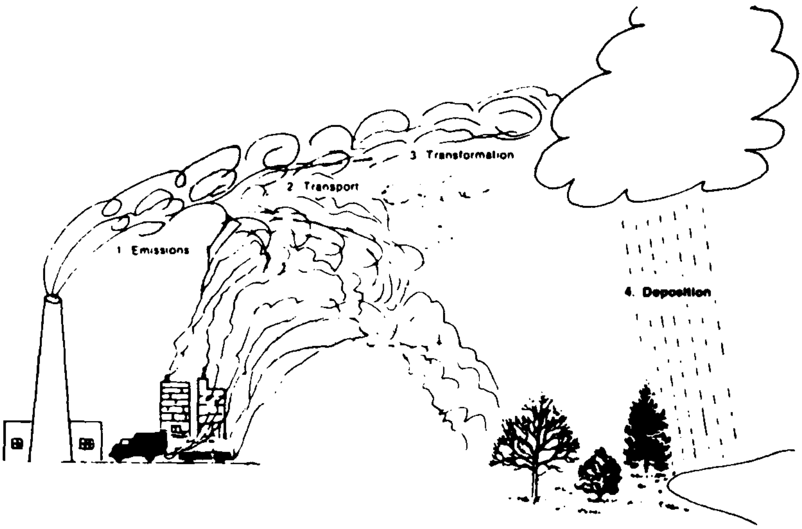


FIGURE 1. Schematic diagram of components of overall process of acid deposition.

It may be noted that while deposition of acidic pollutants represents the end of the process of concern to atmospheric science, it represents the beginning of a second major focus of acid precipitation research, namely research into the effects of deposition of acidic pollutants on biological systems, including human health effects, and, as well, effects on man-made materials. Detailed accounts of current understanding of such effects are given in a compilation of review papers edited by Linthurst,[9] in a report of a United States-Canada work group on trans-boundary air pollution[10] and in a National Research Council Report.[11] A brief resumé of health and environmental consequences of acid fog has been given by Hoffmann.[12]

As may be inferred, there is considerable ongoing research into all aspects of acid deposition. Attention is called to listings of such ongoing research in the public[13] and private[14] sectors.

Precipitation Composition

It is useful briefly to consider precipitation composition as a basis for comparison of cloud composition and also insofar as precipitation represents a major deposition mode of acidic pollutants. Considerable effort has been devoted over the past several years to documentation of the concentrations of major ionic species in precipitation. It should be noted that while the concentration of ionic species in precipitation is highly variable from storm to storm and even within storm events,[15] nonetheless a rather smooth geographic pattern of concentrations is observed for sufficiently long averaging periods, e.g., seasonal or yearly. Examples of such patterns in North America are shown

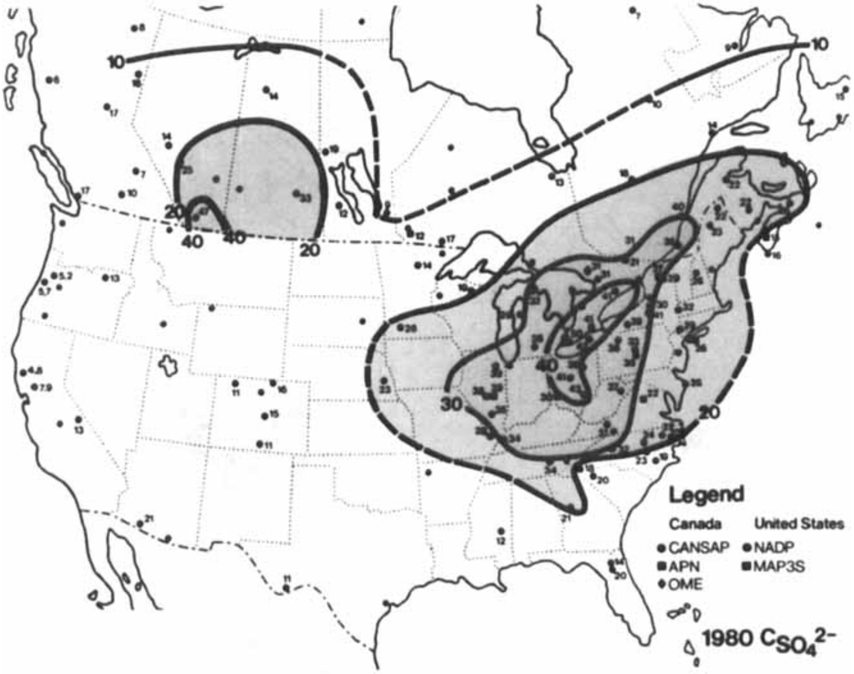


FIGURE 2. Mean concentration (μmol/liter) of sulfate ion in precipitation in North America for 1980, weighted by precipitation amount. (From the United States–Canada Memorandum of Intent on Transboundary Air Pollution. Reprinted by permission.)

in FIGURES 2–5.[10] Concentrations are peaked in the region of the United States east of the Mississippi River and north of the Ohio River corresponding to the region of maximum emission of sulfur and nitrogen oxide precursors. It may be noted that the concentrations of sulfate and nitrate in the regions in which acidic precipitation has its greatest impact exceed those in regions less affected by an order of magnitude or more. It is interesting to note that on a molar basis the deposition of sulfate and nitrate in this region is roughly equal; this equality is roughly matched in emissions of the precursor oxides. Total sulfate plus nitrate concentration (equivalents per liter) is roughly equalled by total hydrogen ion plus ammonium ion; other cations, usually present to a much lesser extent, include calcium and magnesium. Thus precipitation in the northeast United States is seen to consist of a dilute solution of sulfuric and nitric acid, partially neutralized by atmospheric ammonia. The extent of neutralization may be inferred from the ratios of the ionic concentrations to be ~25% in much of the northeastern United States. This is further illustrated in FIGURES 6 and 7,[16] which are frequency distributions of the fractional acidity, $[H^+]/([NO_3^-] + 2[SO_4^=])$, in precipitation samples collected by event. It is seen that the peaks of the distributions represent a 30% neutralization, although substantial variance exists about such a value. We shall return to

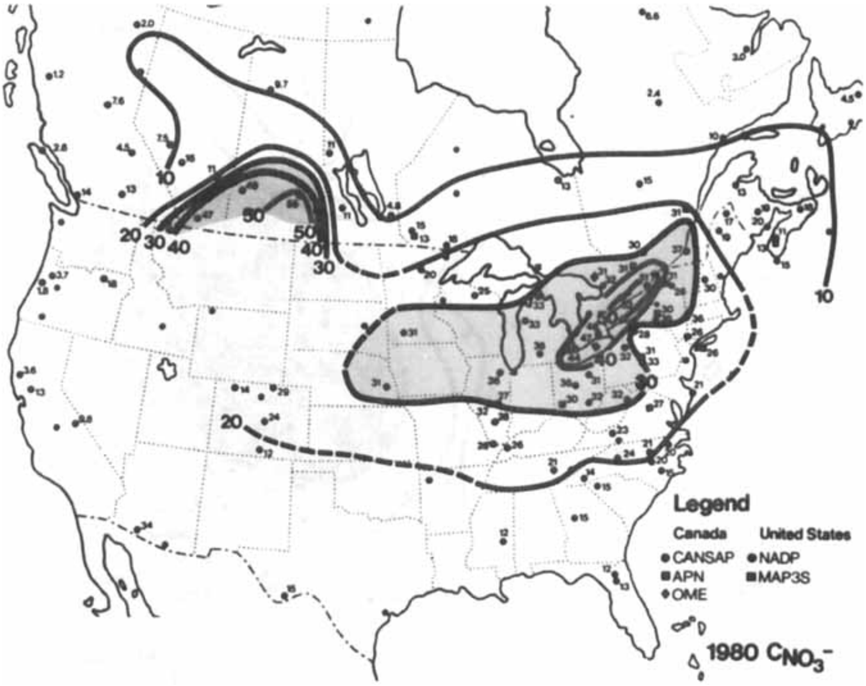


FIGURE 3. Mean concentration (μmol/liter) of nitrate ion in precipitation in North America for 1980, weighted by precipitation amount. (From the United States – Canada Memorandum of Intent on Transboundary Air Pollution. Reprinted by permission.)

consideration of the fractional acidity of rainwater as a point of comparison for cloudwater samples.

One further point of interest in consideration of rain composition is the absolute concentration in comparison to emissions of sulfur and nitrogen oxides. Emissions of sulfur and nitrogen oxides for the region of the United States east of the Mississippi River and north of (and including) Tennessee and North Carolina are given in Table 1. In order to compare emissions with wet deposition, an average composition of precipitation is evaluated assuming that the entire emissions of these species are dissolved in an annual rainfall amount of 100 cm. It is seen that the spatial-average annual deposition of $SO_4^=$, NO_3^-, and H^+ evaluated in this way substantially exceeds (by a factor of perhaps 4 or 5) the magnitude of wet deposition of these species indicated in Figures 2–4. The fate of the fraction of sulfur and nitrogen oxides not deposited in precipitation in this region is not known in detail, but undoubtedly consists primarily of dry deposition and of deposition outside this region.

Transformation Pathways

Returning to consideration of processes responsible for acid deposition,

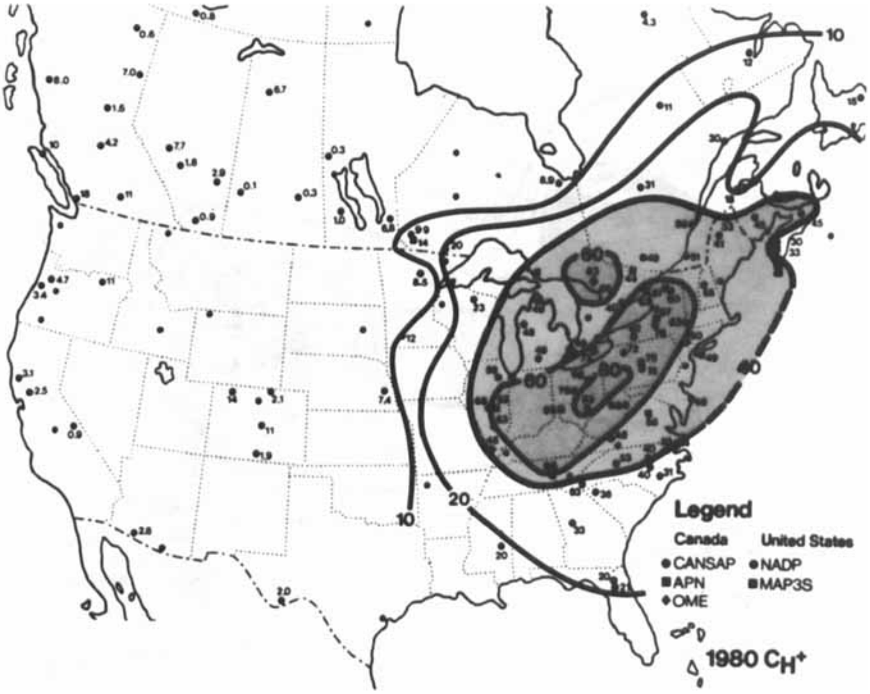


FIGURE 4. Mean concentration (μmol/liter) of hydrogen ion in precipitation in North America for 1980, weighted by precipitation amount. (From the United States—Canada Memorandum of Intent on Transboundary Air Pollution. Reprinted by permission.)

we first observe that the overall process of transformation of sulfur dioxide and nitrogen oxides to sulfuric and nitric acid present in and delivered in precipitation consists of two components: a chemical process, namely the oxidation of the relatively insoluble, lower-oxidation-state oxides initially present in the gas phase to the highly soluble acids; and the physical process of uptake of the gaseous species by cloud- or rainwater. It is thus useful conceptually to distinguish two pathways for this process. These are indicated in FIGURE 8 and are distinguished by the phase in which oxidation takes place, namely the gas phase or aqueous-solution phase. The overall process consists of going from the initially emitted gaseous oxides (upper left on the figure) to the dissolved acids (lower right). We denote the gas-phase path as that consisting of gas-phase oxidation followed by uptake of the high-oxidation-state oxide or acid by cloud- or rainwater, i.e., right and then down on the figure. The aqueous-phase path consists first of dissolution of the oxide followed by aqueous-phase oxidation. Much of our research and that of a number of other groups concerned with the mechanism of acid deposition has been directed to elucidation of the contributions of these two pathways to the overall process. One point that should perhaps be explicitly mentioned here is that in

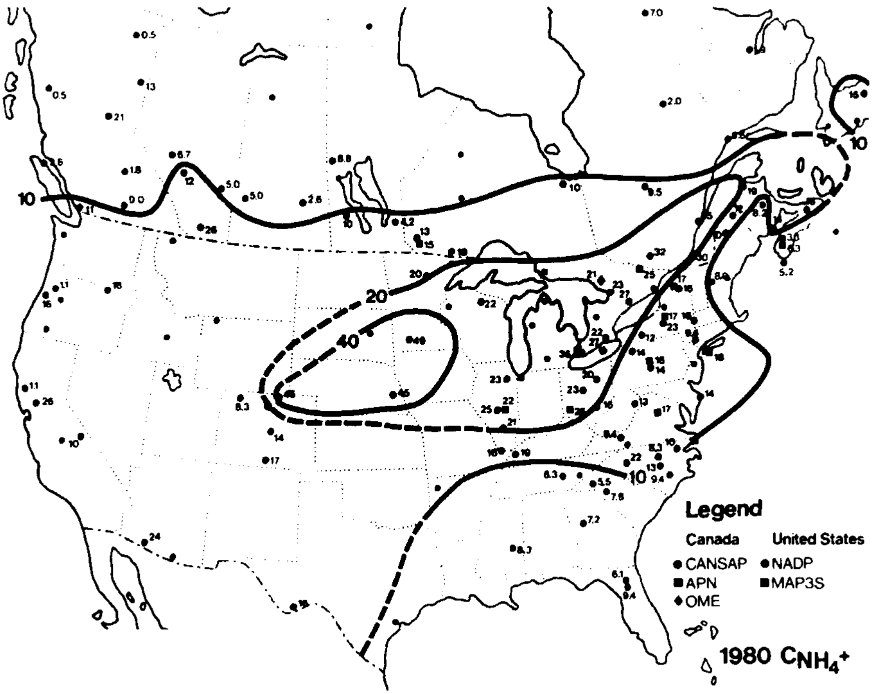
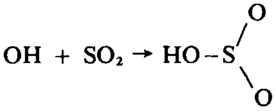


FIGURE 5. Mean concentration (μmol/liter) of ammonium ion in precipitation in North America for 1980, weighted by precipitation amount. (Form the United States—Canada Memorandum of Intent on Transboundary Air Pollution. Reprinted by permission.)

the presence of atmospheric O_2, and all the more so in the presence of oxidant species such as O_3 and H_2O_2, there is strong thermochemical driving force for oxidation of SO_2 and NO_X to the high-oxidation-state acids. The question that must be addressed is therefore not one of chemical equilibrium, but rather of the mechanism and rate whereby the initially emitted oxides are transformed to the acids that are deposited in precipitation.

Of the two pathways for this oxidation that have been outlined here, the gas-phase pathway is much the better understood, the various gas-phase reactions having received much study in a number of laboratories. For a recent review of present understanding see Calvert.[17] A brief synopsis of important gas-phase oxidation reactions of SO_2 and nitrogen oxides is given here.

First, with respect to SO_2, the principal gas-phase oxidation reaction appears to be initiated by the addition of free radical OH,



$$OH + SO_2 \rightarrow HO{-}S\begin{matrix}{}^{/}O \\ {}_{\backslash}O\end{matrix} \qquad [1]$$

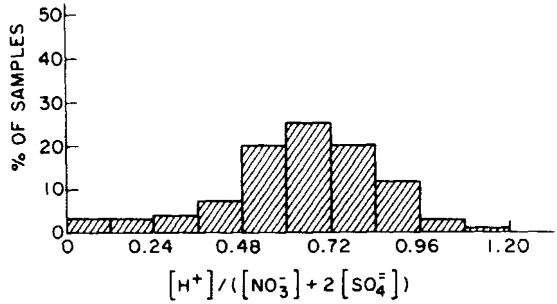
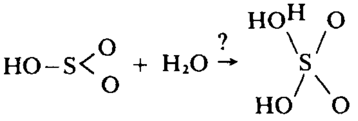


FIGURE 6. Fractional acidity in precipitation samples by event at Brookhaven National Laboratory for the years 1977 to 1981. (From Daum.[16] Reprinted by permission.)

The intermediate $HOSO_2$ is itself a free radical and is presumed to lead with high yield to SO_3 or H_2SO_4. A possible reaction sequence, based on recent work of Stockwell and Calvert[18] is:



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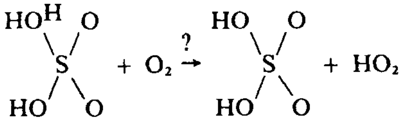

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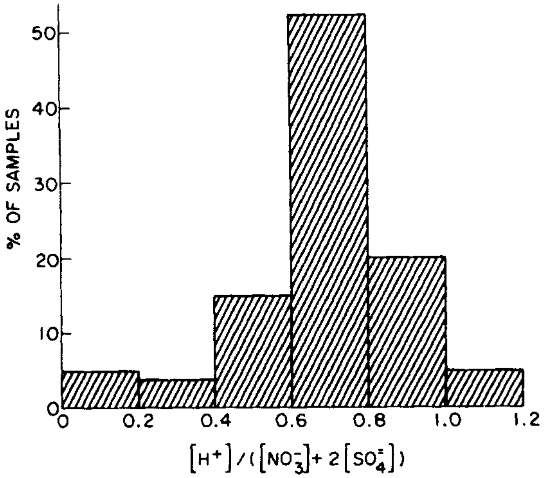

FIGURE 7. Fractional acidity in precipitation samples by event at Lewes, Deleware, summer 1980. (From Daum.[16] Reprinted by permission.)

TABLE 1. Emissions and Maximum Wet Deposition in the Northeastern United States[a]

	SO_2	NO_x	Acid Equivalents[b]
Emissions[c] (mol/yr)	2.4×10^{11}	2.0×10^{11}	6.8×10^{11}
Area (km^2)	- - - -	1.4×10^6	- - - - -
Precipitation amount (cm/yr)	- - - -	100	- - - - -
Precipitation volume (liter/yr)	- - - -	1.4×10^{15}	- - - - -
Average concentration[d] (µmol/liter)	170	140	480

[a] East of Mississippi River and north of (and including) Tennessee and North Carolina.
[b] $NO_x + 2 \times SO_2$.
[c] Reference 7.
[d] Under assumption that all emissions are deposited in precipitation in the region.

The gaseous sulfuric acid product is unstable to formation of an aerosol and apparently readily either adds to existing aerosol particles or nucleates with water vapor to form new aerosol particles. On the basis of the rate constant k_1 for reaction [1] and estimates of representative average OH radical concentration $[(1-2) \times 10^6 \text{ cm}^{-3}]$, the average rate of SO_2 oxidation by this path is perhaps 0.5 to 1% hr^{-1} (Ref. 17), and a rate of this magnitude is consistent with inferences based on field measurements of SO_2 oxidation in various point-source plumes.[19]

Gas-phase atmospheric oxidation of nitrogen oxides is similarly rather well understood. We have noted above that the principal nitrogen oxide emitted as a combustion byproduct is nitric oxide, NO, with nitrogen dioxide, NO_2, present as a relatively minor component. The gas-phase oxidation of NO to NO_2 is strongly coupled to ozone chemistry, which has been the object of much

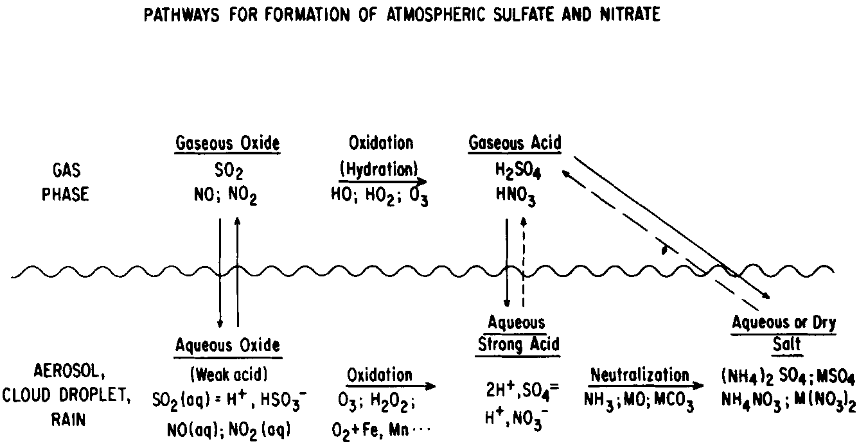

FIGURE 8. Schematic representation of pathways for atmospheric formation of sulfate and nitrate. (From Schwartz.[41])

study as an environmental concern in its own right.[20] Without reviewing that chemistry, suffice it to say that the gas-phase oxidation of NO to NO_2 is a fairly rapid process, taking place on a time scale of one to several hours, depending on the amount of O_3 present and/or on the extent of photochemical activity in the system. The extent of conversion of NO to NO_2 depends as well on insolation, since photolysis of NO_2 sets up a steady-state NO concentration. However, except in areas rather strongly influenced by local source emissions, NO_2 is the dominant of the two species.[21]

Gas-phase oxidation of NO_2 to nitric acid can take place by OH addition, similar to the situation described above for SO_2,

$$OH + NO_2 \rightarrow HONO_2 \qquad [4]$$

In this case the reaction appears to be a simple addition reaction without complication of subsequent steps. The rate of NO_2 oxidation by reaction [4] for estimated representative OH concentrations is perhaps 5 to 10% hr^{-1}, roughly an order of magnitude greater than the SO_2 oxidation rate.[17] In contrast to H_2SO_4, HNO_3 can remain present in the atmosphere as a gas-phase species. However, in the presence of substantial amounts of liquid water (as in clouds) and *a fortiori* in the presence of basic material (e.g., NH_3) nitric acid vapor is efficiently taken up by the condensed phase.[22,23]

The foregoing process involving the photochemically generated free radical species OH, is, of course, essentially entirely a daytime process. An alternative process [24-28] that does not require photochemically generated free radicals consists of reaction of NO_2 with O_3,

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad [5]$$

followed by addition of NO_3 to NO_2 to form N_2O_5

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad [6]$$

N_2O_5 is thought to react rapidly with liquid water to form nitric acid

$$N_2O_5 + H_2O(l) \rightarrow 2HNO_3(aq) \qquad [7]$$

(The corresponding reaction of N_2O_5 with water vapor proceeds only quite slowly or perhaps not at all.[29]) The maximum rate of NO_2 oxidation by this route, evaluated under assumption that reactions [6] and [7] proceed with unity yield for each occurrence of [5], is $2k_5p_{O_3}$. For ozone partial pressure equal to 30 ppb, this rate is about 15% hr^{-1}. Complete description of the reaction must take into account the reversibility of reaction [6],

$$N_2O_5 \rightarrow NO_3 + NO_2 \qquad [-6]$$

as well as competing reactions of NO_3 that do not yield N_2O_5, e.g.,

$$NO_3 \xrightarrow{h\nu} NO + O_2 \text{ or } NO_2 + O \qquad [8]$$

and

$$NO_3 + NO \rightarrow 2NO_2 \qquad [9]$$

Both of these reactions will be more important under daytime conditions than nighttime ones, and thus the sequence [5]–[7] would appear to be a more important process for acid formation at nighttime rather than daytime, thus complementing the OH addition reaction [4]. However, comparison of chemical reaction rates with mass-transport rates governing uptake of gases by cloud droplets[30] suggests that the sequence [5]–[7] may be significant even under daytime conditions.

In contrast to the fairly well-developed understanding of the gas-phase paths, understanding of the aqueous-phase path has been rather less well developed. Reasons for thinking that aqueous-phase oxidation of sulfur and nitrogen oxides in clouds may be important include the strong thermodynamic driving force for such reactions, the high liquid water content of clouds (providing a medium for reaction), high surface-to-volume ratio (promoting interphase mixing), long residence times (permitting time for reactions to proceed significantly), and the prevalence of clouds in the atmosphere. The lack of ability to describe oxidation reactions of sulfur and nitrogen oxides in clouds, which has been described as the "missing link" in our understanding of the chemistry of acid rain formation,[31] has been the impetus behind the work in our laboratory over the past several years directed at elucidation of these processes.

Cloud Properties

Before describing research about chemical reactions in clouds, it is useful to review some of the physical properties pertinent to the uptake and reaction of acidic species. Properties of concern include the liquid-water content, which represents the volume available for aqueous-phase reaction, and the size of drops making up the cloud, which governs the mass-transport rate. For a more complete description of the microphysical properties of clouds reference is made to monographs by Pruppacher and Klett,[32] Mason,[33] and Rogers.[34] A very readable account of the role of clouds in the earth's hydrologic cycle is given by McDonald.[35] In brief: a cloud is a supersaturated suspension of liquid or solid water particles in air. Here "supersaturated" means that the partial pressure of water vapor exceeds the equilibrium partial pressure at the temperature of the cloud; the amount of this supersaturation is quite small, generally a fraction of a percent. Clouds may consist of solid water (i.e., ice) or liquid water. At temperatures above 0°C, of course, clouds consist entirely of liquid water (so-called "warm" clouds). However, liquid water droplets may persist in clouds to temperatures well below 0°C (supercooled clouds). Mixed ice and water clouds can maintain a temperature of 0°C over quite a large volume.[36] From the perspective of cloud chemistry our interest is focused on liquid water clouds because of the ability of liquid water droplets to serve as a medium for chemical reaction.

The most notable characteristic of a cloud is, of course, the presence of condensed-phase water, for it is this property of a cloud that makes it visible.

In an absolute sense, however, the amount of condensed-phase water that is present in a cloud is invariably quite small, typically 0.1 to 1 gram per cubic meter; since the density of liquid water is approximately 1 gram per cm^3, we see that the fraction of volume of the cloud that is occupied by liquid water is in the range 0.1 to 1 parts per million (0.1 to 1 cm^3/m^3, or liquid water volume fraction $L = 0.1$ to 1×10^{-6}). That is, clouds are mostly air! The air between the cloud droplets is denoted the "interstitial" air (i.e., in the interstices between the cloud droplets), although, in view of the fact that the cloud droplets are few and far between, this is a bit of a misnomer. The interstitial air is important in cloud chemistry as the reservoir of gaseous species that may react in the aqueous phase of the cloud. Despite the low fraction of total cloud volume occupied by liquid water, it is important to note in the context of clouds serving as the medium for aqueous-phase reaction that this liquid water content is nonetheless some three to five orders of magnitude greater than that associated with clear-air aerosol.[37]

The amount of water vapor in a cloud is closely approximated by the saturation water vapor content, which is shown as a function of temperature in FIGURE 9. It is seen that over the temperature range 0 to 25°C the saturation water vapor content substantially exceeds the amount of liquid water present in the cloud.

An important feature of clouds is the fact that the liquid water contained in them is in a high state of dispersion. This is illustrated schematically in FIGURE 10, which depicts the sizes of drops characteristic of clouds and of rain. Also indicated for comparison is a typical clear-air aerosol particle that may serve as a nucleus for cloud droplet formation or, alternatively, may remain present in the interstitial cloud air as an unactivated aerosol particle. As may be inferred from FIGURE 10, the drops within a cloud are not all of a single size, but exhibit a range of sizes. FIGURE 11 shows a spectrum of number

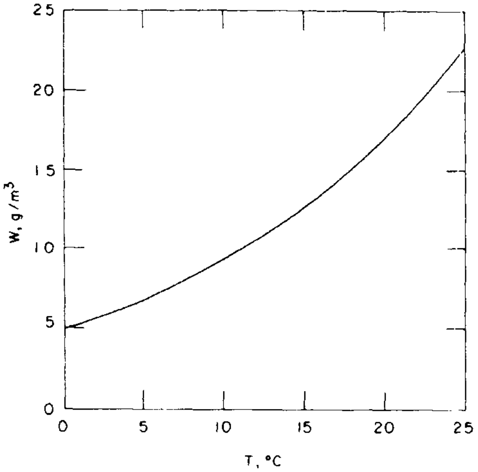

FIGURE 9. Saturation water vapor content of air as a function of temperature.

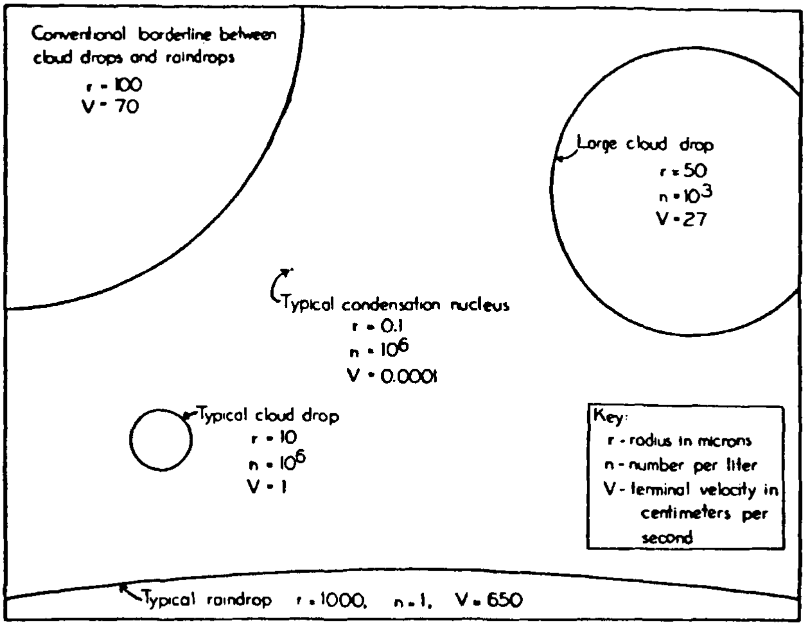

FIGURE 10. Comparative sizes, concentrations, and terminal fall velocities of some particles involved in condensation and precipitation processes. Note for comparison an aerosol particle that serves as nucleus for cloud droplet formation. (From McDonald.[35] Reprinted by permission of Academic Press, Inc.)

of drops as a function of drop radius for a stratus cloud; the sum of drop number density taken over all drop sizes represents the total number density of drops in the cloud, in this instance about 300 cm^{-3}. Also shown is the distribution of liquid water content within the cloud as a function of drop size; the sum of partial water content taken over all drop sizes represents the total liquid water content. In this example the fraction of the total volume occupied by liquid water, L, is about 0.3×10^{-6}.

The question arises: How does a cloud come to exist? It might be observed that a cloud is unstable thermodynamically with respect to a single large drop, in view of the excess free energy associated with the large amount of surface area. In brief answer to a complicated question, cloud formation is a consequence of cooling that results in the actual water vapor content exceeding the equilibrium value. Such a situation most commonly arises from the lifting of an air parcel and the resulting cooling as the rising parcel expands and thereby adiabatically performs work on its surroundings. Alternatively, as in fogs, a vapor-laden air parcel may come into contact with a colder surface. In response to the supersaturation of water vapor, condensation of water takes place on available existing aerosol particles; these particles consist largely of solutions of salts or partially neutralized acids that had been present in clear air prior to cloud formation. The fraction and size distribution of these aerosol parti-

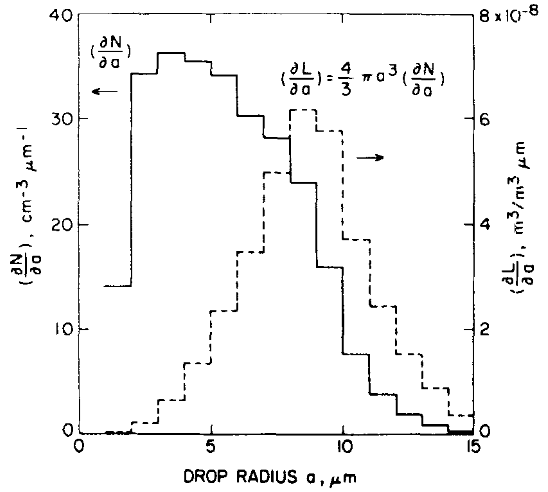

FIGURE 11. Spectra of droplet number density and liquid water volume fraction for aged stratus cloud. $N = 300\ \mathrm{cm}^{-3}$; $L = 0.34 \times 10^{-6}$. (From Schwartz[30] on the basis of data from Knollenberg.[38])

cles that become activated into cloud droplets depend rather sensitively on the rate of cooling and on other properties of the condensing cloud. In any event, despite the thermodynamic instability of a cloud there is little mechanism for interaction of the cloud droplets, and the dispersion is quite stable. It might be observed that the characteristic ratio of interdrop distance to drop dimension is of order $L^{-1/3}$, where L is the liquid-water volume fraction; for $L = 1 \times 10^{-6}$ the characteristic interdrop spacing is 100 times the drop dimension. Cloud droplets can thus to good approximation be treated as noninteracting entities. Coalescence of cloud droplets into rain drops occurs for the most part only by the mechanism of scavenging of smaller drops by larger drops that have acquired an appreciable gravitationally induced fall velocity.

A trivial but important consequence of the low liquid water volume fraction of clouds upon cloud chemistry is the high degree of concentration that results upon dissolving a gaseous species in the aqueous phase. Consider a gaseous species X initially (prior to uptake by cloudwater) having a partial pressure p_X. If this species were to dissolve entirely in cloudwater having volume fraction L, the resulting concentration would be given by

$$[X] = p_X/L\underset{\sim}{R}T, \tag{1}$$

where $\underset{\sim}{R}$ is the universal gas constant and T is the absolute temperature. (For p_X in atmospheres (atm) and [X] in moles per liter (M), $\underset{\sim}{R}T \approx 25\ \mathrm{atm\ M^{-1}}$). It is seen that even a rather low initial partial pressure p_X may lead to a rather high aqueous-phase concentration. Thus for $p_X = 1 \times 10^{-9}$ atm (1 ppb) and $L = 1 \times 10^{-6}$ ($1\ \mathrm{cm^3/m^3}$), $[X] = 40\ \mu\mathrm{M}$.

LABORATORY STUDIES OF CLOUD CHEMISTRY

In this section I outline information that can be derived from laboratory studies that is pertinent to cloud chemistry and review some of this work pertinent to aqueous-phase reactions of SO_2 and NO_2 in clouds. Specifically the objective of such laboratory studies is to determine the fundamental physical and chemical properties necessary to evaluate the rate and extent of gas-aqueous reactions in clouds, based upon measured or modeled reagent concentrations and cloud properties. These fundamental physical and chemical properties include:

- overall chemical equilibrium;
- solubilities of reagent gases;
- mass-transport coefficients; and
- aqueous-phase reaction mechanisms and kinetic rate laws.

These properties are defined and described here with particular reference to the cloud chemistry of SO_2 and NO_2.

Chemical Equilibria

At the outset we might mention, as was noted above, that in an atmosphere containing O_2 and liquid water, there is a strong thermochemical driving force for reaction of SO_2 and NO_2 to sulfuric and nitric acids, respectively, and this driving force is all the stronger in the presence of strong oxidants such as O_3 or H_2O_2. However, it must be stressed that while thermochemical driving force is a necessary condition for reaction to proceed, it is not sufficient. This was emphasized by Lewis and Randall in their 1923 monograph *Thermodynamics*[39] in a passage that remains very appropriate to those of us who are engaged in the study of gas-liquid reactions in the ambient environment:

> We see from the large negative free energy of formation of nitric acid that it should be producible directly from its elements. Even starting with water and air, we see by our equations that nitric acid should form until it reaches a concentration of about 0.1 M where the calculated equilibrium exists. It is to be hoped that nature will not discover a catalyst for this reaction, which would permit all of the oxygen and part of the nitrogen of the air to turn the oceans into dilute nitric acid.

While one shares the wish expressed here that nature not discover such a catalyst, one cannot help noting that should one discover such a catalyst it would be extraordinarily valuable in view of the large industrial usage of nitric acid. (For a delightful account of the history of nitric acid manufacture and of its present industrial manufacture and usage one is referred to the monograph of Chilton.[40]) In any event the foregoing passage from Lewis and Randall serves as a warning that one should not rely solely on thermochemical driving force as a basis for inferring reaction rates, a warning to which we shall return later. (On a longer — geological — time scale one must still face the question why N_2 persists in the atmosphere. As noted by Stedman and Shetter,[21] the presence and maintenance of N_2 in the earth's atmosphere must be attributed to geologic processes.)

Gas Solubilities

The reversible dissolution of a nonreacting gas in a liquid generally obeys a limiting law, valid in the limit of low partial pressure of the gas, that the concentration of the dissolved gas in equilibrium with the gas phase is proportional to the partial pressure of the gas. We denote this proportionality by

$$[X] = H_X \, p_X \tag{2}$$

where [X] represents the liquid-phase concentration of the dissolved gas, p_X represents the partial pressure, and H_X is the proportionality constant. Equation (2) is denoted Henry's law, and H_X the Henry's law coefficient. It should be noted that a variety of units are employed for Henry's law coefficient and, as well, that the sense of the proportionality is often reversed. Consequently care must be exercised whenever Henry's law coefficients are encountered. We have adopted the convention that partial pressures are expressed in units of atmospheres (atm) and solution concentrations in units of moles per liter (M), whence the Henry's law coefficient has units M atm^{-1}. Specializing to aqueous solutions, we observe that H_X represents the equilibrium constant of the reaction

$$X(g) = X(aq)$$

for standard states taken as 1 atm and 1 M. We observe further that the Henry's law coefficient is related to the free energy of dissolution in the usual way for any equilibrium constant,

TABLE 2. Henry's Law Coefficients of Some Atmospheric Gases Dissolving in Liquid Water[a]

Gas	H (M atm^{-1})
O_2	1.3(−3)[b]
NO	1.9(−3)
C_2H_4	4.9(−3)
NO_2[c]	1 (−2)
O_3	1.3(−2)
N_2O	2.5(−2)
CO_2[d]	3.4(−2)
SO_2[d]	1.3
CH_3ONO_2[e]	2.6
PAN[c,e]	3.6
HNO_2	4.9(1)
NH_3[d]	6.2(1)
H_2CO	6.3(3)
H_2O_2	1 (5)
HNO_3[d]	2.1(5)

NOTE: Adapted from Reference 41; PAN and CH_3ONO_2 are from Ref. 42.

[a] T = 25°C except as noted.

[b] The notation 1.3(−3) represents 1.3 × 10^{-3}.

[c] Physical solubility; reacts with liquid water.

[d] Physical solubility, i.e., exclusive of acid-base equilibria.

[e] T = 22°C.

$$H_x = \exp(-\Delta G_{sol}/RT) \tag{3}$$

For gases which dissolve nonreactively Henry's law coefficients may be determined by saturating the solution and measuring the dissolved gas concentration and the gas-phase partial pressure. For Henry's law coefficients of some atmospheric gases see TABLE 2.

In the case of a gas such as SO_2, which undergoes partial and reversible aqueous-phase reaction,

$$SO_2(aq) \overset{H_2O}{=} H^+ + HSO_3^- \qquad [10]$$

both the Henry's law coefficient and the first dissociation constant of sulfurous acid K_{a1} may be determined by suitably varying the gas-phase partial pressure and/or altering the H^+ concentration of the solution with a nonvolatile acid.[43] The pH dependence of the total solubility (i.e., undissociated and ionic forms) of several atmospheric acids and NH_3 is shown in FIGURE 12. This solubility may be represented by an effective Henry's law coefficient, H^*, which is useful if the aqueous solution is sufficiently well buffered that the dissolution of the gas in question does not greatly alter the pH. These effective Henry's law coefficients are conveniently denoted by the oxidation number of the species in question. Thus $H^*_{S(IV)}$ represents the equilibrium ratio of total

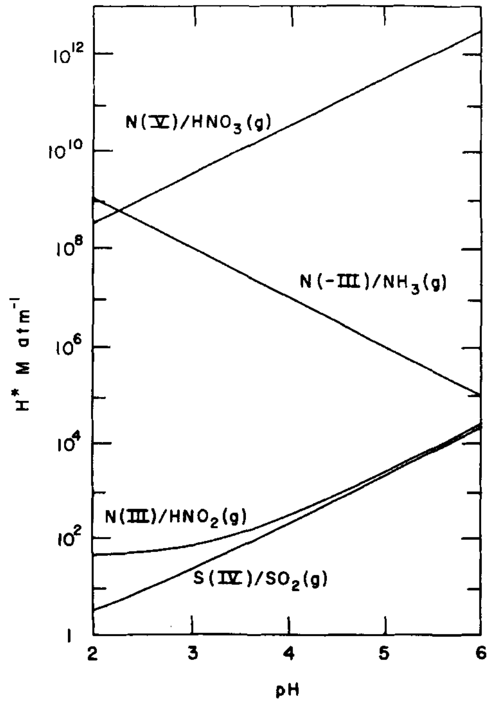

FIGURE 12. Effective Henry's law coefficients for gases that undergo rapid acid-base dissociation reactions in aqueous solution, as a function of solution pH. Buffer capacity of solution is assumed to greatly exceed incremental concentration from uptake of indicated gas. (From Schwartz.[41])

sulfur(IV) concentration, $[S(IV)] \equiv [SO_2(aq)] + [HSO_3^-] + [SO_3^{=}]$, to SO_2 partial pressure.

In the case of gases such as NO_2, which react rapidly and irreversibly in liquid water, the Henry's law coefficient cannot be determined by a direct approach. In such cases Henry's law coefficients may be determined by means of thermochemical cycles and/or from kinetic studies, as discussed below.

It is useful to consider the distribution of material in a cloud between gas and aqueous phases under Henry's law equilibrium. The ratio of material in solution to that in the gas phase within a given volume of a cloud is

$$\frac{C(aq)}{C(g)} = \frac{L[X]}{P_X/\underset{\sim}{R}T} = H_X L \underset{\sim}{R} T \qquad (4)$$

For $H_X << (L\underset{\sim}{R}T)^{-1}$ most of the material is present in the gas phase, whereas for $H_X >> (L\underset{\sim}{R}T)^{-1}$ the opposite is the case. For $L \approx 1 \times 10^{-6}$, $(L\underset{\sim}{R}T)^{-1} \approx 4 \times 10^4$ M atm^{-1}, and correspondingly greater for lower values of L. Examination of the values of Henry's law coefficients in TABLE 2 shows that only for very soluble gases (e.g., H_2O_2) do Henry's law coefficients approach such a value, and thus that most nonreactive gases will be partitioned largely in the interstitial air within the cloud. On the other hand, as indicated in FIGURE 12, dissociative gases such as HNO_3 and NH_3 would be partitioned largely into cloudwater at representative values of pH and liquid water content.

Mass-Transport Kinetics

The overall process of uptake and reaction of gases in cloud droplets may be considered to consist of a sequence of mass-transport processes followed by aqueous-phase reaction. The pertinent mass-transport processes are diffusion from the bulk gas to the surface of the drop, transport across the interface, and diffusion in the aqueous phase. It is useful to think of these processes as taking place in series with each other and as well with chemical reaction, as indicated schematically in FIGURE 13. By identifying the rate-determining process and evaluating the rate of this process it is possible to ascertain the overall uptake rate. The foregoing is somewhat of an oversimplification since one or more of the processes may have a similar rate. Moreover, if aqueous-phase diffusion is controlling, the uptake rate nonetheless does not become independent of the reaction kinetics.[44] Still, this picture is conceptually very useful. Quantitative treatment of various aspects of this problem has been given by a number of groups including our own.[30,44-47]

In terms of laboratory measurements, the important quantities to be determined are the gas- and aqueous-phase diffusion coefficients of the reagent gases, and the so-called mass accommodation coefficient (α), the fraction of gas kinetic collisions of the reagent gas molecules at the air-water interface that result in transfer of the reagent gas across the interface. The diffusion coefficients are fairly well known either from direct measurement or by estimation from semiempirical correlations.[30] However, little is known about the

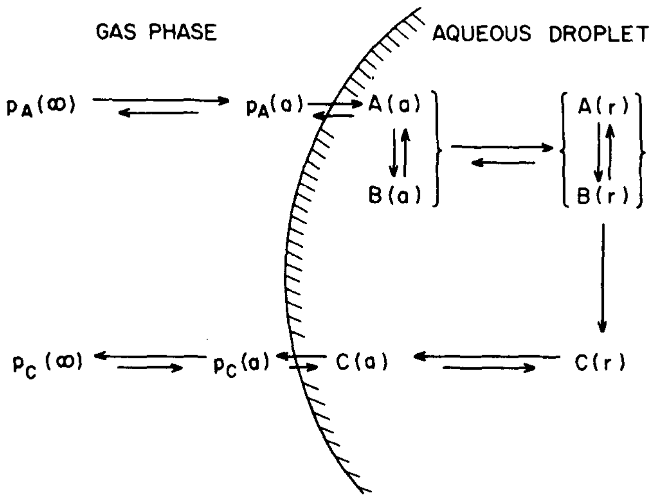

FIGURE 13. Schematic illustration of the subprocesses making up the overall process of reaction of gases in cloud droplets. A represents aqueous-phase reagent species transferred from the gas phase; B, species in rapid equilibrium with A; and C, product species, at the surface of the drop (a) or in the interior (r); P_A and P_C represent gas-phase partial pressures of A and C at the surface of the drop (a) and at large distances from the drop (∞). (From Schwartz.[30])

values of mass-accommodation coefficients on theoretical grounds, and the few experimental measurements appear to be widely inconsistent.[30] My own view, based in part on some recent studies of water vapor on aqueous solution (e.g., Ref. 48), is that values of α are close to unity. However, others (e.g., Chameides[49]) consider α to be substantially lower, perhaps of order 10^{-4}. Ultimately this question must be resolved by further experimental measurement with a variety of gases. It might be noted, though, that for droplets in the size range characteristic of cloud droplets, unless α is of order 10^{-2} or less, interfacial mass-transport is faster than gas-phase diffusion, and thus the overall rate of uptake and reaction is insensitive to the value of α.

An important limiting case in the description of combined mass-transport and aqueous-phase reaction kinetics is attained when mass-transport processes are all sufficiently rapid that the aqueous-phase concentration of the dissolved reagent gas is essentially equal to the value given by Henry's law referred to the bulk gas-phase partial pressure. Under these circumstances description of the mixed-phase reaction kinetics is greatly simplified, since reaction rates can be evaluated using the equilibrium dissolved reagent gas concentration, and the overall rate is insensitive to mass-transport kinetics. Criteria to examine whether this condition is met have been given[30,44] as inequalities involving the Henry's law coefficient of the reacting gas, the aqueous-phase rate coefficient, the gas- and aqueous-phase diffusion coefficients, and the radius of the cloud droplet. As it happens, these criteria appear to be met for reactions of SO_2 and NO_2 in cloud droplets under most situations of interest, although departure from the equilibrium condition may be expected under certain extremes of reagent concentrations.[41]

At the other extreme, for highly soluble and/or highly reactive gases, uptake is controlled entirely by the rate at which the reagent gas can be transported to the cloud droplet by gas-phase diffusion. An example of this situation is the uptake of nitric acid vapor by cloud droplets, which is evaluated to occur on a time scale of several seconds.[23]

Kinetic Studies

We examine here laboratory kinetic studies directed to determination of the mechanism and kinetic rate laws of reactions pertinent to aqueous-phase reactions in clouds and the use of such data to evaluate the rates of these reactions in the atmosphere. An underlying assumption here is that the kinetic rate laws are transferable from the laboratory to the ambient atmosphere. Successful application of this approach requires description of the overall reactions in terms of elementary reactions. In the case of aqueous-phase reactions, such reactions are potentially susceptible to the influence of trace species—catalysts or inhibitors—and this possibility must be borne in mind when applying laboratory rate data to atmospheric systems.

We focus our attention here on aqueous-phase oxidation of SO_2 and NO_2, with oxidants O_2, O_3, and H_2O_2, as possibly important acid-forming reactions in clouds.

SO_2 Oxidation

We first consider oxidation of dissolved sulfur(IV) by O_2. As is well known, the aqueous oxidation of sulfur(IV) by O_2 is an example of a catalytic reaction; indeed it is questionable whether the uncatalyzed reaction proceeds at all.[50] Untold numbers of laboratory investigations of the kinetics of this reaction have been conducted. For a recent review, see Hoffmann.[51] While the details of the kinetics have yet to be resolved, it is apparent that the reaction can be catalyzed by various transition metals either introduced intentionally or present as impurities and is sensitive as well to the presence of other trace species, e.g., organics that may serve as chain terminators, thereby decreasing the reaction rate. Susceptibility to the influence of trace species is often, as is the case for this reaction, manifested by the significant variability in kinetic results from laboratory to laboratory. The sensitivity of this reaction to trace constituents brings into serious question the utility of efforts to model this reaction for real clouds. In view of this it is perhaps fortunate that estimates[52] of the rate of this reaction for representative concentrations of transition metal ions and solution pH indicate that under most conditions this reaction is not of great importance in the atmosphere.

The possible atmospheric importance of O_3 as an aqueous-phase oxidant of S(IV) was suggested by Penkett[53] in 1972 and the kinetics of this reaction have been the subject of several subsequent investigations.[46,52,54–57] The results

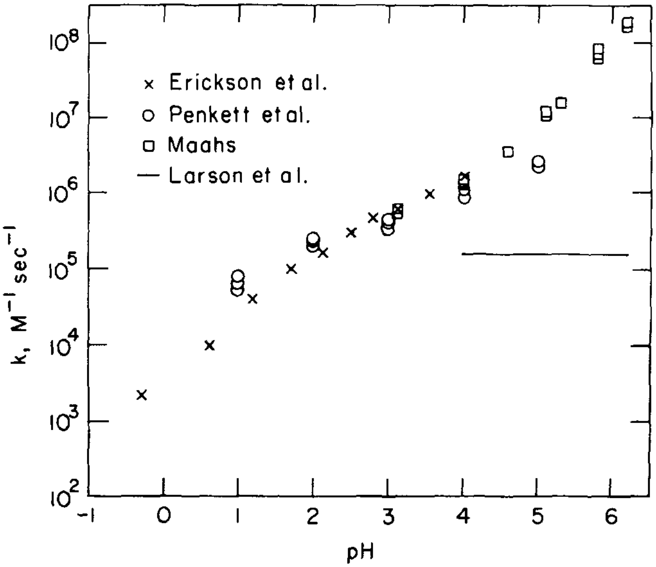

FIGURE 14. Second-order rate constant $k^{(2)}$ for oxidation of sulfur(IV) by ozone according to $d[S(VI)]/dt = k^{(2)}[O_3(aq)][S(IV)]$, as a function of solution pH at 25°C. Data are from References 46, 54, 55, and 57. (Modified from Schwartz.[41])

of these studies are summarized in FIGURE 14, which shows the pH dependence of the second-order rate constant defined as:

$$\frac{d[S(VI)]}{dt} = -\frac{d[S(IV)]}{dt} = k^{(2)}\,[S(IV)]\,[O_3(aq)] \tag{5}$$

It is seen that similar values and pH-dependence were found by Erickson *et al.*,[54] Penkett *et al.*,[46] and Maahs,[56,57] all of whom used a stopped-flow technique, whereas Larson *et al.*,[55] who used a bubbler technique, obtained a substantially lower value of $k^{(2)}$ with little indication of any pH-dependence. Examination of the mass-transport conditions of the latter study suggests that the observed reaction rate may have been restricted by mass transport.[41] As with the O_2 oxidation the question may be asked whether this reaction rate is susceptible to the influence of trace species serving as catalysts or inhibitors; it has been inferred on the basis of isotope exchange studies[58] that the reaction is not a simple bimolecular reaction, but proceeds by way of intermediates. Martin[52] and Maahs[57] report no influence of transition metal ions (up to 5×10^{-5} M) on the rate of this reaction, whereas Harrison *et al.*[59] report a positive influence. Martin and Damschen[60] report no influence on this reaction of ethanol, acetone, formaldehyde, and acetic acid, whereas Maahs[57] finds ∼25–50% apparent decrease in the O^3-S(IV) reaction rate by $(1–5) \times 10^{-5}$ M hydroquinone, an efficient free-radical scavenger. From these studies it is not unambiguous that catalytic or inhibition effects may be neglected for this reaction. On the other hand, the fairly close agreement of the kinetic results from the several laboratories supports the applicability of these results to evaluation of the rate of this reaction in clouds.

Under assumption that the cloudwater concentrations of both O_3 and sulfur(IV) are in equilibrium with the respective gas-phase partial pressures, the rate of aqueous-phase reaction may be evaluated in terms of these partial pressures as

$$\frac{d[S(VI)]}{dt} = k^{(2)} H^{*}_{S(IV)} H_{O_3} p_{SO_2} p_{O_3}. \tag{6}$$

The rate of S(IV) oxidation by O_3 is shown in FIGURE 15 as a function of pH for conditions representative of a liquid water cloud in the ambient atmosphere. In this evaluation[41] I have used the pH-dependence of the rate constant given in FIGURE 14 and, as well, the pH-dependence of the sulfur(IV) solubility given in FIGURE 12. The left-hand ordinate gives the instantaneous aqueous-phase reaction rate (molar per hour) for assumed SO_2 and O_3 partial pressures of 1 ppb and 30 ppb, respectively; this rate scales linearly with either partial pressure. It is seen that at high pH values the rate is quite significant in the context of acidification of precipitation, but that this rate strongly decreases with decreasing pH. The strong pH-dependence of the rate is a consequence of the pH-dependence of both the rate constant and the sulfur(IV) solubility. As a consequence of this strong pH-dependence this reaction tends to become self-limiting; i.e., the generation of strong acid as the reaction proceeds decreases the rate of further reaction. On the right-hand ordinate the reaction rate is expressed in ratio to the SO_2 partial pressure in units of percent hr^{-1} as is commonly given for gas-phase rates. Here a liquid water volume fraction $L = 1\ cm^3\ m^{-3}$ has been assumed; the oxidation rate referred to the gas-phase reagent concentration scales linearly with L. (This rate also scales linearly with p_{O_3}, but is independent of p_{SO_2}). By reference to this ordinate scale it is seen that the oxidation rate can be quite large in comparison to gas-phase oxidation rates ($\sim 1\%\ hr^{-1}$) at high pH, but of course continues to exhibit a strong pH-dependence. Thus from the perspective of both the rate of acidification of cloudwater and the rate of oxidation referred to gas-phase SO_2, this evaluation makes a strong case for the importance of aqueous-phase in-cloud oxidation of SO_2 by O_3.

A second strong oxidant of concern in the in-cloud oxidation of SO_2 is hydrogen peroxide, as suggested initially by Penkett *et al.*[46] The kinetics and mechanism of this reaction have been studied in a number of laboratories.[46,61–67] The reaction is catalyzed by H^+ and, as well, by a number of weak acids and is apparently an example of specific acid catalysis. The pH-dependence of the second-order reaction rate constant, defined according to

$$\frac{d[S(VI)]}{dt} = -\frac{d\,[S(IV)]}{dt} = k^{(2)}\,[S(IV)]\,[H_2O_2] \tag{7}$$

is shown in FIGURE 16. The kinetics of reaction are dependent on buffer concentration and on ionic strength; in preparing FIGURE 16 an attempt has been made to back out this dependence by extrapolation to zero buffer and ionic

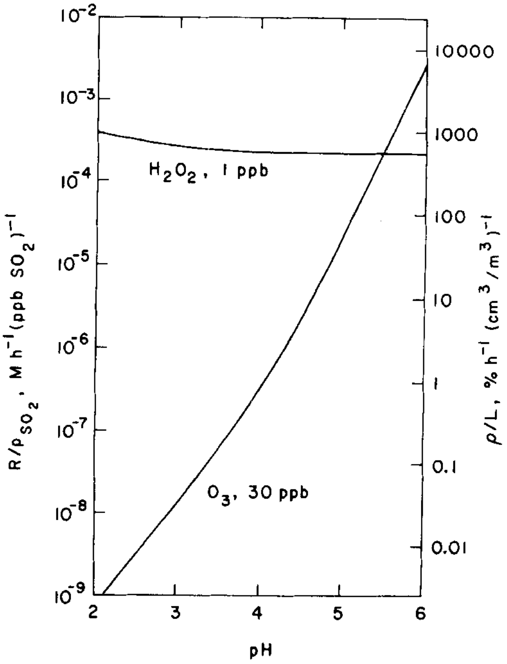

FIGURE 15. Rate of aqueous-phase oxidation of S(IV) by O_3 (30 ppb) and H_2O_2 (1 ppb), as a function of solution pH. Gas-aqueous equilibria are assumed for all reagents. R/p_{SO_2} represents rate of reaction referred to gas-phase SO_2 partial pressure per $cm^3 \cdot m^{-3}$ liquid water volume fraction. Temperature = 25°C. (Modified from Schwartz.[41])

concentration. The residual scatter of the data probably reflects inaccuracies in this procedure, as well as a slight dependence on temperature over the range indicated. The dashed line in Figure 16, which represents a slope of -1 arbitrarily placed through the data, shows the first-order dependence on H^+ concentration in the pH range in which HSO_3^- is the dominant S(IV) species. The reproducibility of the data from the several laboratories and in particular the reproducibility of the $[H^+]$-dependence suggest the lack of susceptibility of this reaction to influence of trace constituents, and this inference is supported by isotope tracer studies[61] that are consistent with a molecular (i.e., non-free-radical) mechanism. We are thus encouraged to apply these data to evaluation of the S(IV)-H_2O reaction rate in the ambient atmosphere. Moreover we would note that recent work in our laboratory[68] measuring the rate of this reaction in precipitation samples gives rates that are generally consistent with the data in Figure 16, albeit with considerable scatter.

Evaluation of the rate of in-cloud oxidation of SO_2 by H_2O_2 with the reaction rate constant represented by the dashed line in Figure 16 is given in Figure 15; here a gas-phase H_2O_2 concentration of 1 ppb is assumed, and the Henry's law coefficient of H_2O_2 is taken as 1×10^5 M atm^{-1}.[64] It is seen that a rather high reaction rate is indicated and that, in contrast to the situation for the O_3 reaction, there is only a slight pH-dependence. This near pH-independence is due to a cancellation of the pH-dependences of the S(IV) solubility and the reaction rate constant. Because of this pH-independence, the reaction can

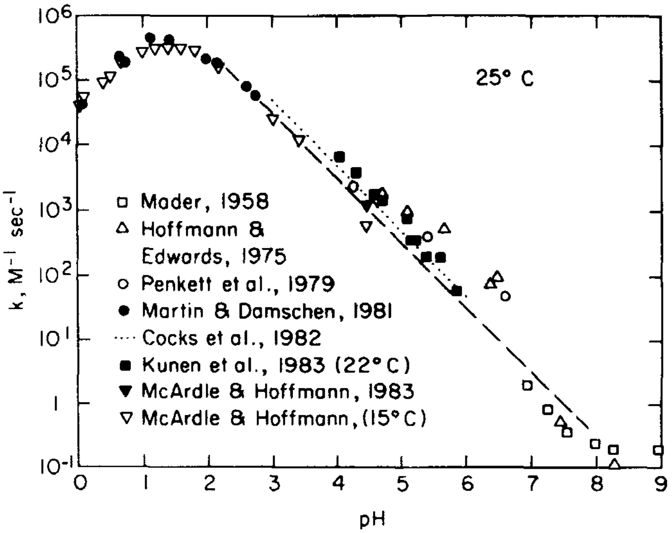

FIGURE 16. Second-order rate constant $k^{(2)}$ for oxidation of sulfur(IV) by hydrogen peroxide according to $d[S(VI)]/dt = k^{(2)}[H_2O_2][S(IV)]$, a function of solution pH. Data are from Refs. 46 and 62–64 (as corrected to zero buffer concentration in Ref. 64) and Refs. 65–67. Temperature 25°C except as indicated. *Dashed line* represents slope of -1 (i.e., $k^{(2)} \propto [H^+]$) arbitrarily drawn through the data. (Modified from Schwartz.[41])

continue to proceed at high rate even at low pH, and thus this reaction assumes major potential importance as a pathway for in-cloud formation of sulfuric acid.

NO_2 Oxidation

I now turn to consideration of aqueous-phase oxidation of NO_2, which has been the subject of much research in our laboratory over the past several years. When we began this work little information was available to permit quantitative evaluation of the rate of this reaction in the ambient atmosphere or even to permit qualitative assessment of its importance. NO_2, of course, is well known[69,70] to react rapidly with liquid water to give a mixture of nitrous and nitric acids,

$$2NO_2 + H_2O(l) \rightarrow HNO_2 + HNO_3 \qquad [11]$$

The nitrous acid produced in this reaction may undergo decomposition to yield additional nitric acid as well as nitric oxide,

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \qquad [12]$$

corresponding to the overall reaction

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad [13]$$

These reactions in fact serve as the basis for the industrial manufacture of nitric acid.[40] Yet another reaction whose importance under atmospheric conditions must be examined is the reaction of NO_2 with NO to form nitrous acid,

$$NO_2 + NO + H_2O \rightarrow 2HNO_2 \qquad [14]$$

The fact that these reactions occur rapidly at high concentrations and also the strong thermodynamic driving force for the production of HNO_3 are probably the basis for the assumption by quite a few investigators that these reactions are rapid also under ambient conditions, i.e., with cloud- or rainwater,[71-77] with liquid-water-containing clear-air aerosols,[78-82] with surface water,[83-86] or with liquid water contained in vegetation.[87-89] The acidity resulting from assumption of these equilibria has been shown as well in model calculations to exert a major influence upon aqueous-phase concentrations of sulfur(IV) and resultant sulfate formation rates as a consequence of the highly pH-dependent solubility of sulfur(IV).[79-81,90] It might be noted as well that reaction of NO_2 to form nitrous and nitric acids has been assumed to be the initial step responsible for the pulmonary toxicity of this substance.[91] In contrast to the studies cited, the work of a few investigators[92-94] has minimized the importance of reaction of NO_2 with liquid water at concentrations representative of the ambient atmosphere.

On the basis of the discussion presented above, it should be evident that the information necessary to evaluate the rate of one or another of these reactions, e.g. [11], in cloudwater is the Henry's law solubility of NO_2 and the aqueous-phase kinetic rate law. In order to determine these quantities we have followed several different approaches, namely, literature review, thermochemical measurements, and direct, mixed-phase chemical kinetic measurements.

As might be inferred from the industrial importance of reaction of NO_2 with liquid water, there has been quite a number of laboratory investigations of the reactive uptake of NO_2 by liquid water. However, such studies have been conducted not only because of practical application but also because of the intrinsic interest of this chemistry. In fact, some of these reactions served as an early proving ground for theories relating reaction kinetics and chemical thermodynamics.[95] In general, studies of reaction kinetics of this system are complicated not only by the interplay between mass transport and chemical reactions, but also by the dimerization of NO_2,

$$2NO_2 = N_2O_4 \qquad [15]$$

which takes place in both the gas and aqueous phases and affects the kinetics of mass transport as well as reaction. As noted above, recognition of the fact that the Henry's law coefficient is an equilibrium constant that must be related to other equilibrium constants by means of thermochemical cycles led us[96] to attempt to evaluate the Henry's law coefficient of NO_2 by such an approach, as summarized in FIGURE 17. In this figure the solid arrows represent reactions whose equilibrium constants we considered to be well established, the dashed arrows represent reactions for which equilibrium constants had been reported but which we did not consider well established, and the dotted arrows

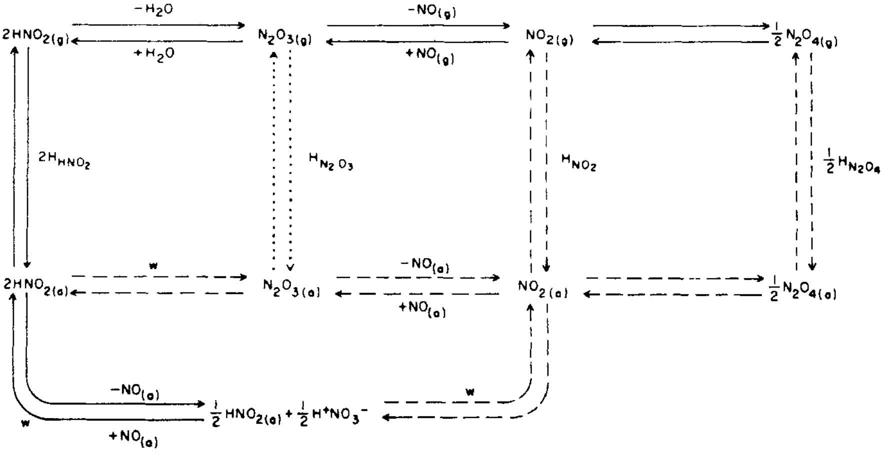

FIGURE 17. Thermodynamic cycles leading to evaluation of Henry's law coefficient of NO_2, N_2O_3 and N_2O_4. *Solid arrows* represent reactions whose equilibrium constants are considered well established. Equilibrium constants represented by *dashed arrows* have been measured directly, but are not considered firm. There are no direct measurements for the equilibrium represented by *dotted arrows*. (From Schwartz and White.[36])

represent a reaction for which no equilibrium constant data were available. Direct measurements of NO_2 solubility from kinetic studies[97,98] yielded values of H_{NO_2} of 1.9×10^{-2} and 4×10^{-2} M atm^{-1}, whereas the several thermochemical paths yielded values of 1.0×10^{-2}, 1.9×10^{-2} and 0.85 M atm^{-1}. A value for H_{NO_2} of order 10^{-2} M atm^{-1} would be consistent with that expected from physical properties of the molecule (cf. $H_{O_3} = 1.3 \times 10^{-2}$ M atm^{-1}), whereas a value of order 1 M atm^{-1} would be anomalously high. The large discrepancy of the latter value suggested to us that the then-accepted[99,100] value for the equilibrium constant for the hydrolysis of N_2O_3,

$$N_2O_3(aq) + H_2O = 2\ HNO_2(aq), \qquad [16]$$

might be incorrect. This prompted us to re-examine this equilibrium constant and in particular to extend the range of examination to lower acid concentrations than had been investigated previously. That study revealed an unexpected dependence of the equilibrium constant K_{16} on $[H^+]$ in several molar perchloric acid, resolving the discrepancy in H_{NO_2}. On this basis we were then able to recommend[96] a value for the Henry's law coefficient of NO_2 of $(1.2 \pm 0.4) \times 10^{-2}$ M atm^{-1}. It is interesting to note that the new measurement of K_{16} also resolved a discrepancy in the interpretation of the kinetics and mechanism of diazotization of amines, which reaction proceeds via N_2O_3 as an intermediate.[96,102]

In a second review [103] we examined studies pertinent to the kinetics of the dissolution reactions. Depending on the nature of the contact between the gas and aqueous phases, which governs the competition between mass transport and chemical kinetics, such studies typically yield products of various

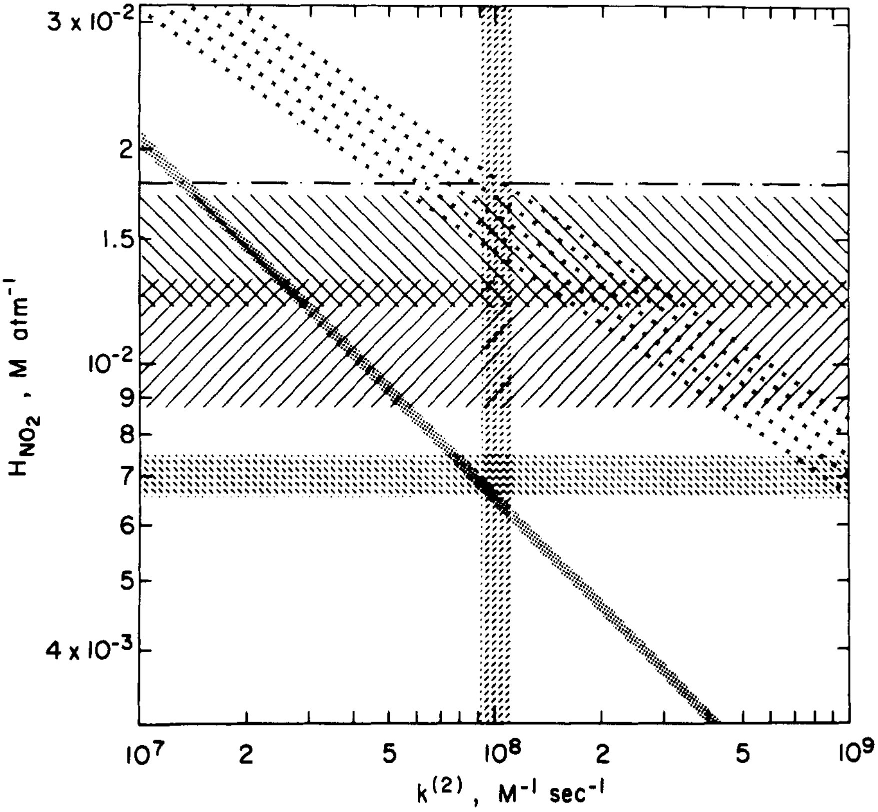

FIGURE 18. Plot of data pertinent to determination of H_{NO_2} and second-order rate constant for reaction [11]. (From Schwartz and White.[103])

powers of the Henry's law coefficient and the reaction rate constant k. Such data, when plotted in a plane whose coordinates are log k and log H, yield straight lines, or, when experimental uncertainties are taken into account, bands whose width corresponds to the error bar on the measured quantity. An example of such a plot is given in Figure 18. Here $k^{(2)}$ represents the rate constant for reaction [11] defined as

$$\frac{d[HNO_2]}{dt} = \frac{d[HNO_3]}{dt} = k^{(2)}\,[NO_2(aq)]^2 \qquad (8)$$

In the absence of error the several lines should intersect at a point whose coordinates represent the values of $k^{(2)}$ and H_{NO_2}; the breadth of the region of intersection shown in the figure is a measure of the uncertainty in values of these quantities to be derived from the several studies. On the basis of this analysis we recommended a value of the rate constant for reaction [11], as (0.7 ± 0.35) × 10^8 M^{-1} sec^{-1}. A rate constant of this magnitude represents quite a high reaction rate, within two orders of magnitude of diffusion controlled.

In parallel with this literature review we embarked on a kinetic study of our own.[104] The distinguishing feature of this study was the low partial pressure of NO_2 employed, as low as 10^{-7} atm. Such low pressures both ruled out any contribution of the dimer N_2O_4 to the reaction and reduced the rate of reaction sufficiently that mass transport could effectively compete with chemical reaction. A sketch of the gas-liquid reactor is given in FIGURE 19. NO_2 in N_2 or air was introduced through a frit as finely dispersed bubbles. In such an approach mass transport between the two phases is promoted by the convection induced by the rise of the bubbles as well as by the high interfacial contact area; the time constant for convective mixing could be measured from the approach to saturation of CO_2 or SO_2. The rate of reaction was followed by the increase in electrical conductivity of the solution associated with formation of ionic products. By measuring the rate of reaction [11] as a function of NO_2 partial pressure and the convective mixing time constant it was possible to determine both the Henry's law coefficient of NO_2 and the rate law for the reaction. The rate law was established to be second order in NO_2 (equation 8) over the pressure range studied, and the Henry's law coefficient and rate constant were in good agreement with the values obtained in the literature review.

On the basis of this study we were able to place a high degree of confidence in the applicability of the rate law and the constants obtained to evaluation of rates of reaction of NO_2 in the ambient atmosphere. This evaluation[105] established that the rate of reaction [11] at representative NO_2 partial pressures is far too low to represent either an appreciable loss route of NO_2 or an appreciable process for the acidification of cloud water. The reason for this is that despite the high reaction rate constant, the second-order rate law and the low Henry's law coefficient conspire to make the overall rate very slow at low NO_2 partial pressures. Furthermore, examination of other possible aqueous-phase atmospheric reactions of NO_2 (e.g., with NO, with transition metal ions, or with O_3 or H_2O_2) has failed to reveal any such reactions that proceed with appreciable rate.[105,106] Thus, on the basis of laboratory studies it appears that the reactive uptake of NO_2 to form cloudwater nitric acid must be dominated by gas-phase rather than aqueous-phase oxidation.

Before concluding the discussion on the kinetics of reaction of NO_2 with water it might be useful to reflect on the shift of reaction order, from first order at high concentrations to second order at low concentrations. The reason for this is the shift in predominant species from N_2O_4 to NO_2. However, we must view this shift as apparent rather than real, since $[N_2O_4]$ is quadratic in $[NO_2]$ throughout the entire concentration range. Thus, the second-order rate law is entirely predictable from consideration of the sequence of elementary reactions that constitute the overall reaction. In fact, a quite accurate rate expression applicable to low NO_2 concentrations under conditions of Henry's law saturation may be derived from the work of Abel and Schmid[95] in the 1920s on the kinetics of decomposition of nitrous acid as interpreted correctly by those authors in terms of elementary reactions.

A spin-off of our laboratory investigations of NO_2 chemistry that might

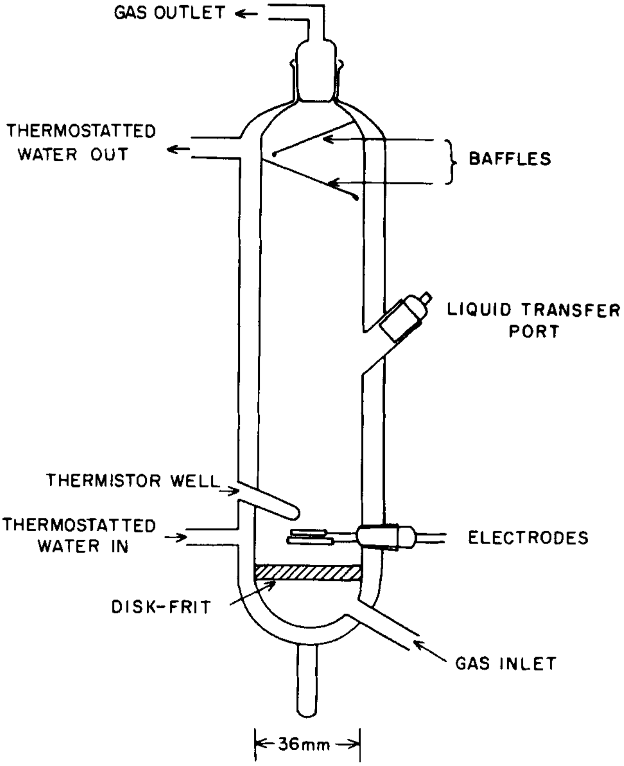

FIGURE 19. Gas-liquid contactor employed in study of reaction of NO_2 with water. (From Lee and Schwartz.[104])

be mentioned here is a revision of thinking of the mechanism of NO_2 toxicity in pulmonary systems. Again, in view of the low solubility and second-order rate law, reaction [11] seems improbable at low NO_2 partial pressures. As an alternative it has been suggested[107] that NO_2 may serve as a one-electron oxidizing agent leading to the formation of organic free radicals by abstraction of an allylic hydrogen from unsaturated molecules. The relevance of research conducted for a particular application to other areas of application is a major strength underlying the approach of carrying out research directed to determination of fundamental chemical and physical properties. Just as our research into cloud chemistry has benefited from a long history of research carried out for other purposes, so will our research serve as the basis for future work in still further areas of application.

FIELD MEASUREMENTS

I turn now to an account of the second "side" of our examination into cloud chemistry, namely measurement of the chemical composition of clouds and evaluation of the processes responsible for establishing that composition. Again, emphasis will be given here to results obtained by our group at Brookhaven National Laboratory, but it should be noted that several other research groups are actively engaged in measurements of the composition of clouds and fogs, most prominently the National Center for Atmospheric Research,[108] the National Oceanic and Atmospheric Administration,[109] the State University of New York at Albany,[110,111] the California Institute of Technology,[112,113] the University of Washington,[114,115] and Sonoma Technology, Inc.[116] in this country, the Atmospheric Environment Service of Canada,[117] the Central Electric Research Laboratories in Britain,[118] and KEMA N.V. in the Netherlands.[119] Attention is called as well to earlier measurements of cloud composition to which reference is made in the articles cited here.

The platform for our measurements of cloud chemistry has been a twin-engine high-wing STOL-type aircraft (Fig. 20) that has been outfitted with sampling and measurement equipment suitable for characterization of the composition of cloudwater and interstitial air.[120] The aircraft is fully equipped for instrumented flight as is required for flying in clouds. Personnel onboard the aircraft during such flights consist of the pilot, copilot, and two members of our scientific staff. Cloud-sampling missions require considerable cooperation and assistance from aviation authorities. We have found that FAA Air Traffic Control has been highly cooperative whenever possible.

Air for the chemical measurements is ducted into the aircraft through intakes located on the side of the cabin (Fig. 21) under "ram" pressure induced by the forward motion of the aircraft. For measurements of the composition of interstitial air in clouds it is necessary to remove cloud droplets from the inlet air stream. This is effected by a cloudwater separator[121] mounted in the sampling line. This separator, which was developed at the Central Electric Research Laboratories in Britain, contains a set of static blades (Fig. 22) set at an angle to induce a swirl downstream that in effect centrifuges the cloud droplets to the walls while transmitting gases and aerosol particles that have

FIGURE 20. The Britten-Norman Islander research aircraft that has been employed in our cloud-composition measurements.

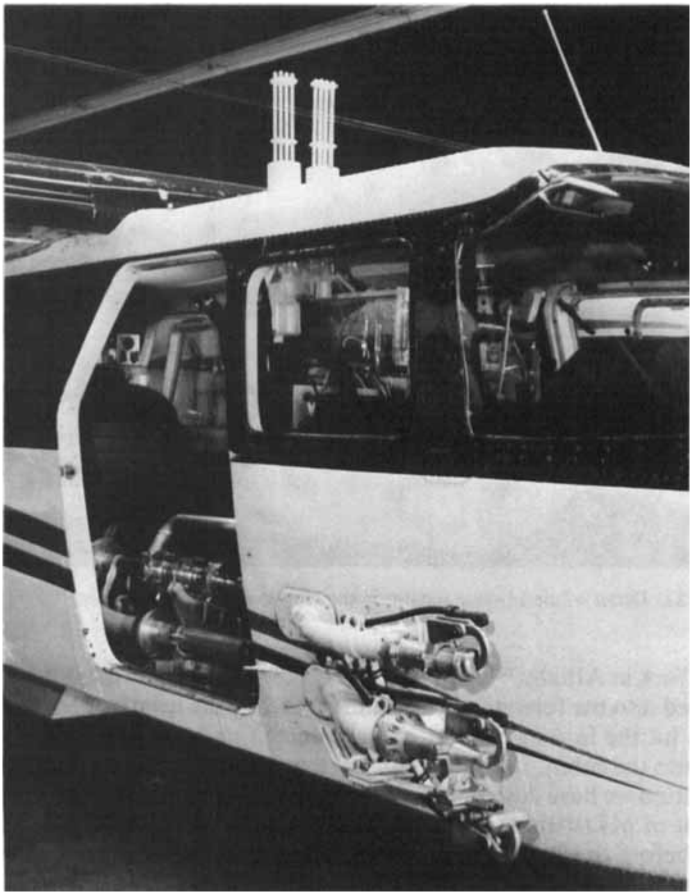

FIGURE 21. Detail of research aircraft showing inlets for air samples (*lower right*, with remote-operated covers), cloudwater separator (in cabin), cloudwater collectors (protruding through cabin roof) and collection bottles (in cabin).

not been incorporated into cloud droplets. A portion of this air stream is passed through a series of filters that collect aerosol particles and gaseous HNO_3 and SO_2 for subsequent analysis.[122] The time required for collection of sufficient sample for analysis is about half an hour. Additional portions of the interstitial air stream are sampled by various "real-time" instruments on board the aircraft. These instruments, which for the most part are modified from commercially available instruments[123,124] to enhance sensitivity or chemical selectivity, are mounted in two instrument racks located fore and aft of the scientific observers (FIGS. 23 and 24). Interstitial species measured continuously include SO_2, aerosol sulfate, NO, NO_X, HNO_3, O_3, and NH_3.

Cloud liquid water is collected by means of collectors projecting through the cabin roof (FIG. 21). These collectors, developed at the State University

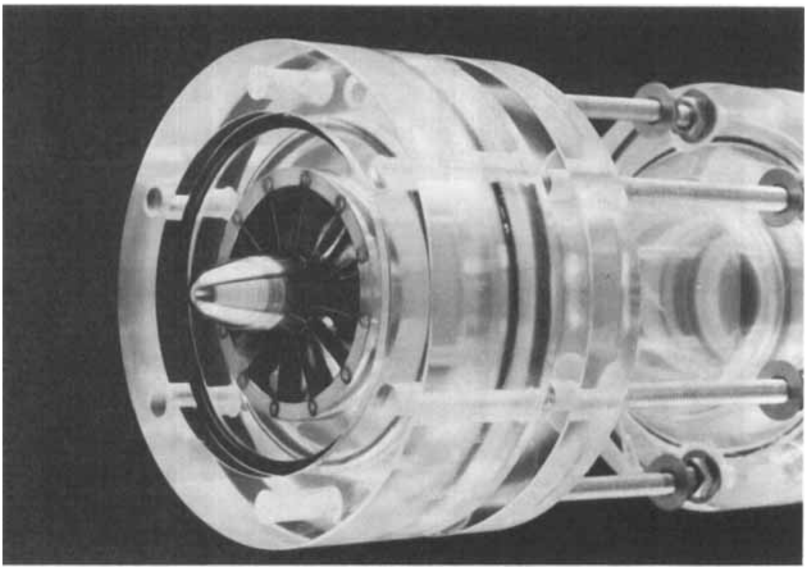

FIGURE 22. Detail of cloudwater separator showing static blade assembly.

of New York at Albany,[125] consist of arrays of rods, each rod having a vertical slot milled into the forward surface and extending the length of the rod. Cloud droplets hit the face of the slot and are ducted under slight suction through tubing into the cabin. In order to obtain a real-time assessment of cloudwater composition we have designed flow-through cells that permit continuous measurement of pH (with a glass electrode) or conductivity (with platinum electrodes) before the sample is ducted into the collection bottle. Collection of sufficient sample for analysis (about 5 cm^3) requires 5 to 15 minutes or more, depending on cloud liquid water content.

Physical and meteorologic measurements made onboard the aircraft include liquid water content (by a hot-wire indicator[126]), relative humidity, temperature, light-scattering, and total and ultraviolet insolation. Signals from the several real-time instruments, from the flowmeter used with the filter sampler, and from navigational instruments are recorded digitally for subsequent processing. Additionally, strip-chart records are available for display of the several chemical concentrations and liquid water content during the conduct of the flight. The continuous measurements, having time-resolution typically of a few seconds, provide much more detailed information on the spatial variability of cloud composition than can be obtained from the collected samples.

Cloud Composition Measurements

I present here some of the highlights of our measurements of cloud composition; for details of these measurements see References 127–129. To date

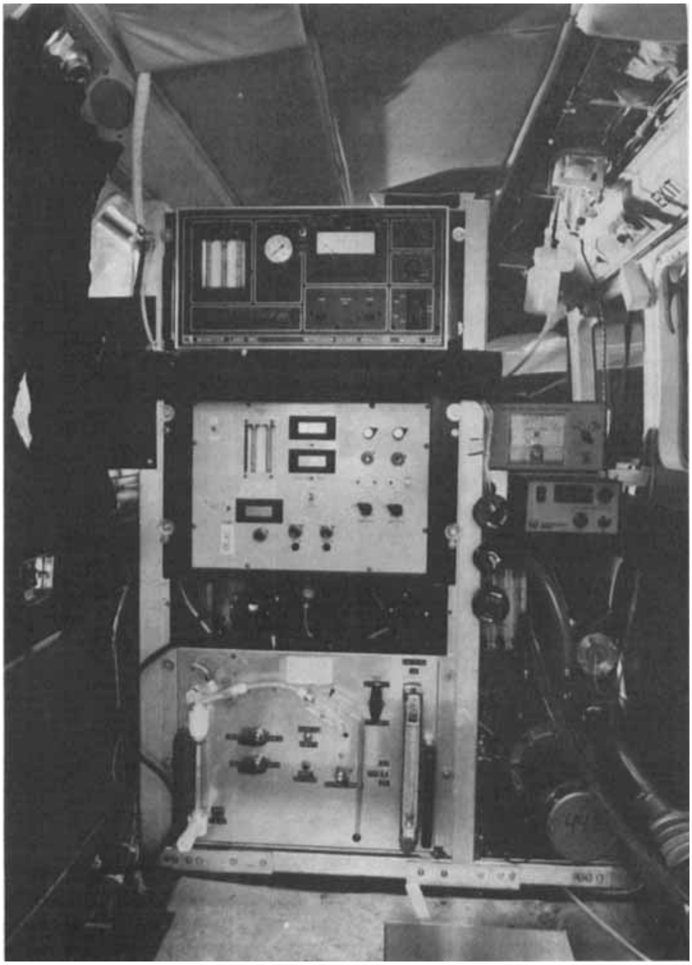

FIGURE 23. View of front instrument rack in aircraft, showing chemiluminescence NO_x analyzer, dual-channel flame photometric sulfur analyzer, and fluorescence derivatization NH_3 analyzer. Mounted to *right* of rack are read-out units for relative humidity and conductivity. Collected bottles and pH/conductivity cell for use with cloudwater collector are visible at *upper right.*

we have concentrated our efforts on warm (i.e., having temperatures greater than 0°C) stratiform clouds, and the results presented here are restricted to such clouds. This type of cloud has been selected for our initial study because these clouds are prevalent, responsible for delivery of much precipitation to the surface, amenable to forecasting, widespread and spatially uniform, and subject to dynamic interpretation.[130] Measurements have been made at several locations in the eastern United States, including Long Island, NY; Salisbury, MD; Charleston, SC; and Birmingham, AL. Altitudes were typically

FIGURE 24. View of rear instrument rack in the aircraft, showing on the *left*, the data acquisition system, navigational instrument read-outs, Doppler radar, and the integrating-nephelometer. On the *right* are the chemiluminescence ozone monitor, the high-volume flowmeter and integrator, radiation thermometer and the turbulence monitor. Strip-chart recorders are on top of the rack.

in the range 500–1500 m above mean sea level, i.e., within the lower portion of the planetary boundary layer.

Cloudwater Composition

As an initial means of displaying concentration measurements of cloudwater species, it is convenient to present these data as frequency distributions, the percent of the samples measured exhibiting concentrations of the several ionic species within specified ranges. Such frequency distributions are given in FIGURE 25 for H^+, $SO_4^=$, NH_4^+, and NO_3^-. Concentrations of other cations (Na^+, K^+, Ca^{++}, Mg^{++}) and anions (Cl^-) have been almost invariably well below

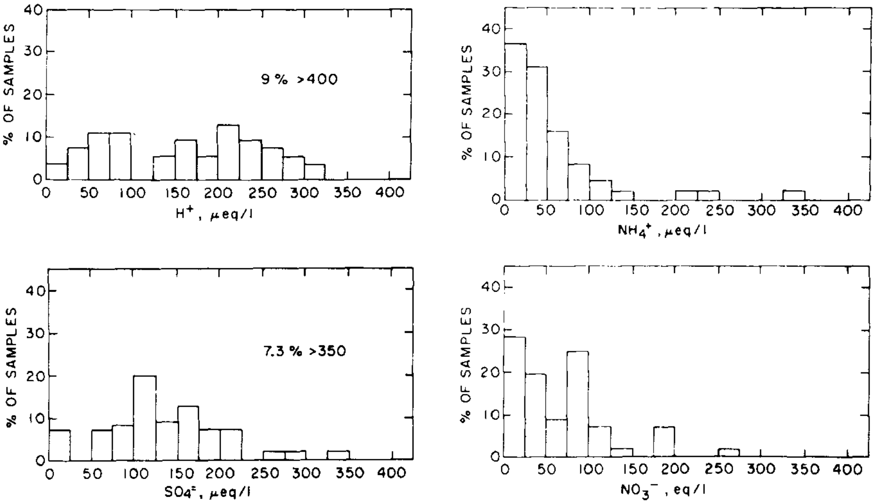

FIGURE 25. Frequency distributions of concentrations of principal ions in cloudwater samples. (From Daum *et al.*[127] Reprinted by permission.)

those of these principal ionic species. Examination of cloudwater composition and comparison with that of rainwater samples indicates that the composition of cloudwater is, not surprisingly, similar to that of rainwater, with a possible indication that for the clouds sampled concentrations were somewhat greater than are typical in precipitation samples.

Further insight into cloudwater composition may be gained by examination of fractional acidity, $[H^+]/([NO_3^-] + 2[SO_4^=])$. The frequency distribution of this quantity for cloudwater samples given in FIGURE 26 indicates that for most samples H^+ is the principal cation associated with sulfate and nitrate anions. Comparison of the distribution of fractional acidity of cloudwater samples with those for rainwater samples (FIGS. 6 and 7) shows a general

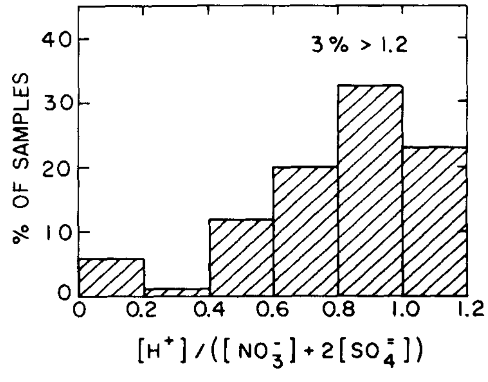

FIGURE 26. Frequency distribution of the fractional acidity of cloudwater samples. (From Daum *et al.*[129] Reprinted by permission.)

similarity, but with cloudwater samples, if anything, exhibiting a somewhat greater fractional acidity than the rainwater samples.

The relatively high fractional acidity of cloud and rainwater samples contrasts dramatically with that characteristic of clear-air (i.e., noncloud) aerosol. Figure 27 shows distributions of fractional acidity obtained by our group in aircraft sampling of clear air during the summer 1980 NEROS (NorthEast Regional Oxidant Study) project in the vicinity of Baltimore, MD.[131] The distribution in Figure 27a represents the fractional acidity of the collected aerosol sample. It is clear that the sulfate and nitrate present in these aerosol samples are not mainly associated with H^+, but rather represent acids that have been mostly neutralized by NH_3. It is clear further that the composition of rainwater (cf. Fig. 6 and 7; the latter representing summer precipitation at nearby Lewes, DE, is particularly pertinent) cannot be derived simply by dissolution into rainwater of aerosol of composition exhibited by these samples. This conclusion holds all the more strongly for cloudwater, which, as noted above, appears to exhibit greater fractional acidity than rainwater. These observations therefore give strong indication of the participation of gaseous species

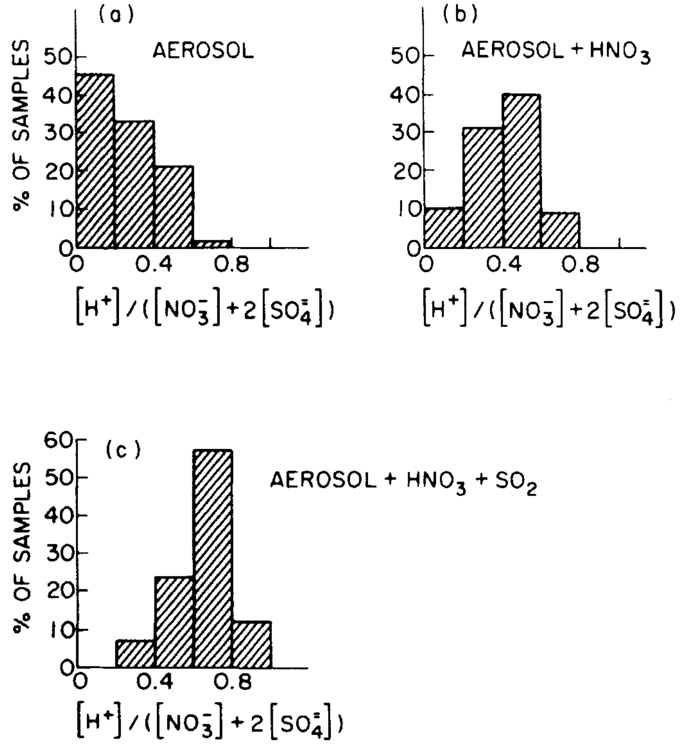

FIGURE 27. Frequency distribution of fractional acidity of clear-air samples taken in Baltimore, Maryland, summer 1980. (a) Aerosol only; (b) aerosol + HNO_3; (c) aerosol + HNO_3 + SO_2, with SO_2 assumed to yield $2H^+ + SO_4^=$. (From Daum.[131] Reprinted by permission.)

in establishing the composition of the cloudwater samples. To explore this further, FIGURE 27b shows the frequency distribution of fractional acidity for the clear-air NEROS samples evaluated under the assumption that nitric acid (which was sampled simultaneously with the aerosol) would contribute both to the H^+ and NO_3^- concentrations upon dissolution of the material present in the clear air in cloud- or rainwater. This assumption seems most reasonable in view of the fact (as discussed above and also in Ref. 23) that HNO_3 would completely and rapidly partition into cloudwater. It is seen that the distribution of fractional acidity is shifted to somewhat greater values, but still does not match that of the cloud- or rainwater distributions. However, if the SO_2 that was present is also included in evaluating the fractional acidity under assumption that SO_2 reacts to form H_2SO_4 (FIG. 27c), then a distribution of fractional acidity is obtained that much more closely matches those of cloud- and rainwater. Considerations such as these give strong support to the hypothesis (e.g., Newman[132]) that rainwater in the eastern United States must derive its sulfate and acidity largely from aqueous-phase oxidation of SO_2.

I now turn to consideration of reasons for variability in concentrations of cloudwater-dissolved substances. A major reason for this variability is the variability of liquid water content within clouds. As may be seen by reference to FIGURE 9, slight changes in temperature may lead to changes in liquid water content that are quite large relative to typical liquid water content of 0.1 to 1 cm^3/m^3. An instance of the effect of variable liquid water content on dissolved species concentrations can be seen in FIGURE 28, which presents ionic concentration data obtained in a series of measurements in Charleston, SC, in February 1982. FIGURE 28a presents aqueous-phase concentrations, whereas FIGURE 28b presents these concentrations multiplied by liquid water content. Attention is called in particular to the measurements on missions 1 and 2, which were made in morning and afternoon of the same day, the afternoon measurements being in clouds of lower liquid water content. From compar-

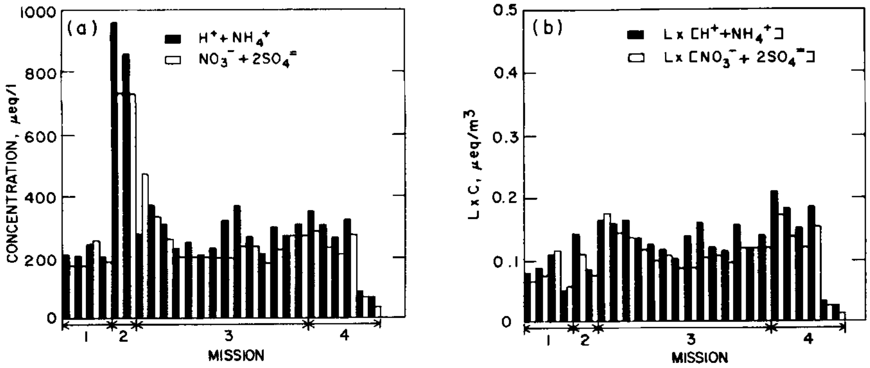

FIGURE 28. Cation ($[H^+]$ + $[NH_4^+]$) and anion ($[NO_3^-]$ + $2[SO_4^=]$) concentrations for cloudwater samples collected in Charleston, South Carolina, February 1982. (a) Aqueous concentrations; (b) concentrations per cubic meter of air. (From Daum *et al.*[128] Reprinted by permission.)

isons of the two figures it is seen that much of the apparent increase in concentrations between the two missions is due simply to a decrease in liquid water content.

In order to remove the effect of variable liquid water content on reported concentrations and as well to permit comparison of concentrations of species in the several phases (gas, aerosol, aqueous solution), we have taken to expressing the concentrations of cloudwater-dissolved species as potential partial pressure, the partial pressure the species would exhibit as an ideal gas-phase species. From Equation (1) it is seen that this potential partial pressure is evaluated as

$$\hat{P}_X = L\underset{\sim}{R}T[X] \qquad (9)$$

This quantity is equivalent to the partial pressure of a gaseous constituent or the mole fraction of an aerosol constituent and thus constitutes a common currency for comparison of concentrations in the several phases.

Having defined the potential partial pressure, we proceed to examine frequency distributions of cloudwater concentrations expressed in this way. Such frequency distributions are given in FIGURE 29. The potential partial pressures of the principal ions are found to exhibit values up to several parts per billion, comparable to nonurban gas-phase concentrations of SO_2 and NO_X in these regions. This comparability offers no support, at least for the stratiform clouds

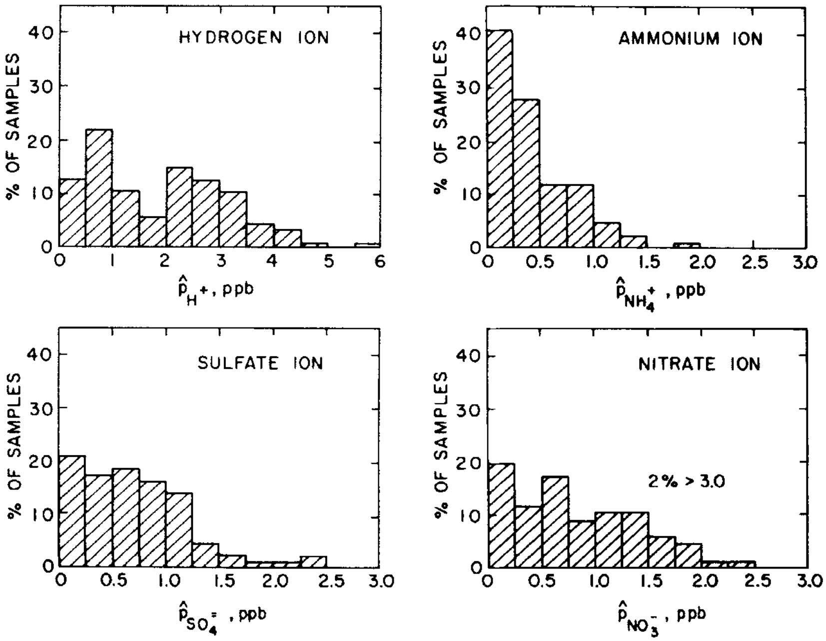

FIGURE 29. Frequency distributions of the potential partial pressures of the major ions in cloudwater samples. Number of samples (N) = 88. (From Daum *et al.*[129] Reprinted by permission.)

that have been studied to date, to the suggestion[133,134] that clouds may process and accumulate within their cloudwater materials from a volume of air substantially greater than that contained within their physical boundaries. Rather, these observations are consistent with the more customary picture of cloud droplets remaining with and interacting with only the air in which the droplets are initially formed.

Of course, variability in species concentrations may be due simply to variability in the amount of solute present. An instance of this is found in the final sets of samples collected on mission 4 (FIG. 28) in comparison to the earlier samples obtained on that mission. For the earlier samples the aircraft was at an altitude-of 0.6 km above mean sea level, whereas for the later samples the aircraft had climbed to 0.9 km. The difference in concentrations between the two altitudes is reflected in both the aqueous solution concentrations (FIG. 28a) and the absolute concentrations (FIG. 28b). The altitude-dependence is reflected as well in the pH trace registered on this mission (FIG. 30), which

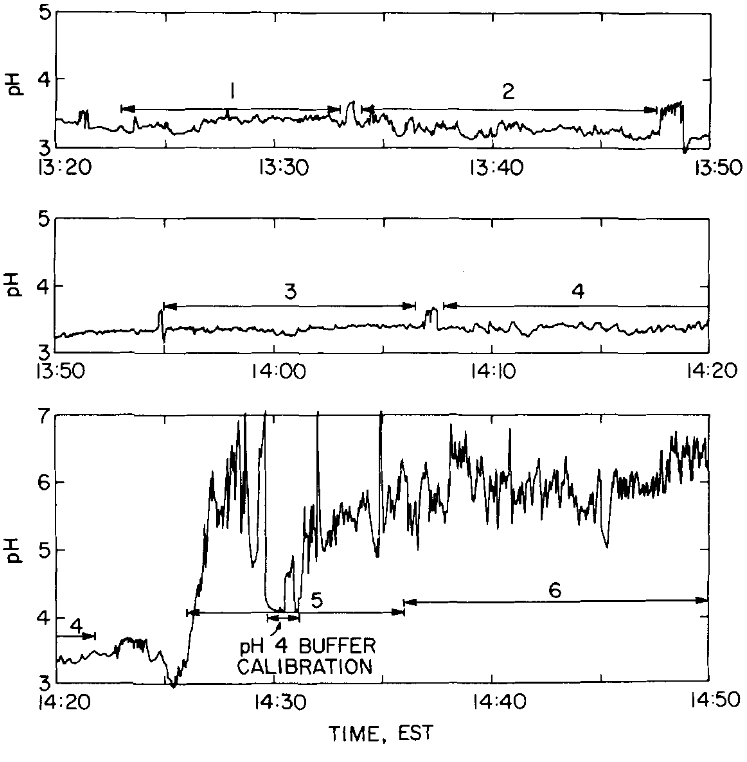

FIGURE 30. Continuous cloudwater pH obtained during aircraft measurements in the vicinity of Charleston, SC, February 28, 1982 (cf. FIGURE 28, mission 4). Values from 1320 to 1425 were obtained at an altitude of 600 m above mean sea level. Values from 1425 to 1450 were obtained at an altitude of 900 m above mean sea level. *Arrows* indicate collection times and pH values of collected samples. Note pH calibration at 1430. (From Daum *et al.*[128] Reprinted by permission.)

shows a sharp increase in pH at about 1425, when the aircraft made the ascent. In fact, the dramatic change in pH led us initially to question the performance of the pH meter; however, in-flight calibration (at 1430) confirmed that the pH meter was behaving properly, as was later substantiated by the chemical analysis of the collected samples.

Interstitial Composition

I have emphasized that the great majority of the volume of a cloud consists of air. Our interest in cloud composition is thus directed as much to the composition of this air as to the composition of the cloudwater. As with clear air, our interest is focused both on gaseous and particulate species.

Concentrations of principal ionic species in aerosol particles present within the interstitial air in clouds are shown in FIGURE 31. (Here, a negative concen-

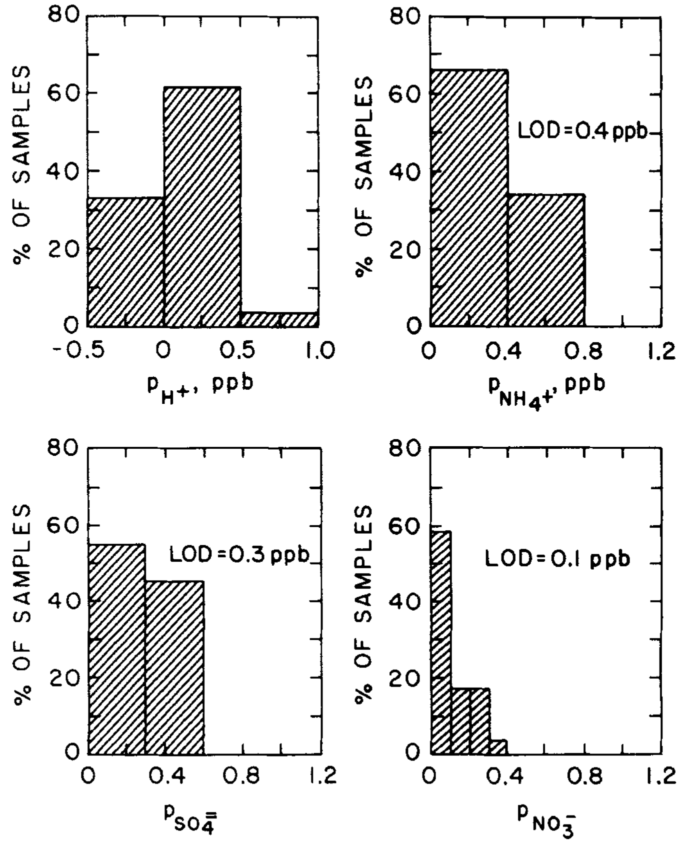

FIGURE 31. Frequency distributions of the concentrations of interstitial aerosol constituents. N = 29. (From Daum *et al.*[129])

tration represents net basicity in comparison to blanks for H^+ determined by Gran [pH] titration[135] following leach of the filter by 10^{-4} *N* acid solution.) Interstitial aerosol composition is quite distinct from that of cloudwater, e.g., in the ratios of concentrations of the several ionic constituents, being similar in that respect rather to composition of clear-air aerosol. Concentrations of interstitial aerosol species are seen also to be typically quite low in comparison to concentrations of the same species in cloudwater, FIGURE 29. This point is illustrated by FIGURE 32, which presents the fractional distribution η_X of each of the several ionic species, defined as

$$\eta_X = \frac{\hat{p}_X(\text{c.w.})}{\hat{p}_X(\text{c.w.}) + p_X(\text{a.p.})} \qquad (10)$$

where c.w. and a.p. denote cloudwater and aerosol particle, respectively. (In these diagrams, the hatched areas represent η values that could be determined unambiguously, whereas the open values represent situations where only a lower limit value could be determined for η because the interstitial concentration was below the limit of detection. Thus these diagrams must be interpreted such that an open area might appear anywhere to the right of the indi-

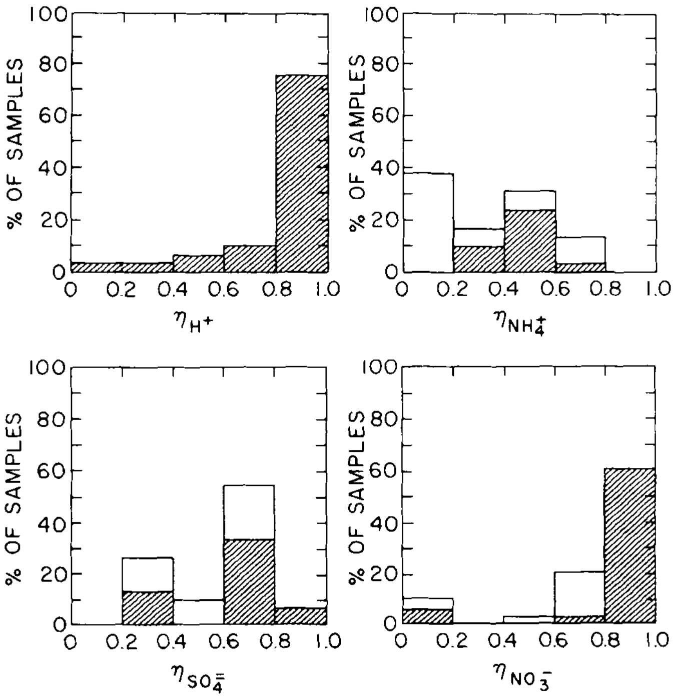

FIGURE 32. Frequency distribution of the scavenging efficiencies η_X, for H^+· NH_4^+, $SO_4^=$, and NO_3^-. $\eta_X = \hat{p}_X/(\hat{p}_X + p_X)$ where $\hat{p}_X$ is the cloudwater potential partial pressure of species X and p_X is the concentration of the interstitial aerosol expressed as a partial pressure. N = 29. (From Daum *et al.*[129] Reprinted by permission.)

cated location.) Despite the ambiguity in these figures introduced by limits of detection, it is nonetheless quite clear with the possible exception of NH_4^+, that the several ionic species are preferentially distributed into the cloudwater. This preferential distribution may be a consequence of uptake of ionic species into the cloudwater from pre-existing aerosol particles and/or of uptake and reaction of gases, which we consider presently.

Interest in concentrations of interstitial gases is focused on the role of these gases as precursors of cloudwater acidity, as neutralizing agents, and as oxidants. HNO_3 and NH_3 have invariably been below detection limits (0.4 ppb), consistent with rapid and complete uptake of these gases by cloudwater as expected from solubility and mass-transport considerations as discussed above. At the other extreme, in-cloud O_3 concentrations have been found to be comparable to those in clear air, consistent with the low solubility of this gas. It must be conceded, however, that since concentrations of O_3 are typically much greater ($\sim$ 40 ppb) than concentrations of potential reducing species with which it might react (e.g., SO_2, typically in the range up to several ppb), it would be difficult to discern any depletion of O_3 due to in-cloud reaction. In-cloud concentrations of nitrogen oxides (mainly NO_2) have been found to be comparable to clear-air concentrations, establishing that NO and NO_2 can persist in clouds for considerable periods of time (of the order of an hour or more). On the other hand, in-cloud SO_2 concentrations appear quite variable—sometimes rather high, comparable to clear-air concentrations, and at other times quite low (below the limit of detection 0.2 ppb), often in the presence of several ppb NO_X, which would suggest that SO_2 should have been present had it not reacted.

It is useful to display these results as distribution efficiencies, as were presented above for ionic constituents. Here we define

$$\eta_S \equiv \frac{\hat{p}_{SO_4^=}\,(\text{c.w.})}{\hat{p}_{SO_4^=}\,(\text{c.w.}) + p_{SO_2}(g)} \tag{11}$$

the fraction of sulfur present at cloudwater sulfate versus gaseous SO_2, and similarly for nitrogen,

$$\eta_N \equiv \frac{\hat{p}_{NO_3^-}\,(\text{c.w.})}{\hat{p}_{NO_3^-}\,(\text{c.w.}) + p_{NO_X}(g)} \tag{12}$$

Frequency distribution diagrams for these quantities are given in FIGURE 33. Looking first at the distribution of nitrogen we see that the weight of the distribution is largely in favor of the gaseous species, with only 20% of the samples exceeding 40% cloudwater nitrate and none exceeding 60%. In contrast it is seen that the fractional uptake of sulfur for the same set of samples was broadly distributed over the entire range of possible values; i.e., there is a significant percentage of the samples (14%) in which η_S was less than 0.2 and, as well, a significant percentage in which the aqueous fraction exceeded 0.6 (at least 10% and perhaps as great as 50%). The broad distribution for sulfur must reflect differing conditions characterizing the various samples, e.g., the extent of oxidation that had occurred in pre-cloud air, the amount

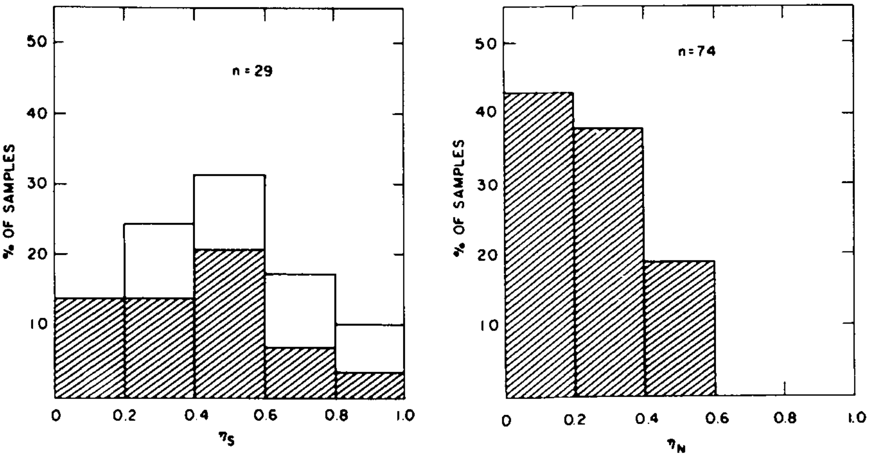

FIGURE 33. Frequency distributions of the scavenging efficiencies η_S for sulfur compounds (N = 29) and η_N for nitrogen compounds (N = 74). $\eta_S = \hat{p}_{SO_4^=}/(\hat{p}_{SO_4^=} + p_{SO_2})$ where $\hat{p}_{SO_4^=}$ is the cloudwater potential partial pressure of $SO_4^=$ and p_{SO_2} is the interstitial SO_2 partial pressure; $\eta_N = \hat{p}_{NO_3^-}/(\hat{p}_{NO_3^-} + p_{NO_X})$. (From Daum *et al.*[129] Reprinted by permission.)

of time in cloud prior to sampling, or the amount of oxidant available for reaction with SO_2. Comparison of the frequency distributions for sulfur and nitrogen establishes that NO_X is much less efficiently converted to cloudwater nitrate than SO_2 is to cloudwater sulfate in the clouds sampled here and/or in the pre-cloud air. Since available information (e.g., Refs. 17, 136, 137) suggests that oxidation of NO_X to HNO_3 in clear air is more rapid than oxidation of SO_2 to $SO_4^=$, these measurements give strong evidence, at least under some circumstances, for the rapid and complete in-cloud oxidation of SO_2 to $SO_4^=$.

As discussed above, laboratory experiments suggest that strong oxidants, O_3 and H_2O_2, may be responsible for this oxidation, so it is of interest to examine concentrations of these species in clouds. As noted already, measurement of O_3 in interstitial cloud air presents no problem. On the other hand, measurement of H_2O_2 in air or in cloud- or rainwater has proved to be a vexatious undertaking, plagued with artifacts in sampling and interferences in determination. In view of the magnitude of the Henry's law coefficient of H_2O_2, which leads to the presence of comparable amounts of this material in the gas and aqueous phases, one might consider determination of this species in either of the two phases. Because of unresolved problems in sampling gaseous H_2O_2, we have chosen to measure this species in collected cloudwater samples.

A fairly convincing approach to the determination of H_2O_2 in cloud- or rainwater is that taken by Guilbault *et al.*[138] as modified for flow systems by Lazrus *et al.*,[139] which makes use of the specificity of enzyme reactions to eliminate interferences. The approach is to assay H_2O_2 by means of the peroxidase-catalyzed dimerization of *p*-hydroxyphenylacetic acid (PHOPAA) and to determine the amount of dimer by spectrofluorimetry. This technique is quite sensitive (limit of detection ∼ 0.2 μM). As it turns out, however, the dimerization is induced as well by organic peroxides; in order to obtain a specific H_2O_2 signal, a second measurement must be made in which H_2O_2 has been destroyed by addition of a second enzyme, catalase. From the difference of the two signals, a specific measure of H_2O_2 concentration is obtained.

We began measurement of H_2O_2 in collected cloudwater samples in late 1982 and have continued such measurements to the present time. In some of the early measurements we were assisted by personnel and equipment from the National Center for Atmospheric Research. Later on, using equipment of our own, which had only a single channel, we obtained for the most part only total peroxide signals, although in a few instances concentrations of organic peroxides have been comparable to those of H_2O_2.[140]

A synopsis of measured concentrations of peroxide expressed as potential partial pressure is presented in FIGURE 34. In the evaluation of $\hat{p}_{H_2O_2}$ we have included not only the concentration of dissolved H_2O_2, but also the concentration of gaseous H_2O_2 in equilibrium with the measured aqueous concentration, evaluated as

$$\hat{p}_{H_2O_2} = [H_2O_2]\,(L\underline{R}T + \tilde{H}_{H_2O_2}) \tag{13}$$

It is seen that H_2O_2 concentrations that we have observed are of the order of 0.1 up to occasionally as great as ∼ 1 ppb. Such values are within the range expected to be present as a consequence of gas-phase photochemical reactions,[141,142] although such a coincidence of values should not be taken as proof of the predominance of the gas-phase pathway for formation of H_2O_2.

It is possible on the basis of measured O_3 and H_2O_2 concentrations to evaluate rates of SO_2 oxidation by either of these species. Such evaluations yield instantaneous oxidation rates for SO_2 of the order of 100% hr^{-1} by H_2O_2 for the higher H_2O_2 concentrations in this range, and some two to three orders

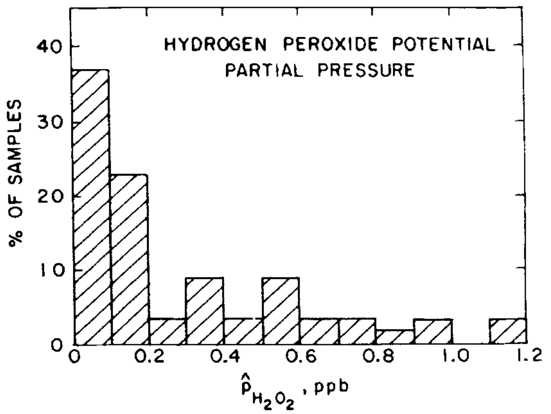

FIGURE 34. Frequency distribution of the potential partial pressure of peroxide in cloudwater samples, $\hat{p}_{H_2O_2}$, evaluated as discussed in the text. N = 57. (From Daum *et al.*[129] Reprinted by permission.)

of magnitude lower for O_3.[124,140] On this basis it would appear that aqueous-phase oxidation of SO_2 by H_2O_2 is a rapid process and perhaps the major pathway for in-cloud oxidation of SO_2.

In order to examine this process further we have plotted a "scatter diagram" of gas-phase SO_2 partial pressures against aqueous-phase H_2O_2 concentrations (expressed as potential partial pressure) (FIG. 35). Most striking in this figure is the division of the data points into two classes, those with appreciable H_2O_2 but with very low SO_2, near or below the limit of detection, and those with appreciable SO_2 but with very low H_2O_2, near or below the limit of detection for that species. These data suggest a near mutual exclusivity of the two species in clouds, which we interpret as indicating that reaction had proceeded until the reagent initially present in lesser concentration (the "limiting reagent") has been exhausted. We consider these findings to be an exciting and important confirmation from field measurements of the occurrence of in-cloud reaction of SO_2 and H_2O_2, as has been anticipated from evaluations based on laboratory studies. It must be stressed that our measurements thus far have been restricted to warm stratiform clouds, for the most part not in the immediate vicinity of sources, and it will thus be interesting to see how generally the mutual exclusivity of $SO_2(g)$ and $H_2O_2(aq)$ holds. We would note that Richards *et al.*[116] have found these species to be simultaneously present in clouds in the Los Angeles urban area.

An additional consideration that is suggested in these data concerns the capacity of ambient concentrations of H_2O_2 for oxidation of SO_2. Since reaction of SO_2 with H_2O_2 depletes H_2O_2 on a one-to-one (molar) basis for every SO_2 oxidized, it is seen from FIGURE 34 that H_2O_2 concentrations such as we have observed are capable of oxidizing only a limited amount of SO_2. It thus seems plausible that in regions of high SO_2 concentrations (i.e., near sources) H_2O_2 would be exhausted by reaction with SO_2, whereas in regions well re-

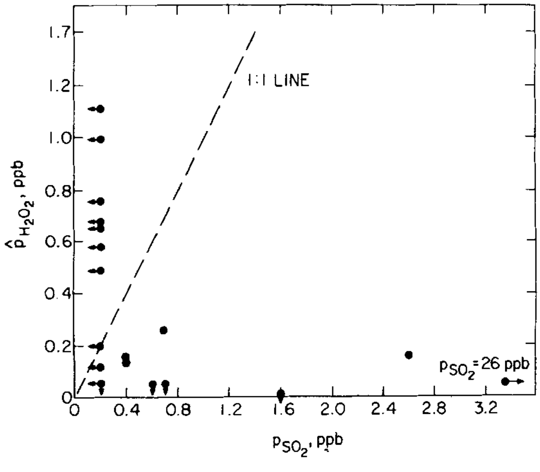

FIGURE 35. Scatter diagram of cloudwater peroxide potential partial pressure versus interstitial SO_2 partial pressure. (From Daum *et al.*[129] Reprinted by permission.)

moved from sources H_2O_2 would be present in excess. Thus the rate or extent of SO_2 oxidation and incorporation into precipitation would be dependent on the SO_2 concentration in relation to the H_2O_2 concentration prior to reaction. Considerations such as these bear directly on the development of strategies for control of acid deposition and in particular on the question of linearity of acid deposition in response to changes in SO_2 emissions such as might be imposed by regulation.[2,143] Unraveling the details of these processes is the task of future research.

CONCLUSION

This article has covered a lot of ground, ranging from fundamental laboratory studies of chemical thermodynamics and kinetics to highly empirical measurements of the concentrations of chemicals in the ambient atmosphere. However, the unifying theme of the article, and for that matter of our work on cloud chemistry, has been an underlying faith in the pertinence and transferability of laboratory-determined quantities to description of chemical reactions in the atmosphere. Of course, this approach must be taken with caution and wisdom. In the case of chemical thermodynamics, we have noted that a strong driving force for a given reaction does not necessarily imply that the reaction will proceed to completion. Similarly, in the case of chemical kinetics one must be careful to describe the system in terms of appropriate elementary reactions in order to permit confident application of laboratory-determined rate expressions to field evaluations. Additionally, one must always be alert to the possibility of catalysts or inhibitors that can alter the rate of reaction from that determined in laboratory studies. However, such processes are themselves amenable to laboratory study; they just represent a more complicated sequence of reactions.

With respect to the chemistry of clouds, a level of understanding of cloud acidification processes has been attained, from both laboratory studies and field measurements, that is substantially greater than that previously available. Ultimately, information derived from studies such as these will be incorporated into the description of source receptor relationships in acid deposition and, it is hoped, lead to development of more efficient strategies for the mitigation of acid deposition that might otherwise have been obtained.

SUMMARY

The process whereby sulfur and nitrogen oxides are transformed in the atmosphere and deposited to the surface in precipitation is of current interest in atmospheric science because of concern over apparent widespread environmental effects associated with such deposition. A key component of this process is the oxidation of SO_2 and NO_x ($\equiv NO + NO_2$) to form sulfuric and nitric acids that are deposited in precipitation. This article presents two complementary approaches to the study of this chemistry as it occurs in liquid water clouds. The first approach relies upon laboratory determination of fun-

damental physical and chemical properties (such as overall reaction equilibria, gas solubilities, chemical kinetic rate expressions, and diffusion coefficients) and evaluation of rates of dissolution and reaction for representative reagent concentrations and physical situations. The second approach consists of measuring concentrations of relevant reagent and product species and other pertinent quantities (most importantly, cloud liquid water content) in and about clouds and of drawing inferences from these measurements about the rate and extent of processes responsible for establishing cloudwater composition.

On the basis of laboratory studies, the following inferences may be made: (1) Aqueous-phase oxidation of SO_2 by H_2O_2 or O_3 may be sufficiently rapid to contribute significantly to cloudwater acidity for representative concentrations of these oxidants; however, the rate of the O_3 reaction decreases strongly with decreasing pH and is therefore of relatively little importance below about pH 4.5. (2) Despite strong thermochemical driving force for oxidation of NO_2 to nitric acid in cloudwater, this reaction appears to be negligibly slow for representative concentrations of NO_2, largely because of the low Henry's law solubility of this species in water. These inferences gain support from field measurements of the composition of liquid water stratiform clouds at various locations in the eastern United States, which indicate that the fractional uptake of SO_2 (as $SO_4^=$) by cloudwater is frequently quite high, whereas a corresponding high fractional uptake of NO_x as NO_3^- is never observed. A near mutual exclusivity of gaseous SO_2 and dissolved H_2O_2 in clouds supports the inference that reaction of these species in clouds is rapid and can represent a major process for cloudwater acidification.

[**Note added in proof:** The period since June 1984, when this article was submitted for publication, has been a time of extraordinary activity and productivity in research directed to both "sides" of cloud chemistry. Attention is called here to pertinent new papers dealing with laboratory studies (References 144–184) and field studies (References 185–224) and as well to interpretive and modeling studies that deal with cloud chemistry (References 225–270). Attention is called as well to two recent textbooks that extensively discuss cloud chemistry (References 271 and 272).]

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