

CLOUD CHEMISTRY

S. E. Schwartz
Atmospheric Sciences Division
Brookhaven National Laboratory
Upton, NY 11973-5000

March 2001

For inclusion in
"Handbook of Weather, Climate, and Water",
McGraw-Hill, 2001.

By acceptance of this article, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper.

Research by BNL investigators was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-98CH10886.

CLOUD CHEMISTRY

INTRODUCTION

The term "cloud chemistry" is considered here to comprise both cloud composition and reactions that take place in clouds. Clouds are a very special subset of the atmosphere because they present substantial amounts of condensed-phase water (liquid or solid) that can dissolve gases that would otherwise be present in the gas phase, and as a consequence of condensed-phase reactions permit reactions to occur that would not otherwise occur or which would be much slower. In this sense clouds may be considered to serve as catalysts of atmospheric reactions.

The uptake and reaction of material in clouds, especially sulfur and nitrogen oxides and acids, has received particular attention in the context of gaining improved understanding the processes responsible for acid deposition. Consequently the examples developed here focus on these chemical systems. However much of the resulting understanding of these phenomena is applicable more generally to other systems.

CLOUD PHYSICAL PROPERTIES PERTINENT TO CLOUD CHEMISTRY

Clouds consist of a suspension of liquid or solid (ice) particles in air. Thus, formally, a cloud is an aerosol, a suspension of particles in air. However it is useful to distinguish clouds from clear-air (non-cloud) aerosols. The cloud environment is slightly supersaturated with respect to liquid water or ice, respectively. The typical amount of condensed-phase water is 0.1 to 1 g m⁻³ (roughly equivalent to 0.1 to 1 g per kg of air). The amount of condensed-phase water is substantially lower in cirrus clouds and in polar stratospheric clouds. For condensed-phase amount substantially exceeding 1 g m⁻³, coagulation occurs and precipitation rapidly develops, removing condensed-phase water from the cloud.

A liquid water content of 1 g m⁻³ corresponds (within the approximation that the density of water is 1 kg m⁻³) to a liquid water volume fraction $L = 1 \times 10^{-6}$, or one part per million by volume. On dimensional grounds the separation between cloud droplets is $\sim L^{-3}$ times the diameter of the droplets; for $L = 1 \times 10^{-6}$, the average inter-drop separation is ~ 100 times the drop diameter. Thus clouds must be considered a sparse suspension of condensed phase water. Clouds are mostly air. Thus any consideration of cloud chemistry must deal with both the gas phase and the condensed phase.

Despite this sparseness, clouds still contain much more condensed-phase material than cloud-free air. Consider a clear-air aerosol of mass loading of 100 $\mu\text{g m}^{-3}$; within the approximation of density equal to 1 kg m⁻³, the corresponding condensed phase volume fraction is 1×10^{-10} . The much greater mass loading of a cloud leads among other things to its greater light scattering, the most distinguishing feature of clouds.

Clouds form when air, containing water vapor, is cooled to a temperature below its dew point. Typically this occurs when air is lifted, for example buoyant rise of a convective parcel, or larger scale gentle upward motion of warm air over denser cooler air. Cooling by conduction can also be important, for example in ground fogs, as can radiative cooling. The condensation process defines the number concentration of cloud droplets by activating a certain fraction of pre-existing aerosol particles into cloud droplets [**CROSS REFERENCE:** Microphysical processes in the atmosphere *Raubert*; Wet Deposition *Walcek*] This number concentration is typically 100 to 1000 per cm³ or 10⁸ to 10⁹ per m³. Thus within the cloud the condensed-phase water is finely suspended. For droplet concentration of $1 \times$

10^9 per m^3 and liquid water volume fraction of $1 \times 10^{-6} m^3/m^3$, the corresponding volume of an individual droplet is $1 \times 10^{-15} m^3$ and the corresponding diameter $\sim 1 \times 10^{-5} m$ or $10 \mu m$.

Invariably there is a dispersion in the diameter of drops; that is, there is a spectrum of cloud droplet sizes. This influences mass-transport processes, which are faster for smaller droplets, affecting uptake and reaction of gases in clouds. Typically cloud droplet distributions are rather sharply peaked. This is a consequence of the fact that mass transport of condensing water is faster for smaller droplets thereby allowing the smaller droplets to "catch up" with the larger ones early in the cloud formation process.

Clouds persist in the atmosphere for a few tens of minutes (short-lived cumulus) to a few tens of hours (persistent stratus). Most clouds evaporate, rather than precipitate, thereby returning dissolved nonvolatile material to the clear air as aerosol particles.

SOURCES OF CLOUDWATER COMPOSITION

Cloudwater composition is very much a function of location, being dominated by availability of soluble ionic species. Principal ionic species present in cloudwater include sodium and chloride, from seawater, sulfate and nitrate anions, and ammonium and hydrogen ion as cations. In regions influenced by industrial emissions of sulfur and nitrogen oxides, cloudwater concentrations of H^+ are commonly $10^{-4} mol L^{-1}$ (molar, M) and not uncommonly $10^{-3} M$ or higher [Daum et al., 1984].

The fact that cloud droplets form on existing aerosol particles has immediate implications for cloudwater composition. Consider an ammonium sulfate aerosol particle of dry diameter $0.1 \mu m$ that serves as a nucleus of a cloud droplet of $10 \mu m$ diameter. The volume of the particle is $\sim 10^{-21} m^3$. For density $\sim 1000 kg m^{-3}$ and molecular weight $100 g mol^{-1}$ ($\sim 0.1 kg mol^{-1}$), the amount of ammonium sulfate contained in the particle is $10^{-17} mol$. For this material dissolved in a $10 \mu m$ droplet ($\sim 10^{-15} m^3$) the solution concentration is $\sim 10^{-2} mol m^{-3}$ or $\sim 10^{-5} M$. This concentration is at the low end of the range of concentrations of sulfate in cloudwater (and also in precipitation) in regions influenced by industrial emissions [**CROSS REFERENCE** Acid Rain - Galloway]. It should be stressed that this figure varies as the third power of the particle diameter, that is, an order of magnitude for a factor of 2 in particle diameter. Thus for the particle diameter $0.2 \mu m$, the concentration is $10^{-4} M$.

Consider the correspondence between aqueous-phase concentration and the equivalent mixing ratio of the material in air. For 1000 $0.1 \mu m$ -diameter, unit-density particles per cm^3 , the corresponding mass loading is $1 \mu g m^{-3}$, a loading that is rather low in the context of industrialized regions [**CROSS REFERENCE** Visibility - Husar], albeit still substantially greater than that characteristic of regions remote from industrial sources. For molecular weight 100, this corresponds to a molar mixing ratio relative to air, $x \approx 0.3 nmol/mol(\text{air})$ (ppb). For a substance S that dissolves entirely in cloudwater, the relation between mixing ratio of the substance x_S in air and concentration in cloudwater is:

$$[S] = x_S p_{\text{atm}} / LR_g T$$

where [S] is aqueous concentration, p_{atm} is the atmospheric pressure, R_g is the universal gas constant, and T is the absolute temperature. In SI units p_{atm} is in units of pascal and $R_g = 8.3 J mol^{-1} K^{-1}$. The resulting concentration [S] is in units $mol m^{-3}$. In practical units (concentration in $mol L^{-1}$ and pressure in bar; $1 bar = 10^5 Pa$)

$$[S](mol L^{-1}) = 10^2 x_S p_{\text{atm}}(bar) / LR_g T$$

In general the fractional uptake of soluble (ionic) aerosol species into cloudwater is fairly high, approaching unity at low aerosol loading and/or high updraft velocities leading to fairly high maximum

supersaturation governing activation of aerosol particles (Leitch et al., 1996). However in the case of gases the uptake varies substantially depending on the solubility and/or reactivity of the gas in question.

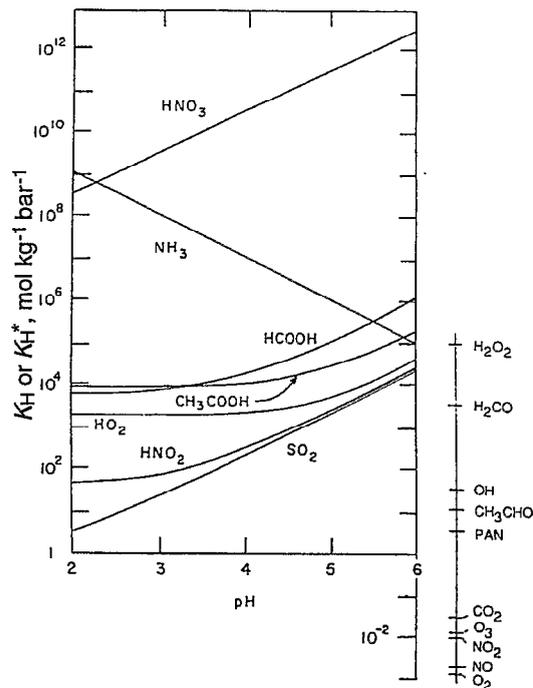
UPTAKE OF GASES INTO CLOUDWATER

In general a gaseous substance does not dissolve entirely in cloudwater in view of the rather limited solubility of most atmospheric gases in water--if the gas were highly soluble in cloudwater it would be rapidly rained out and no longer in the atmosphere. The equilibrium concentration of a gaseous substance S physically dissolved in a liquid is given by Henry's law (**CROSS REFERENCE WALCEK - Wet deposition**)

$$[S(\text{aq})] = H_S p_S = H_S x_S p_{\text{atm}}$$

where H_S is the Henry's law solubility coefficient of the gas. (In practical units, p_S in bar and $[S(\text{aq})]$ in mol L^{-1} i.e., M, H_S has units M bar^{-1} .) Abundance of a gas-phase species is expressed in terms of the molar mixing ratio in air x , which is applicable equivalently to substances in gas, aerosol, or solution phases (Schwartz and Warneck, 1995). Characterization of the Henry's law solubility is the first step to understanding the uptake and reaction of a gas in cloudwater. Henry's law solubility coefficients of many gases of atmospheric importance are given in Figure 1.

Figure 1. pH-Dependence of the effective Henry's law coefficient for gases which undergo rapid acid-base dissociation reactions in dilute aqueous solution, as a function of solution pH. Buffer capacity of solution is assumed to greatly exceed incremental concentration from uptake of indicated gas. Also indicated at the right of the figure are Henry's law coefficients for non-dissociative gases. $T \approx 300$ K. Modified from Schwartz (1986).



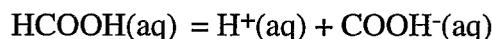
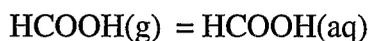
The ratio of the amount of material in solution to gas phase (distribution ratio), under assumption of Henry's law equilibrium, is given by

$$D_{\text{aq/g}} \equiv \frac{\text{moles in aqueous phase}}{\text{moles in gas phase}} = 10^{-2} L H (\text{M bar}^{-1}) R_g T$$

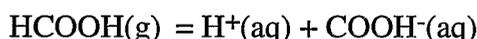
If this is written as $D_{\text{aq/g}} = H / H_{1/2}$ where $H_{1/2} = 10^{-2} L R_g T$ then for any specified value of L , the value of Henry's law solubility coefficient for which the gas is equally distributed between the gas phase and cloudwater is given by $H_{1/2}$. Consider a cloud of rather high liquid volume fraction $L = 10^{-6}$ (i.e., $\sim 1 \text{ g m}^{-3}$ liquid water content); the corresponding value of $H_{1/2}$ is $\sim 4 \times 10^4 \text{ M bar}^{-1}$; $H_{1/2}$ would be

correspondingly higher for lower value of L . Comparison with the values of Henry's law solubility coefficients given in Figure 1 shows that virtually all such coefficients are orders of magnitude less than this value, supporting the assertion that reaction of the dissolved gas is required for substantial uptake into cloudwater.

In the case of gases that undergo rapid reversible reaction with water, for example hydration or acid dissociation, it is necessary to consider the overall solubility equilibrium, not just the Henry's law equilibrium. Consider the solubility equilibrium for the dissolution of an acidic gas, for example formic acid, HCOOH. The overall equilibrium for this dissolution may be thought to consist of the following steps:



These reactions sum to give the overall reaction



The corresponding equilibrium expressions are

$$H_{\text{HCOOH}} = \frac{[\text{HCOOH(aq)}]}{x_{\text{HCOOH}}P_{\text{atm}}}, K_a = \frac{[\text{H}^+][\text{COOH}^-]}{[\text{HCOOH(aq)}]}, \text{ and } K_{\text{eq}} = \frac{[\text{H}^+][\text{COOH}^-]}{x_{\text{HCOOH}}P_{\text{atm}}}$$

where K_a is the acid dissociation constant of aqueous formic acid. Depending on the situation it may be more useful to deal with the overall solubility or with the individual equilibria.

The total concentration of the dissolved gas can be written (here staying with the example of formic acid) as

$$[\text{Formic acid}] \equiv [\text{HCOOH}] + [\text{COOH}^-] = H_{\text{HCOOH}}x_{\text{HCOOH}}P_{\text{atm}} \left(1 + \frac{K_{\text{eq}}}{[\text{H}^+]} \right)$$

It is often a good assumption that the cloudwater is well buffered against change in acid concentration $[\text{H}^+]$ resulting from the incremental uptake of gases present at low partial pressures characteristic of the ambient atmosphere. Under this assumption, $[\text{H}^+]$ is a constant and hence the aqueous concentration is linear in gas-phase partial pressure with an effective Henry's law solubility coefficient defined as:

$$H_{\text{HCOOH}}^* \equiv H_{\text{HCOOH}} \left(1 + \frac{K_{\text{eq}}}{[\text{H}^+]} \right)$$

so that one obtains a Henry's law-like expression for the overall solubility,

$$[\text{Formic acid}] = H_{\text{HCOOH}}^* x_{\text{HCOOH}} P_{\text{atm}}$$

In the case of SO_2 there are two acid dissociation equilibria. The effective Henry's law solubility coefficient for S(IV) (the Roman numeral IV denotes the oxidation state) is

$$H_{\text{S(IV)}}^* \equiv H_{\text{SO}_2} \left(1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}^+]^2} \right)$$

where K_{a1} and K_{a2} denote the first and second dissociation constants, respectively.

Values of effective Henry's law solubility coefficients are shown in Figure 1 as a function of solution pH for the range of pH values typical of cloudwater. The effective solubility coefficient can greatly exceed the Henry's law coefficient for physical dissolution, especially for strong acids, such as nitric acid, and also for ammonia, which is highly soluble in the form of ammonium ion NH_4^+ . These effective Henry's law solubility coefficients can also substantially exceed $H_{1/2}$, indicating that at equilibrium, such highly soluble gases as HNO_3 are essentially entirely taken up by cloudwater.

Because the chemical kinetics of acid dissociation reactions are generally quite rapid, the uptake of acidic gases such as HNO_3 is itself quite rapid, under control of mass-transport processes rather than chemical kinetics. The mass -transport processes governing this uptake are essentially identical to those governing the transfer of water vapor itself to and from cloud droplets, and the solubility of a gas such as HNO_3 is so that the uptake of soluble gases occurs on the time scale of cloud droplet activation and growth, that is taking place on a time scale of a few seconds to a few tens of seconds. This can result in such soluble gases being preferentially concentrated in the initially formed drops rather than being distributed uniformly throughout the cloud droplet spectrum [Wurzler et al, 1995]; this can influence subsequent uptake and reaction of less soluble gases such as SO_2 . A gas such as HNO_3 that dissolves in a growing cloud droplet contributes soluble material to the droplet thereby adding to the Raoult effect of the solute already serving as the cloud condensation nucleus and increasing its cloud nucleating potential. This can have a further influence on cloud droplet composition and can also lead to situations of free cloud droplet growth at relative humidity slightly below 100% (Kulmala et al, 1997).

REACTIVE UPTAKE OF GASES BY CLOUDWATER

Without further reaction the fractional uptake of SO_2 into cloudwater is low, even at fairly high pH. The same is true *a fortiori* for NO_2 , which does not undergo acid dissociation reaction in aqueous solution. However there is strong thermodynamic driving force in clouds for the reactive uptake of these gases to form sulfuric and nitric acids, respectively, the principal species contributing to acid deposition. This situation has stimulated substantial research interest in the processes whereby these gases are transformed into the acids and incorporated into cloudwater. The present understanding of these reactive uptake processes is that in the case of SO_2 , the process consisting of uptake of SO_2 followed by aqueous-phase oxidation contributes substantially to the uptake of sulfuric acid by cloudwater and to the deposition of this material in precipitation. In contrast, the uptake process for NO_2 to form nitric acid appears to be dominated by gas-phase oxidation followed by uptake of the oxidized species. This section presents the formalism by which the rate of aqueous-phase reaction in cloudwater may be evaluated treating these two gases as examples.

Consider the rate of aqueous-phase reaction of dissolved sulfur-IV to be given by

$$-\frac{d[\text{S(IV)}]}{dt} = \frac{d[\text{S(VI)}]}{dt} = k^{(1)}[\text{S(IV)}]$$

where $k^{(1)}$ denotes an effective first-order rate coefficient, which in general may be equal to a second-order rate coefficient times the concentration of a second reagent. The reaction need not be first-order in the reagent sulfur-IV; additional power(s) of $[\text{S(IV)}]$ could be incorporated within the effective first-order rate coefficient $k^{(1)}$. It is useful to refer the reaction rate to the total S(IV) concentration because of equilibration of individual sulfur-IV species within solution, $\text{SO}_2(\text{aq})$, HSO_3^- or bisulfite, and SO_3^{2-} or sulfite, that is rapid relative to depletion by reaction. The aqueous-phase reaction rate can be related to the gas-phase mixing ratio of SO_2 by solubility equilibria between aqueous-phase concentration of S(IV) and gas-phase partial pressure of SO_2 , under assumption that these equilibria apply. This phase equilibrium is expected to hold if mass-transport rates coupling the two phases are sufficiently fast to

replenish the aqueous-phase material that is depleted by reaction, a situation that is normally expected to obtain, as discussed below. Hence

$$-\frac{d[\text{S(IV)}]}{dt} = \frac{d[\text{S(VI)}]}{dt} = k^{(1)} H_{\text{S(IV)}}^* x_{\text{SO}_2} p_{\text{atm}}$$

Under assumption that the aqueous-phase rate is uniform within a given region of a cloud, then the rate of reaction, expressed as a rate of decrease in the mixing ratio of SO₂, is

$$\frac{dx_{\text{SO}_2}}{dt} = -\left\{10^{-2} LR_g T k^{(1)} H_{\text{S(IV)}}^*\right\} x_{\text{SO}_2} = -k_{\text{eff}}^{(1)} x_{\text{SO}_2}$$

The quantity in braces is an effective first-order rate coefficient of aqueous-phase reaction, referred to the gas-phase mixing ratio; this quantity may be directly employed in evaluating rates of reactions or in comparison to rate coefficients for loss by gas-phase reactions. Note that $k_{\text{eff}}^{(1)}$ scales linearly with liquid water content and with Henry's law solubility coefficient. The more water that is present to serve as volume of reactor, the faster the reaction. Likewise, the more soluble the reagent gas, the faster the reaction. Evaluation of the rate of a specific reaction requires knowledge of the effective first-order rate coefficient of aqueous-phase reaction, $k^{(1)}$. For this one must identify the mechanism and rate of aqueous-phase reaction.

There is a strong thermodynamic driving force for oxidation of dissolved SO₂ by molecular oxygen, which, because of its abundance, might be thought to be the key oxidant of SO₂ in cloudwater. However this reaction is quite slow unless catalyzed, for example by transition metal ions. Although catalyzed oxidation of dissolved sulfur-IV by dissolved molecular oxygen may be of some importance in some circumstances, the species that have been identified as of principal importance in oxidation of sulfur-IV in cloudwater are the strong oxidants ozone (O₃) and hydrogen peroxide (H₂O₂). Ozone is commonly present in the atmosphere at a mixing ratio of 30-50 nmol/mol. Hydrogen peroxide is present at much lower abundance, ~ 1 nmol/mol. These mixing ratios compare with those for SO₂ of order 10 nmol/mol in regions influenced by industrial emissions, to much lower at locations well removed from sources.

Consider first the ozone reaction. The rate of aqueous-phase reaction is given as

$$-\frac{d[\text{S(IV)}]}{dt} = \frac{d[\text{S(VI)}]}{dt} = k^{(2)} [\text{S(IV)}][\text{O}_3], \text{ i.e., } k^{(1)} = k^{(2)} [\text{O}_3]$$

where $k^{(2)}$ is a second-order rate constant that must be determined by laboratory measurement, and has been found to exhibit a strong pH-dependence, increasing with increasing pH, Figure 2a. The concentration of dissolved ozone is related to the gas-phase mixing ratio of this species again under assumption of solubility equilibrium, as

$$[\text{O}_3] = H_{\text{O}_3} x_{\text{O}_3} p_{\text{atm}}$$

so that

$$k_{\text{eff}}^{(1)} = 10^{-2} LR_g T k^{(2)} H_{\text{O}_3} x_{\text{O}_3} H_{\text{S(IV)}}^* p_{\text{atm}}$$

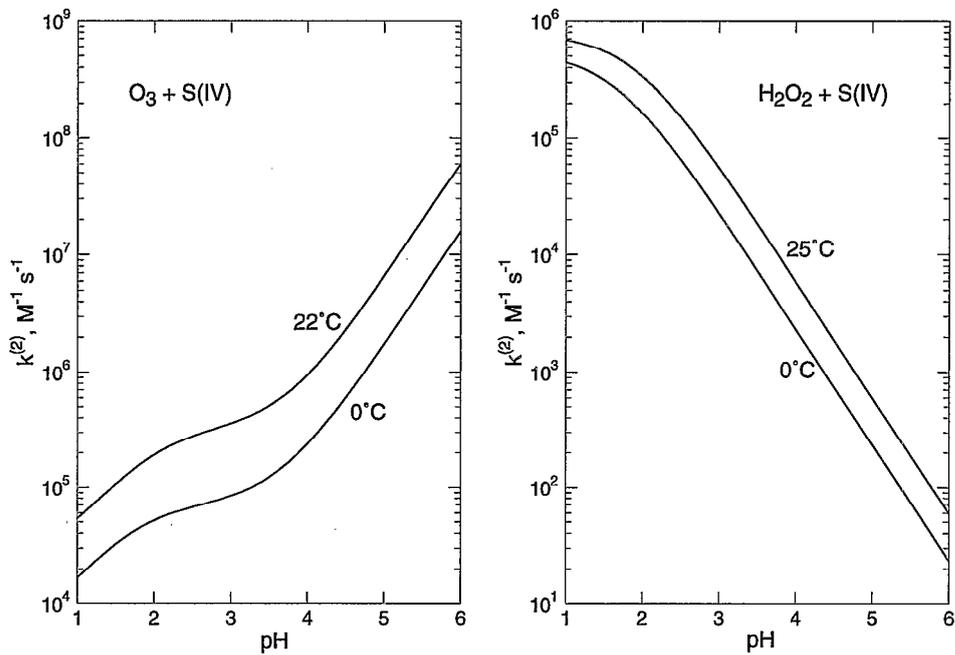
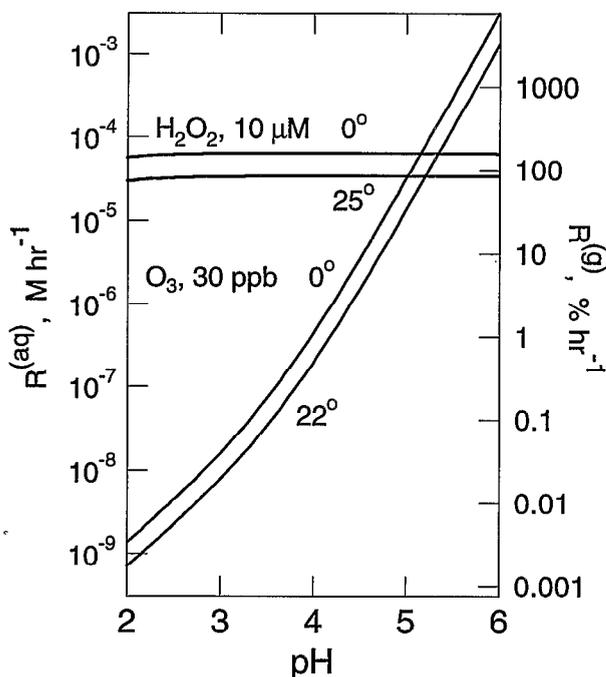


Figure 2. Effective second-order rate coefficients for aqueous-phase reaction of S(IV) with O₃ and with H₂O₂ as a function of pH. Modified from Schwartz (1988).

Combining the kinetic and solubility data permits the rate of reaction to be evaluated for known or assumed conditions of cloud liquid water content and partial pressures of reagent gases, Figure 3. Here the left-hand ordinate gives the rate of aqueous-phase reaction. The right-hand ordinate gives the effective first-order rate coefficient of aqueous-phase reaction, referred to the gas-phase mixing ratio; $k_{eff}^{(1)}$ for indicated conditions, expressed in units of percent per hour. Note the strong pH-dependence, rate increasing with pH, resulting from the pH dependences of sulfur-IV solubility (Figure 1) and kinetic rate constant (Figure 2). The ozone reaction is quite rapid at high pH. However because of production of sulfuric acid as the reaction proceeds, the pH rapidly becomes lower decreasing the rate. Although a strong acid concentration of 10 μ M (pH 5) is quickly reached, in perhaps 10 minutes, a much greater time, \sim 10 hours, is required to reach an acid concentration of 50 μ M. For this reason the ozone reaction is unlikely to account for cloudwater acidities of 10^{-4} to 10^{-3} M commonly observed in regions influenced by industrial emissions of SO₂.

Figure 3. Instantaneous rate of aqueous-phase oxidation of S(IV) by H₂O₂ and O₃, evaluated as a function of pH for representative non-urban reagent concentrations. The rates scale approximately linearly with reagent concentrations. The right hand ordinate gives the oxidation rate of SO₂ referred to the gas-phase partial pressure and expressed as percent per hour for a liquid water content $L = 1 \times 10^{-6}$ (1 cm³ m⁻³); the rate scales approximately linearly with L . For the H₂O₂ reaction the indicated aqueous-phase concentration of H₂O₂ corresponds to total mixing ratio of this species (gas-plus aqueous-phase; the two are comparable) of $\sim 0.6 \times 10^{-9}$.



Now consider the hydrogen peroxide reaction, whose aqueous-phase rate is given by:

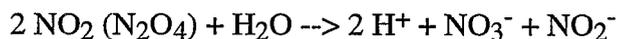
$$-\frac{d[\text{S(IV)}]}{dt} = \frac{d[\text{S(VI)}]}{dt} = k^{(2)}[\text{S(IV)}][\text{H}_2\text{O}_2]$$

This reaction is acid-catalyzed; that is, the second-order aqueous-phase rate constant increases with decreasing pH, Figure 2b. The pH dependences of solubility and reaction kinetics now cancel to yield a reaction rate that is roughly independent of pH throughout the pH range pertinent to cloudwater acidification, Figure 3. For the conditions given in Figure 3 the rates of the O₃ and H₂O₂ reactions are equal roughly at pH 5. An effective first-order reaction rate of 100 % hr⁻¹ corresponds to a 1/e lifetime of SO₂ of one hour; the actual lifetime would depend on actual conditions. The H₂O₂ reaction is the only identified atmospheric reaction capable of maintaining the SO₂ oxidation rate sufficiently rapid to produce observed cloudwater H⁺ and SO₄²⁻ concentrations on time scales pertinent to cloud acidification.

In the case of the ozone reaction, ambient mixing ratios of O₃ are generally sufficiently in excess of those of SO₂ that depletion of O₃ need not be considered. However ambient concentrations of H₂O₂, which are typically below 3 nmol/mol are often well less than ambient SO₂ mixing ratios. This leads to a situation where the reaction proceeds rapidly to completion by exhausting the H₂O₂ reagent. If on the other hand SO₂ mixing ratios are the lesser, then the reaction can rapidly and completely exhaust ambient SO₂. The time scale of this process, a few tens of minutes for representative mixing ratios in the nmol/mol region, leads to a situation where the extent of reaction is controlled by the limiting reagent. Such appears to be the case as indicated by field measurements simultaneously examining H₂O₂ and SO₂ mixing ratios in clouds. A survey of nonprecipitating stratiform clouds indicated that although either species is frequently present at nmol/mol mixing ratios, appreciable mixing ratios of the two species are virtually never simultaneously present. [Daum, 1990]. The contribution of this reaction to cloudwater acidification has been directly confirmed by field measurements under well defined flow conditions, including experiments with artificially introduced SO₂ and inert tracers, showing concomitant decreases in SO₂, and H₂O₂ and increases in H⁺ and SO₄²⁻ consistent with this reaction. This reaction is now thought to be the major contributor to atmospheric oxidation of SO₂, contributing

both to acid precipitation and, in the likely event of cloud evaporation to sulfate aerosol, a principal component of atmospheric aerosols.

Based on laboratory and industrial experience nitrogen dioxide (NO₂) is known to be highly reactive with liquid water forming nitric and/or nitrous acids, the initial reaction being

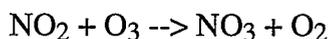


for which there is strong thermochemical driving force; the N₂O₄ in parentheses indicates the possible participation of the NO₂ dimer, dinitrogen tetroxide. (This reaction is the basis for industrial manufacture of nitric acid.) It was therefore assumed by many atmospheric chemists that NO₂ would be rapidly taken up in cloudwater in the ambient atmosphere. Consideration of the mechanism of this reaction gives the aqueous-phase rate expression,

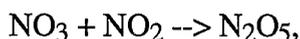
$$-\frac{d[\text{NO}_2]}{dt} = 2k^{(2)} H_{\text{NO}_2}^2 x_{\text{NO}_2}^2 p_{\text{atm}}^2$$

Determination of the Henry's law coefficient for NO₂ and the second order reaction rate constant permitted evaluation of this rate for atmospheric conditions. Such evaluations have indicated that this rate is much too slow to contribute appreciably to NO₂ uptake by cloudwater at ambient concentrations. The reason for this, and for the great difference with experience at high NO₂ concentrations, is that the reaction is second-order in the concentration of a very weakly soluble gas. Comparisons of NO₂ mixing ratios in clouds with those in clear air in the vicinity of clouds indicates that the fractional uptake of NO₂ into cloudwater is quite small, lending confirmation to the above picture. Alternative possible mechanisms for NO₂ uptake include reaction with reducing species dissolved in cloudwater, as NO₂ is a fairly strong oxidant.

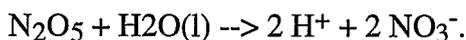
An alternative mechanism that may be important, especially at night is initiated by the gas-phase reactions



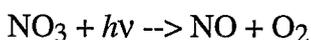
followed by



with N₂O₅ being taken up by cloudwater by reaction to form nitric acid:

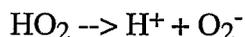


The rate of reaction is controlled by the rate of the initiation reaction of NO₂ with O₃, which is several percent per hour at typical ozone mixing ratios of a few tens of nmol/mol. The reason that this appears to be important at night but not during the day is that photolysis of NO₃ by visible radiation



is the major sink of NO₃ during the day, thereby cutting off the overall reaction.

In addition to these acidification reactions several other in-cloud reactions have been identified as of importance or potential importance in atmospheric chemistry. The hydroperoxy radical, HO₂, which plays an important role in gas-phase photochemistry as part of the chain of reactions leading to ozone formation by oxidation of NO and hydrocarbons, is thought to be rather soluble in water because of its weak-acid dissociation



The dissolved material undergoes rapid self-reaction to form hydrogen peroxide. It has been suggested that the occurrence of this process can substantially influence the ozone budget in the remote troposphere. However the process remains somewhat speculative in view of the lack of firm information on the solubility of the HO₂ radical.

Several studies have demonstrated substantial aqueous-phase formation of H₂O₂ by photochemical reactions in collected cloudwater. The exact processes are not yet elucidated, but evidently involve trace organic species, which are difficult to characterize. Such reactions may contribute substantially to SO₂ oxidation in situations where this oxidation is limited by the amount of H₂O₂ initially present. More generally, it may be noted that photochemical reactions, in both gas and solution phases, may be enhanced in the tops of clouds because of enhanced photolysis fluxes, by a factor of 5 or more, that result from multiple scattering of solar radiation within clouds.

COUPLED MASS-TRANSPORT AND CHEMICAL REACTION

As indicated above quantitative evaluation of the rates of aqueous-phase reactions in clouds are predicated on the assumption that the rate of mass-transport processes coupling the gas-phase reservoir of reagent gas to the solution phase within individual cloud droplets is sufficiently fast to maintain the Henry's law equilibrium in competition with the sink of dissolved material by aqueous-phase reaction. The pertinent mass-transfer processes are gas-phase diffusion, from the bulk of the gas-phase to the gas-liquid interface; transfer across the interface, as governed by the gas-kinetic collision rate and the mass-accommodation coefficient, the fraction of collisions resulting in transfer of material across the interface, a property characteristic of individual gases and solutions; and aqueous-phase diffusion of the dissolved gas occurring concomitantly with aqueous-phase reaction. In general, if the reaction is sufficiently slow, mass transport is sufficiently rapid to maintain the solubility equilibria, but departure from equilibrium occurs for sufficiently rapid reaction rates. Criteria for the onset of this "mass-transport limitation" of the rate of aqueous-phase reactions in clouds have been developed in terms of drop radius, Henry's law coefficient, effective first-order reaction rate coefficient, diffusion coefficients, and mass-accommodation coefficients. For the most part, the rate of reaction of SO₂ in cloudwater appears only minimally limited by mass-transport rates, the exception being the ozone reaction at high pH, under which condition both the solubility and effective first-order rate coefficient are quite large.

SUMMARY

Clouds present substantial concentrations of liquid-phase water, which can potentially serve as a medium for dissolution and reaction of atmospheric gases. The important precursors of acid deposition, SO₂ and nitrogen oxides NO and NO₂ are only sparingly soluble in clouds without further oxidation to sulfuric and nitric acids. In the case of SO₂ aqueous-phase reaction with hydrogen peroxide, and to lesser extent ozone, are identified as important processes leading to this oxidation, and methods have been described by which to evaluate the rates of these reactions. The limited solubility of the nitrogen oxides precludes significant aqueous-phase reaction of these species, but gas-phase reactions in clouds can be important especially at night.

REFERENCES

- Daum, P. H., Kelly, T. J., Schwartz, S. E., and Newman, L. (1984) Measurements of the chemical composition of stratiform clouds. *Atmos. Environ.* **18**, 2671-2684.
- Daum, P. H. (1990) Observations of H₂O₂ and S(IV) in air, cloudwater and precipitation and their implications for the reactive scavenging of SO₂. *Atmos. Research* **25**, 89-102.
- Kulmala M., A. Laaksonen, R. J. Charlson and P. Korhonen: Clouds without supersaturation, *Nature* **388** (1997) 336-337.
- Leaitch W. R., Banic C. M., Isaac G. A., Couture M. D., Liu P. S. K., Gultepe I., Li S.-M., Kleinman L. I., Daum P. H., and MacPherson J. I. (1996) Physical and chemical observations in marine stratus during the 1993 North Atlantic Regional Experiment: Factors controlling cloud droplet number concentrations. *J. Geophys. Res.* **101**, 29123-29135.
- Schwartz, S. E. (1986) Chemical conversions in clouds. In *Aerosols: Research, Risk Assessment and Control Strategies*, S. D. Lee, T. Schneider, L. D. Grant, and P. J. Verkerk, Eds., Lewis Publishers, Chelsea, MI, pp. 349-375.
- Schwartz, S. E. (1986). Mass-transport considerations pertinent to aqueous-phase reactions of gases in liquid-water clouds. In *Chemistry of Multiphase Atmospheric Systems*. Edited by W. Jaeschke, pp. 415-471. Springer, Heidelberg.
- Schwartz, S. E. (1988). Mass-transport limitation to the rate of in-cloud oxidation of SO₂: Reexamination in the light of new data. *Atmos. Environ.* **22**, 2491-2499.
- Schwartz, S. E. and Warneck, P. Units for use in atmospheric chemistry. *Pure Appl. Chem.* **67**, 1377-1406 (1995).
- Wurzler S., Flossmann A. I., Pruppacher H. R. and Schwartz S. E. (1995) The scavenging of nitrate by clouds and precipitation. I. A theoretical study of the uptake and redistribution of NaNO₃ particles and HNO₃ gas by growing cloud drops using an entraining air parcel model. *J. Atmos. Chem.*, **20**, 259-280 (1995).