Solubility data requirements and new experimental methods in atmospheric aerosol research

C.E. Kolb,[a] J.T. Jayne,[a] D.R. Worsnop[a] and P. Davidovits[b]

[a]*Center for Chemical and Environmental Physics, Aerodyne Research, Inc.,
Billerica, MA 01821-3976*
[b]*Department of Chemistry, Boston College, Chestnut Hill, MA 02167-3860*

Abstract: The uptake of trace gases by atmospheric aerosols and cloud droplets plays a critical role in the atmospheric chemistry of both the troposphere and stratosphere. The transfer of gaseous species through the interfacial boundary layer and into the liquid phase involves a number of closely entwined processes, including: gas phase diffusion, mass accommodation, evaporation, Henry's law solubility, liquid phase diffusion, and, in some cases, chemical reaction at the gas/liquid interface or in the bulk liquid. In the atmosphere or in the laboratory these physical processes are seldom isolated and must be addressed together for many trace gases of interest. Mathematical parameterizations of trace gas uptake for cloud droplets and aerosols will be discussed. During the past decade several new experimental approaches have been developed to investigate trace gas uptake by aqueous/acid liquid and ice surfaces and to distinguish and quantify the physical and chemical parameters governing the uptake process. Here, particular emphasis is on three techniques: the droplet train/flow reactor, the bubble column reactor, and the bubble train reactor, all jointly developed in our laboratories. Examples of measured temperature dependent kinetic uptake parameters and their dependence on the measured Henry's law solubility will be presented for trace species important in stratospheric ozone depletion, tropospheric ozone production and tropospheric sulfate aerosol formation.

INTRODUCTION

During the past decade the critical role played by heterogeneous processes involving trace gas interactions with aerosols and cloud droplets has been a key theme of atmospheric chemistry research. Heterogeneous processing is now recognized as an important component of the chemistry characterizing major environmental issues such as acid deposition (acid rain), stratospheric ozone depletion, tropospheric ozone production and oxidative capacity, and the formation and growth of tropospheric aerosols which impact both climate and human health. The solubility of trace gaseous species in aqueous and aqueous acid (principally sulfuric and nitric acid) aerosols and cloud droplets clearly plays a major role in these and other issues facing the atmospheric environment.

Unfortunately, solubility alone seldom governs the partitioning of trace gaseous species between the atmosphere's gas and condensed phases. Since, the atmospheric condensed phase components are so disperse, with liquid volume/gas volume ratios ranging from 3 x 10^{-7} for typical tropospheric clouds to 3 x 10^{-14} for background stratospheric sulfuric acid aerosol, gas phase diffusion to and/or mass accommodation on atmospheric aerosol particles/droplets can limit gas/liquid uptake (Refs.1,2). Furthermore, for relatively insoluble species heterogeneous uptake can be limited by liquid phase diffusion or surface and/or bulk chemical reactions such as hydrolysis. All of these processes can play important roles in the heterogeneous processing of trace atmospheric gases and in the design and execution of laboratory experiments to study those processes.

Even when solubility is a critical parameter governing heterogeneous uptake, simple Henry's law constants (usually defined in the atmospheric chemistry community as H=n_l/p, where n_l is the equilibrium liquid phase concentration in mole/L and p is the equilibrium trace gas partial pressure in atmospheres) are insufficient. First, because many important atmospheric trace species undergo

reversible dissociation reactions in aqueous solutions so their solubility must be described in terms of an effective Henry's law constant, H*, which accounts for the additional solubility due to these dissociative channels; and second, because atmospheric aerosol usually contains significant concentrations of dissolved acids or salts, and the solubility of many trace gases displays a Setchenow type dependence on the concentration of these ionic species. Since the activity of water and dissolved acid/salt ions can vary over many orders of magnitude in atmospheric aerosols a complete thermodynamic description of their solubility characteristics can be quite complex. Recent modeling work by Clegg, Brimblecombe and coworkers on trace gas solubilities in aqueous acid solutions well illustrate the current state-of the-art and the utility of effective Henry's law and Setchenow coefficient representations (Refs.3,4). Another interesting attribute of liquid atmospheric aerosol particles and cloud droplets is the fact that they are frequently in a supercooled state, so traditional bulk liquid experimental techniques are often not able to yield solubility or other uptake parameters over the full range of atmospherically relevant temperatures.

Fortunately, recent progress in the design and execution of laboratory techniques to characterize and quantify atmospheric heterogeneous interactions has been impressive (Ref.1) and methods to measure the role of solubility parameters in many atmospherically important heterogenous systems are now available. After a brief discussion of the quantitative relations among the transport, kinetic and solubility parameters which control atmospheric heterogeneous processing, experimental techniques jointly developed in our laboratory will be discussed and representative data presented.

INTERACTION OF ATMOSPHERIC TRACE GASES WITH AEROSOL DROPLETS

Several recent publications have presented a consistent theoretical framework for the interaction of trace gases with atmospheric aerosol and cloud droplets (Refs.1,2,5). This framework assesses the roles of the following processes: 1) gas phase diffusion to the droplet; 2) mass accommodation at the gas/liquid interface; 3) liquid phase diffusion in the droplet; 4) chemical reaction in the droplet; and 5) solubility. All of these processes can be closely coupled and are described by complex differential equations initially presented by Danckwerts (ref.6), Carslaw and Jaeger (ref.7) and Fuchs and Sutugin (ref. 8). The framework presented in Refs. 1,2,5 is based on useful approximate solutions tailored for specific parameter combinations with atmospheric relevance. Several key approximations from this framework are presented below.

The net flux of gas into the condensed phase, J, (molecules cm^{-2} s^{-1}) is given by:

$$J = \frac{n_g \gamma \bar{c}}{4} \qquad (1)$$

where $n_g \bar{c}/4$ is the molecular collision rate of gas (with an equilibrium Boltzmann velocity distribution) through a planar surface; n_g is the gas concentration (molecules cm^{-3}), $\bar{c}$ the mean molecular speed (cm s^{-1}) and γ is a net uptake coefficient which takes into account the effect on gas uptake of all the processes listed above. A resistance model of the transport and uptake processes (Refs. 1,2) yields:

$$\frac{1}{\gamma} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sol} + \Gamma_{rxn}} \qquad (2)$$

Where α is the mass accommodation coefficient, which is defined as the probability that a molecule striking the droplet's surface enters the droplet and the uptake coefficients Γ_g, Γ_{sol} and Γ_{rxn} represent normalized rates, rather than probabilities; of gas phase diffusion, dissolution of the gaseous species and liquid phase reaction, respectively. Thus, in the limit of large Γ_g, Γ_{sol} and/or Γ_{rxn}, their resistances become negligible and the maximum value of γ approaches α. Below we present expressions for the uptake coefficients associated with gas transport and condensed phase solubility and reaction.

The gas transport coefficient, Γ_g, accounts for the fact that the actual gas collision rate at the surface of the condensed phase is not always given by the Boltzmann gas kinetic flux, ($n_g \bar{c}/4$) where n_g is

the bulk gas concentration far away from the surface. As defined (Refs.1,2), Γ_g is given by the sum of two terms:

$$\frac{1}{\Gamma_g} = \frac{\bar{c}d}{8D_g} - \frac{1}{2} \tag{3}$$

where the first term accounts for gradients in gas concentration above the surface arising from gas diffusion to the surface. Here D_g is the trace gas diffusion coefficient ($cm^2 s^{-1}$) and d is the droplet diameter. The second term (-1/2) accounts for distortion of the Boltzmann collision rate ($\bar{c}/4$) when there is significant net gas uptake at the surface.

Solubility limitations in the resistance model are represented by the uptake coefficient, Γ_{sol}:

$$\Gamma_{sol} = \frac{4\,HRT}{\pi^{1/2}\,\bar{c}} \left(\frac{D_l}{t}\right)^{1/2} \tag{4}$$

where D_l is the condensed phase diffusion coefficient ($cm^2 s^{-1}$) and t is the time, in seconds, of exposure of the liquid to the gas (from the liquid frame of reference). Eq. (4) is explicitly formulated for liquids, expressing the gas/liquid equilibrium in terms of the Henry's law constant H(mole L^{-1} atm^{-1}).

At equilibrium (i.e. $t = \infty$ in the absence of reaction), $\Gamma_{sol} = 0$; in other words, net uptake is zero because fluxes due to accommodation and evaporation are equal. This can be seen by re-writing Eq. (5) in kinetic terms:

$$\frac{n_g\alpha\bar{c}}{4} = n_{liq}\left(\frac{\alpha}{HRT}\right)\frac{\bar{c}}{4} \tag{5}$$

Thus, at equilibrium, the gas flux in and out of the droplet is determined by α. Equation (5) explicitly indicates there is an interfacial collision rate from the condensed phase, $n_{liq}\bar{c}/4$, analogous to $n_g\bar{c}/4$ from the gas phase. The collision efficiency from the condensed phase is given by an "evaporation coefficient," α/HRT. For non-equilibrium conditions, Γ_{sol} accounts for the rate of evaporation ($\alpha/HRT\ n_{liq}\bar{c}/4$) which determines the net gas uptake. Equation (4) approximates the gradient in liquid concentration below the interface by assuming that a surface layer of thickness $\sim(D_l t)^{1/2}$ in the condensed (liquid) phase is saturated with dissolved gas (i.e. $n_{liq} = HRT\ n_g$). The magnitude of Γ_{sol} decreases with time, reflecting the increasing rate of evaporation of dissolved molecules back into the gas phase as n_{liq} approaches $HRTn_{gas}$ limit. Thus, the resistance ($1/\Gamma_{sol}$) increases with time and the net uptake (measured by γ) decreases. Equation (4) is an approximation to the exact solution given by Danckwerts (Ref.6) for uptake into a flat surface of infinite depth. This solution assumes that n_g at the surface is constant. Application of Eq. (4) requires that the condensed phase is deeper than $\sim(D_l t)^{1/2}$; when $(D_l t)^{1/2}$ exceeds the dimension of the droplet, which is often true for submicron aerosol particles, Eq. (4) is not appropriate; then $n_{liq} = n_g\ HRT$ (see Ref. 5 for further discussion.)

Reactive uptake occurs in a surface layer whose depth is given by $\sim(D_l / k_{rxn})^{1/2}$; for aerosol or cloud droplets with dimensions larger than this depth, the reactive uptake coefficient, Γ_{rxn}, can be expressed as:

$$\Gamma_{rxn} = \frac{4\,HRT}{\bar{c}} (D_l\,k_{rxn})^{1/2} \tag{6}$$

where k_{rxn} (s^{-1}) is the first order reaction rate of the dissolved gas in the liquid droplet (Refs.1,2). This derivation of Γ_{rxn} assumes either that the reaction is irreversible or that the solubility of the reaction product is large (as measured by Γ_{sol}). Corrections to Eq. 6 which are relevant to reaction in small liquid aerosol particles where this constraint is not met are presented by Hanson et al (Ref.5). Several useful limiting cases for Eqs. 4 and 6 are presented in Ref.1. For cases with reversible reactive processes, overall uptake can be expressed as a more complex resistance model (Ref.9). Ref.10 extends this model to include surface reaction as well.

ATMOSPHERIC CHEMISTRY DATA REQUIREMENTS

To understand the current state of the atmosphere and predict its future course and composition, it is necessary to model the atmospheric fate of many soluble or semi-soluble atmospheric trace gases and the formation and growth of cloud and aerosol droplets. Detailed atmospheric chemistry and aerosol microphysics models are required for studies of acid rain/deposition, stratospheric ozone depletion, tropospheric ozone formation and oxidative capacity, and the formation and/or growth of tropospheric aerosols which impact both climate and human health. The fidelity and reliability of atmospheric models is strongly dependent on the availability of high quality input data.

Solubility parameters such as Henry's law constants and Setchenow coefficients for many trace atmospheric species, ranging from reactive free radicals such as OH, HO_2, NO_3, as well as organic RO and RO_2 radicals, to a wide variety of stable inorganic and organic trace species are required for models of the atmospheric chemical processes listed above. Both basic Henry's law constants representing simple physical solvation and effective Henry's law constants accounting for reversible reactions such as ionic dissociation are needed for trace species which undergo reversible reactions with aerosol/cloud droplet liquids. Stratospheric heterogeneous processes are characterized by interactions with low temperature (185-240 K) aqueous acid aerosols (often supercooled) composed of sulfuric acid (40-80 wt.% H_2SO_4) and, under the coldest stratospheric conditions, ternary $H_2O/H_2SO_4/HNO_3$ solutions. Tropospheric aerosol and cloud droplets are generally less acidic than stratospheric droplets, but still may contain high levels of sulfate, nitrate, chloride and other acid anions as well as appreciable ammonium and hydrogen cations. Marine aerosols can also contain substantial sea salt components; most importantly, sodium and chloride ions. High concentrations of ions can alter gas solubility through a "salting out" effect. The degree of this ionic influence on solubility is quatitatively expressed by Setchenow coefficients. Setchenow coefficients for ammonium sulfate/bisulfate, ammonium nitrate and sodium chloride at a minimum are often required to modify aqueous Henry's law constants in order to predict trace gas solubilities in high ionic strength tropospheric aerosols. Some specific examples of recently determined solubility data of interest to the atmospheric chemistry community are presented in the next section.

For many years atmospheric chemists have relied on ongoing efforts by NASA and IUPAC panels to tabulate and evaluate kinetic parameters for atmospheric reactions. While some Henry's law data have also been tabulated and evaluated by NASA (Ref.11), particularly for aqueous acid solutions and trace gas species of specific interest to stratospheric ozone models, no systematic tabulations/evaluations of solubility data for atmospherically relevant systems are currently available. An IUPAC effort to provide such reviews would be a boon to atmospheric scientists.

MEASUREMENT OF HETEROGENOUS UPTAKE PARAMETERS

The challenge of measuring accurate heterogeneous uptake parameters for atmospheric systems has spurred a number of innovative experimental approaches during the past decade. These include Knudsen cell, coated and flowing wall flow tube, aerosol flow tube, liquid jet, levitated droplet, droplet train/flow tube and bubble column or bubble train techniques. Many of these techniques have complimentary capabilities and properly employed can yield accurate uptake parameters, including Henry's law constants and Setchenow coefficients, for important atmospheric systems. The capabilities and limitations of each of these experimental approaches are reviewed in Ref.1. Three of these techniques, the droplet train/flow tube, the bubble column reactor and the bubble train reactor techniques were jointly developed in our laboratories. A description of these techniques, along with representative data from several recent studies utilizing them, are presented in this section.

A schematic of the droplet train apparatus is shown in Fig. 1. In this technique a fast moving (~2000 cm s⁻¹) train of droplets is generated using a vibrating orifice which produces well characterized monodisperse droplets with diameters ranging from ~100 to 250 μm. The droplets traverse a flow reactor containing one or more trace gaseous species of interest entrained in a carrier gas flow. The contact time between the droplet train and flow reactor atmosphere are varied systematically providing millisecond time resolution over the range of 2 - 20 msec. Both the chemical composition and surface temperature can be controlled. Droplets ranging from 85 wt% H_2SO_4 to pH 14 can be generated. The droplet surface temperature is controlled by precooling the source liquid and by evaporation after droplet formation, allowing experiments with supercooled water droplets as cold as 260 K. However, upon entering the flow tube the water vapor is maintained near equilibrium with the droplet surface temperature to assure that the droplet surface
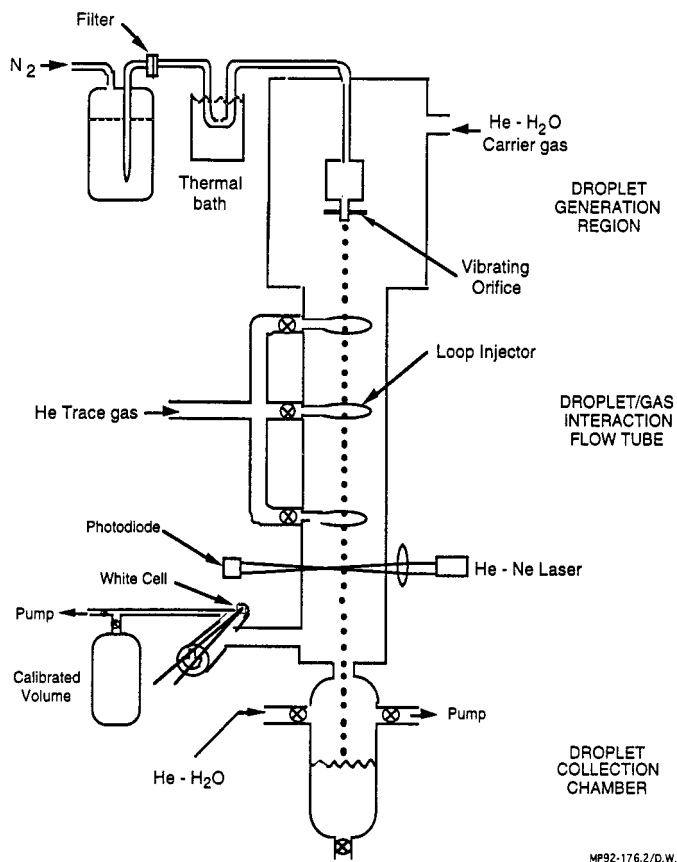
Fig. 1 Schematic of the droplet train/flow tube apparatus.

temperature is steady and the droplets neither grow nor shrink during the uptake experiment. Measurement of trace gas uptake is achieved by monitoring the concentration of trace gas remaining in the gas flow after exposure to the droplets. The trace gas is monitored with either a tunable infrared laser or mass spectrometer. Details of this experimental technique are presented in Ref. 1 and references therein.

Determination of soluble, non-reactive trace gas uptake coefficient as a function of droplet/trace gas contact time leads to determination of both the mass accommodation coefficient and the Henry's law constant through an analysis based on Eqs. 2, 3 and 4. In the case where the species solubility is large and the limiting effects of gas transport are minimized uptake coefficients measured using the droplet train apparatus provide an almost direct measure of mass accommodation coefficient. For gases which have a reduced solubility the uptake coefficient varies with the gas/liquid interaction time. Due to the relatively short experimental time scale of this technique (2 - 20 ms) only the outer shell of the droplet saturates to a depth of $(D_l t)^{1/2}$ (~ 1um) giving rise to an uptake coefficient with a $t^{1/2}$ time dependence. The rate at which the dissolved gas diffuses to the interior of the droplet coupled with its solubility determine the extent of the measured time dependence. A plot of the inverse of the time dependent uptake coefficient, Γ_{sol}, as a function of the $t^{1/2}$ provides a measure of the quantity $H(D_l)^{1/2}$ (Eq. 4). An independent measure of the liquid phase diffusion coefficient allows determination of the Henry's law coefficient. As an example, Fig. 2 plots the measured time dependence for the uptake of methanol at three different droplet temperatures. From the slope of a linear least squares fit line through the data the quantity $H(D_l)^{1/2}$ can be extracted. The intercept of the plot is the uptake coefficient free of solubility limitations and can be used to determine the mass accommodation coefficient through the use of Eq. 2. As can be seen from Fig. 2 both the slope and intercept vary with temperature indicating that α, H and D_l are all temperature dependent parameters. Note that both H and D_l have opposing temperature dependencies, the value of H increases and D_l decreases with decreasing temperature. In general, we find that α also increases with decreasing temperature. Many other examples of uptake studies of this type for organic alcohols, acids and ketones are presented in Refs. 12 and 13.

This same experimental approach can also be applied to the determination of solubility parameters for reactive trace gases. Droplet train studies of formaldehyde (Refs.9,10) and acetaldehyde (ref.9) both show relatively small, solubility controlled uptake behavior, described by Eq. 4, on near neutral pH droplets. At high pH uptake of both aldehydes is reactively controlled by hydroxyl catalyzed hydrolysis to form the diol, a process well characterized by Eq.6. At low pH (moderate acidities) the uptake of formaldehyde increases and is controlled by surface chemisorption. At high acidities in sulfuric and/or nitric acid solutions the uptake increases further driven by formation of
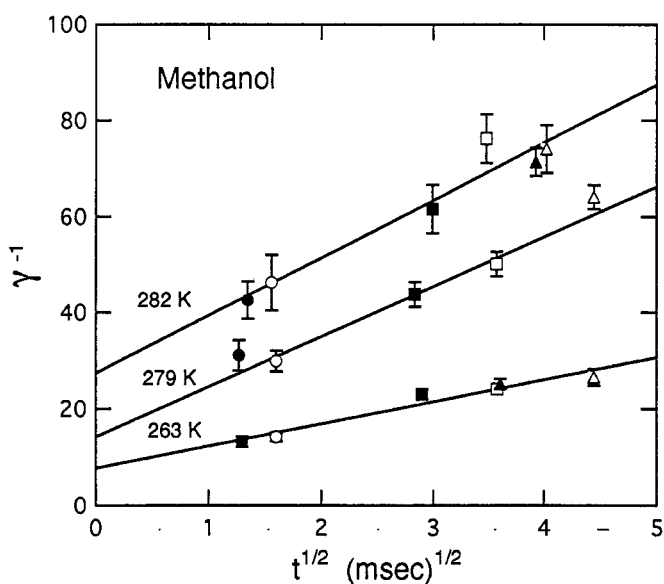
Fig. 2 Plots of $1/\gamma$ versus the square root of gas/liquid interaction time for CH_3OH
droplets at three temperatures.

protonated formaldehyde (CH_3O+) which can be characterized by an effective Henry's law constant
based on the physical Henry's law modified by Setchenow coefficients for each acid (Ref.10). The
model we present for the temperature dependent uptake of CH_2O by concentrated sulfuric and/or
nitric acid solutions representative of stratospheric aerosols in ref. 10 is based on the strong acid
solubility modeling framework pioneered by Clegg, Brimblecombe and co-workers (Refs. 3,4).
The powerful combination of this solubility modeling framework, the theoretical uptake coefficient
descriptions presented above, and our temperature, composition and time dependent uptake
coefficient measurements allows the reliable determination of effective Henry's law constants and
Setchenow coefficients for a reactive species like CH_2O in cold, concentrated acid solutions. In
Fig. 3 we show measured uptake coefficients and the model fit to these data (ref. 10). The ability
of the uptake model to fit measured uptake parameters for acid concentrations varying over six
orders of magnitude is apparent in Fig. 3.

Another stratospheric issue is the uptake and hydrolysis reaction of chlorine nitrate ($ClONO_2$) on
sulfuric and sulfuric/nitric aerosol droplets. Reference 14 presents our droplet train uptake
measurements of $ClONO_2$ uptake on sulfuric acid droplets as a function of droplet temperature and
sulfuric acid concentration. It also presents an uptake model similar to that described above and
published in Ref.10 for CH_2O. However, in the case of $ClONO_2$ we have fit the model not only to
our data but also to uptake data from a stirred Knudsen cell reactor at SRI, International and both
coated wall flow tube and aerosol flow tube reactors at the NOAA Aeronomy Laboratory.
Descriptions of these experimental techniques can be found in Ref.1. Fig. 4 shows the uptake data
from these four separate experimental techniques grouped by approximate sulfuric acid
concentration and plotted as a function of temperature; it also shows the model fit to these data. The
data fit shown in Fig. 4 does not unambiguously determine the effective Henry's law coefficient,
H^*, for $ClONO_2$ in sulfuric acid, but does determine the product of $H^*(k_{hyd})^{1/2}$ where k_{hyd} is the
first order hydrolysis rate constant. Information about k_{hyd} from the aerosol flow tube studies of
Hanson and Lovejoy (Ref.15) at NOAA allows us to estimate an H^* for $ClONO_2$ in 60 wt.%
H_2SO_4 at 250 K of 22 mole $L^{-1}atm^{-1}$ and a physical H for pure water at 250 K of 7 mole $L^{-1}atm^{-1}$
(Ref.14).

For heterogenous studies of relatively insoluble and/or slowly reacting species a method which
allows a longer contact time between the trace gases and liquids of interest is required (Ref.1). To
meet this need we have jointly developed bubble column and bubble train reactors in our
laboratories. The bubble column reactor, described in detail in Ref.16, employs a vertical column
of the liquid under study and passes a single line of bubbles up through the column. We have used
this reactor to measure Henry's law constants for biogenically produced reduced sulfur gases in
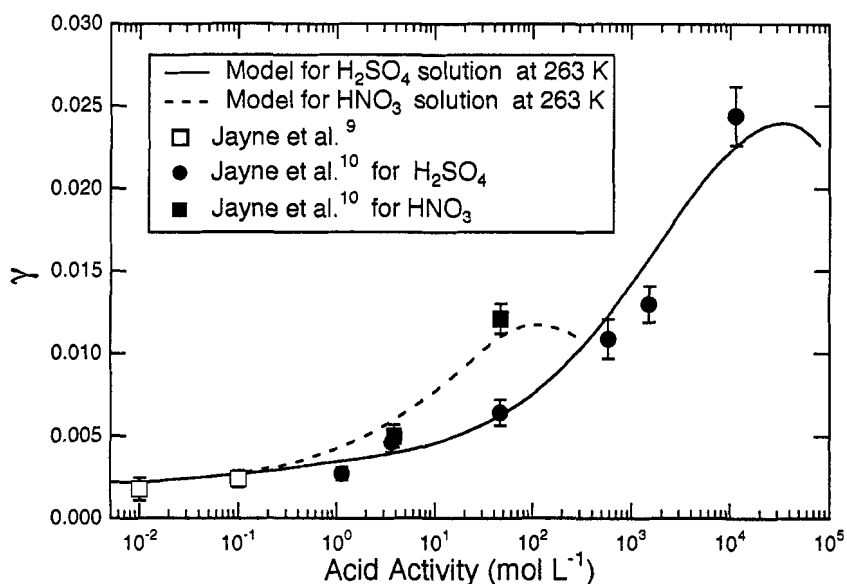pure water as well as their Setchenow coefficients for aqueous sodium chloride and ammonium

Fig. 3 Measured CH_2O uptake coefficients and uptake model fit as a function of H^+ activity.
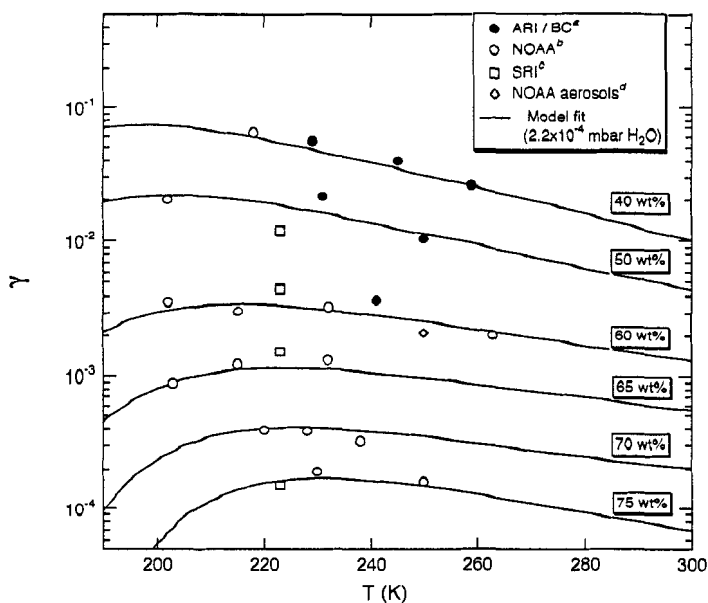

Fig. 4 Temperature dependent $ClONO_2$ uptake coefficients on sulfuric acid surfaces grouped by acid weight percent and model fit to data

sulfate solutions (Ref. 17). This study yielded the first measured Henry's law constants for CH_3SH and CS_2 and the first reported Setchenow coefficients for these gases as well as for H_2S and CH_3SCH_3. We have used both the bubble column reactor and the droplet train/flow tube to study the uptake of reactive carbonyl halides (CF_2O, CCl_2O) and haloacetyl halides (CCl_3CClO, CF_3CClO, CF_3CFO) which are produced by atmospheric gas phase oxidation of manmade hydrohalocarbons used as solvents or refrigerants. Initial studies with our droplet train/flow tube method yielded aqueous uptake coefficients too small to measure except at high pH (Ref.18). However, measurements with the bubble column reactor, with its longer contact times, yielded

reproducible uptake coefficients which could be analyzed to yield values of $H(k_{hyd})^{1/2}$ for all of the species at pH levels typical of tropospheric cloud droplets (Ref.19). Mirabel and co-workers used a droplet train/flow apparatus which captured the droplet stream and used liquid ion chromatography to measure uptake coefficients for most of the same species with greater sensitivity than that allowed by our gas phase depletion method (Refs.20, 21). Although the $H(k_{hyd})^{1/2}$ values measured by Mirabel and co-workers were systematically larger than those from our studies, the combined results clearly show that all of the compounds studied will be removed from the atmosphere on time scales of ~30 days or less by absorption into cloud droplets (a process whose rate is proportional to the product of H and k_{hyd})(Ref.19).

Recently we have improved the bubble column concept by designing a horizontal bubble train reactor, illustrated in Fig. 5. Its principal advantages include greater control over bubble site and trajectory and, if desired, an even longer gas/liquid contact time. Typical uptake data from the horizontal bubble train reactor for trace gases with a wide range of solubilities is shown in Fig. 6 and a plot of the resulting Henry's law constants against accepted literature values is shown in Fig. 7 (see Ref. 16 for references to literature values).

SUMMARY

A wide range of solubility parameters, including physical and effective Henry's law constants and appropriate Setchenow coefficients for atmospheric aerosol systems, is required to understand many current atmospheric issues of concern to the environmental research community. The recent development of an effective theoretical framework to describe the coupling of transport, kinetic and solubility parameters governing heterogeneous atmospheric interactions combined with new laboratory techniques to measure heterogeneous kinetic processes has allowed the determination of solubility parameters for important reactive atmospheric trace species. As both novel and traditional methods for measuring relevant solubility parameters yield data appropriate to atmospheric issues a systematic effort to archive and evaluate solubility data for atmospheric systems will be required to maximize its value to the atmospheric science community.
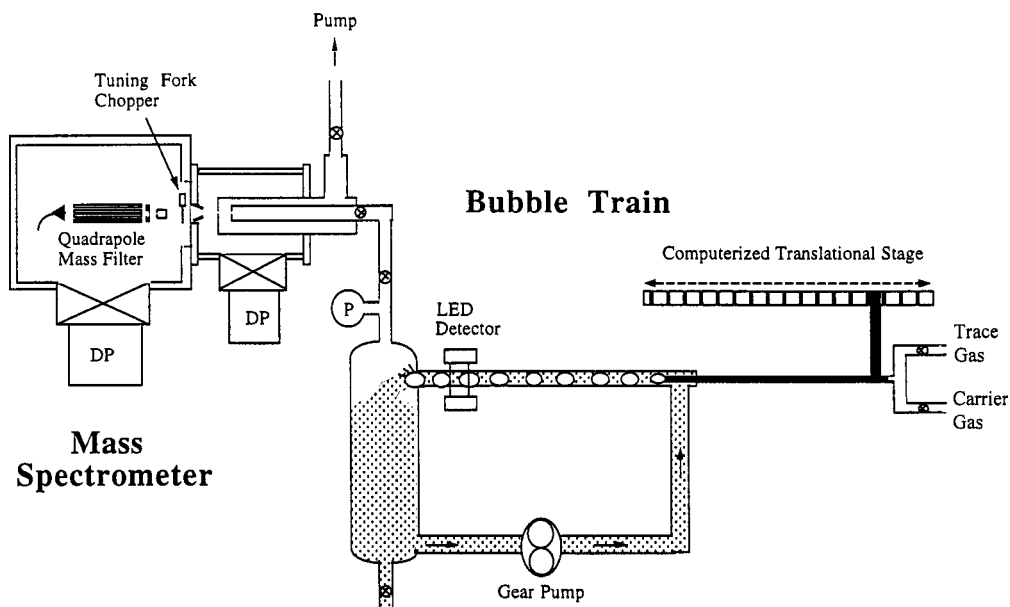

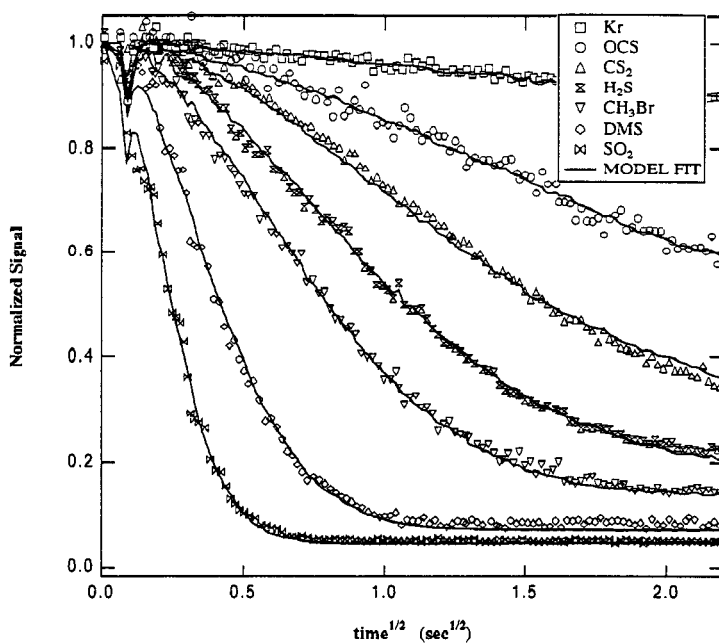Fig. 5 Schematic of the horizontal bubble train reactor

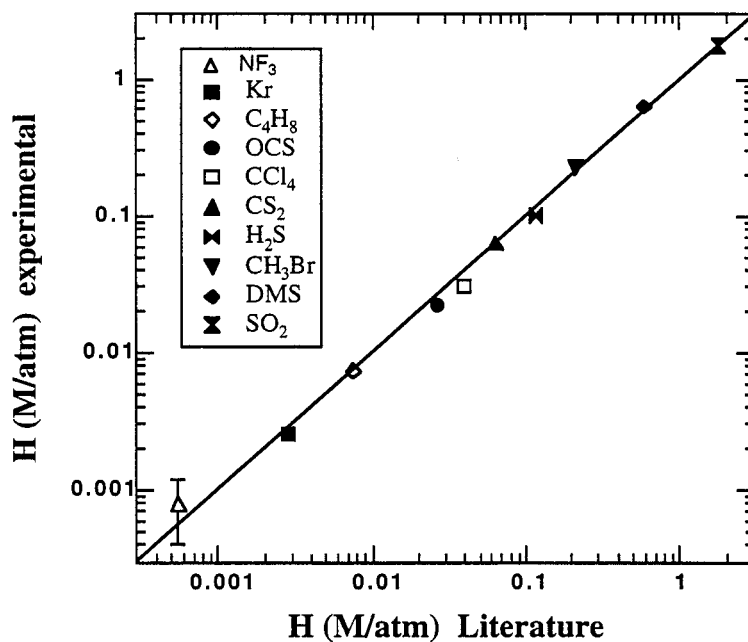Fig. 6 Horizontal bubble train reactor uptake data for test trace gases

Fig. 7 Experimental Henry's Law constants (H) from horizontal bubble train reactor experiments plotted against literature values.

ACKNOWLEDGEMENTS

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