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Heterogeneous and Multiphase Chemistry in the Troposphere

A. R. Ravishankara

Heterogeneous and multiphase reactions on solids and in liquids, respectively, have the potential to play a major role in determining the composition of the gaseous troposphere and should be included in models for understanding this region and assessing the effects of anthropogenic emissions. Making a distinction between reactions on solids (heterogeneous reactions) and those occurring in liquid droplets (multiphase reactions) is convenient for understanding, describing, and including them in models of the troposphere. Frameworks are available for including multiphase reactions in numerical models, but they do not yet exist for heterogeneous reactions. For most of these reactions, water not only provides the medium but it is also a reactant. Other substrates such as sulfate and organic and sea-salt aerosols may also be important, but their effects cannot currently be accurately assessed because of a lack of information on their abundance, nature, and reactivities. Our ability to accurately predict the composition of the troposphere will depend on advances in understanding the microphysics of particle formation, laboratory investigations of heterogeneous and multiphase reactions, and collection of field data on tropospheric particles.

Earth's atmosphere, made up mostly of gases, has suspended in it liquid and solid particles that affect its radiation field and chemical composition. One of the most intense areas of current research in atmospheric sciences is the effect of these particles, natural and anthropogenic, on the radiative balance of Earth and its climate. Here I concentrate on the changes in the composition of the gaseous atmosphere induced by the presence of condensed matter (*1*). I adopt a "gas phase–centric" perspective of the atmosphere, because the atmosphere is primarily gaseous, and what is often of interest is what controls the composition of this medium, particularly how human activity influences this medium.

In the context of tropospheric chemistry involving condensed species, it is important to distinguish between heterogeneous chemistry as that which is constrained to the surface of a solid, and multiphase chemistry as that which takes place in the bulk of the liquid medium (Fig. 1). I focus mostly on the global-scale heterogeneous and multiphase chemistry of the troposphere (*2*). Heterogeneous and multiphase reactions have been studied for a long time, often for practical reasons such as chemical production. However, the field of atmospheric heterogeneous and multiphase chemistry is, in a sense, young. Recently it received a boost by the recognition of the crucial role played by these processes in the dramatic Antarctic ozone hole and the stratospheric ozone depletion (*3*). The evidence for the occurence of heterogeneous and multiphase reactions in the stratosphere is very strong, and it has been possible to identify and quantify their role by using laboratory data, field observations, and modeling calculations.

There is also evidence for tropospheric heterogeneous and multiphase reactions. For example, wet deposition is a mechanism for the ultimate removal of chemicals from the atmosphere and thus terminates the reactions of the removed species in the atmosphere. Two decades ago Penkett *et al.* (*4*) showed that SO_2 could be oxidized by H_2O_2 and O_3 in liquid droplets in the atmosphere, and it is now accepted that a significant fraction of SO_2 is oxidized by multiphase reactions (*5*). However, because it is not associated with any global-scale disasters, heterogeneous and multiphase chemistry in the troposphere has not received as much notoriety as its stratospheric counterpart. Changes in the tropospheric composition due to heterogeneous and multiphase processes can be subtle and hence more difficult to diagnose and understand. Analysis of tropospheric heterogeneous and multiphase chemistry is further complicated by two factors: (i) very rapid mixing in the troposphere, which makes it difficult to attribute a change to a specific process, and (ii) as noted later, the variety of condensed matter and gaseous species that can participate in the reactions.

Role of Heterogeneous and Multiphase Reactions in the Troposphere

The most visible forms of condensed matter in air are clouds (including fog), which are primarily solid or liquid water (Fig. 2). Water is also the most abundant reactant for heterogeneous and multiphase reactions. If their volatility is low, other less abundant species may also condense to form particles, as exemplified by stratospheric sulfuric acid aerosols, which are made of sulfuric acid ($\sim$5 to 35 M). How does the presence of small amounts of this suspended material alter the composition of the gaseous atmosphere? The composition can be altered by the following means:

(i) Gas-phase species dissolve in the liquid droplets or coat the solid particles and are thereby removed from the gas phase. If the particles sediment, the gaseous species may be removed from the troposphere or transported to lower altitudes.

(ii) Two gas-phase species can react on or in the suspended particle, or a gas-phase species can react with a constituent of the condensed medium. Reactions between "filled-shell" molecules, which are very slow in the gas phase because of high energy barriers, may be greatly facilitated with condensed media because of lower barriers or the availability of an ionic reaction pathway. One of the most important of these reactions is hydrolysis, which is a reaction between a molecule and water; water is present in almost all suspended particles in the troposphere. Hydrolysis reactions, such as that with N_2O_5, are typically very slow in the gas phase (*6–8*) but can be very efficient in or on condensed matter (*8*).

(iii) A liquid medium suspended in air removes soluble species from the gas phase and thus separates insoluble species from the soluble ones (*9*). Such a separation can lead to interesting changes in the gas-phase chemistry. For example, the photochemical production of ozone from the reaction of HO_2 with NO will be suppressed because HO_2 is incorporated into the liquid phase whereas the less soluble NO (and NO_2) is not. Furthermore, HO_2 leads to O_2^- in the liquid phase, where it can destroy ozone.

(iv) The atmospheric photochemistry of a species may be different in the presence of particles because of alterations in the available actinic flux, changes in the absorption spectra (spectral shifts and generation of new absorbers), and the production of different products. The photon density in the gas phase may be enhanced at or near the top of thick clouds, whereas it can be greatly reduced below (*10*). For example, the gas-phase NO_2 photolysis rate constant near the top of a cloud can be five times as large as the rate constant in clear air (*10*). Photolysis rates within liquid droplets may also be enhanced near the top of clouds (*10*).

The combination of altered photolysis rates and the separation of reactants between gaseous and liquid phases can lead to processes and products that in clear air would not be possible or would be much slower. Because stratospheric ozone filters out light at wavelengths of less than $\sim$290 nm, the solar actinic radiation in the troposphere is limited to longer wavelengths. Because the solar flux increases very rapidly above 290 nm, even small spectral shifts may lead to large changes in the photolysis rates for species that absorb around 300 nm. For example, O_3, whose ultraviolet (UV) spectrum in water is red-shifted (*11*), will photodissociate more rapidly in liquid droplets than in air. Different photolysis products are also possible when a species is taken up into a liquid or on to a solid surface. For example, dissolution of N_2O_5 in water leads to the formation of NO_3^-, whose photodissociation leads to OH (*12*), an important oxidant not produced directly from N_2O_5. Photochemistry in the liquid or on the solid phase will be important only if it leads to a product that is not formed in the gas phase or if it occurs at a much faster rate.

The area of liquid-phase photochemis-

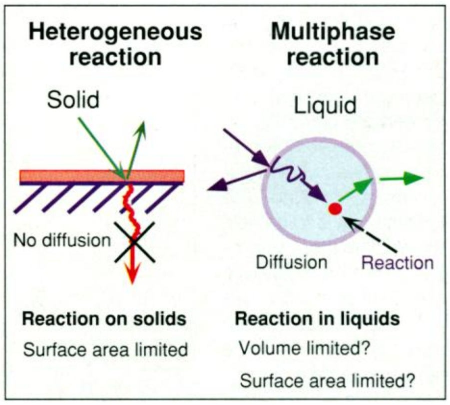

Fig. 1. Distinction between heterogeneous and multiphase reactions. The slab on the solid is meant to represent a quasi-liquid layer, if it is present. Diffusion into and out of the bulk of the solid is assumed to be too slow to effect the concentrations at the surface; thus, the reaction is confined to the surface. In the case of the liquid, it is assumed that the reaction takes place after the molecule has been incorporated into the bulk of the liquid.

The author is at the Aeronomy Laboratory, Environmental Research Laboratories, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80303, USA. He is also associated with the Department of Chemistry and Biochemistry, and The Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA.

try and photocatalysis briefly outlined above is of great importance to atmospheric chemistry. Faust and co-workers (*13*, *14*) have shown that solar irradiation of rainwater produces H_2O_2, presumably because of the presence of dissolved organic chromophores, and this production can overwhelm the gas-phase transport of H_2O_2 or HO_2 into liquid droplets. A more detailed discussion of this topic, even though of great importance to atmospheric chemistry, is beyond the scope of this article [see Gunz and Hoffmann (*15*) and Faust (*14*) for reviews].

It is important to consider which chemical species are likely to be affected by heterogeneous and multiphase reactions. Most tropospheric species removed by heterogeneous and multiphase reactions can also be lost through gas-phase processes. If the gas-phase removal is fast, heterogeneous reactions are unlikely to compete. For example, the concentrations of low-abundance short-lived free radical species, whose production rate is slow relative to their removal rate, are unlikely to be affected by heterogeneous removal. Even though their gas-phase concentration is thus not greatly affected by heterogeneous reactions, free radicals can be important sources of reactants to the condensed medium and sometimes can be key to initiating chain reactions in liquids [see, for example, (*16*)]. The consequences to the atmosphere of the two paths may also not be the same. For example, SO_2 can be oxidized by OH in the gas phase or by oxidants such as H_2O_2 and O_3 in a liquid droplet; however, only the formation of gaseous H_2SO_4, by means of the OH reaction, can lead to new particles. The largest concentration changes as a result of heterogeneous and multiphase reactions are expected when a species is not as easily produced by gas-phase reactions. The observed larger concentrations of H_2O_2 (*17*) and cloud condensation nuclei (*18*) above clouds could be indicators of such processes.

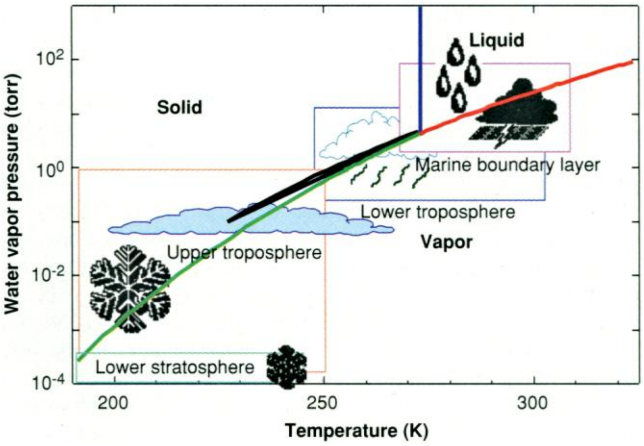

Fig. 2. The vapor pressure of water as a function of temperature over ice (green), supercooled water (black), and liquid water (red). The blue vertical line separates liquid from solid phase. Various atmospheric condensed phases of water are depicted in the approximate regimes of their existence in the atmosphere.

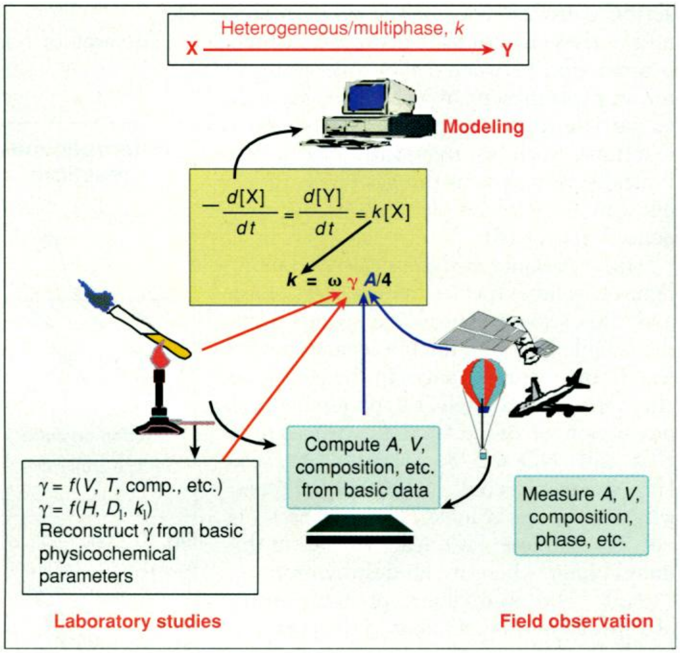

Fig. 3. A pictorial flow chart of the calculation of the rates of heterogeneous and multiphase reactions in the troposphere. *A* and *V* are the surface area and volume of the condensed matter per cubic centimeter of air and are currently obtained from field observations carried out in situ or by remote sensing. The ultimate aim is to be able to calculate these quantities from atmospheric composition (comp.). ω is the mean speed of the molecule X, and γ is the reactive uptake coefficient, which can be either measured in the laboratory under atmospheric conditions or calculated from various physicochemical parameters. The parameters needed to calculate the reactive uptake coefficients are *H*, the Henry's law solubility constant; D_l, the liquid-phase diffusion coefficient; and k_l, the first-order rate coefficient for the reaction of reactant X in the droplet. With these data and a suitable framework, heterogeneous and multiphase reactions can be included in atmospheric models.

Rates of Heterogeneous and Multiphase Reactions

To calculate a heterogeneous or multiphase reaction rate in the troposphere (Fig. 3), one needs (i) the surface area and, for some multiphase reactions, the volume of condensed matter; (ii) the phase of the condensed matter; (iii) the composition of the bulk (for liquids) and the surface (for solids); (iv) the identity and concentrations of the gas-phase species that can undergo heterogeneous or multiphase reactions; and (v) the reactive uptake coefficient on the specific substrate under atmospheric conditions for the reaction. In principle, these quantities should be calculable; however, as will become clear in the following sections, limited observations and understanding of the microphysics of particle formation severely restrict our current ability to model these systems. After discussing the different condensed media available for reactions, I will return to the question of reaction rates and their assessment.

Media for Heterogeneous and Multiphase Reactions

Condensed water is likely to be the predominant form of suspended material in the troposphere. However, sulfuric droplets in various stages of neutralization, sea-salt particles, soot, silicates, and organic aerosols also provide media for important transformations. The current understanding of the microphysics of particle formation in the atmosphere, a focus of much current research, is not sufficiently developed to calculate the surface area (and volume), phase, and composition adequately enough to estimate the rates of heterogeneous and multiphase reactions with an accuracy comparable with those calculated for gas-phase reactions. Such accuracy is essential with regard to the troposphere because the time scales for gas-phase processes and transport are comparable with those for heterogeneous and multiphase reactions. Some of the elements of the microphysics are discussed by Baker (*1*). In my opinion, for at least the next few years, we will have to rely on observations more than on prediction to define the condensed matter for heterogeneous and multiphase reactions in the troposphere. However, even the observations on the nature, amount, phase, variability, and time trend of condensed matter in the troposphere are currently insufficient to quantify their influence on a global scale with an accuracy comparable with that achieved for the stratosphere. Therefore, assessment of the global-scale effects of tropospheric heterogeneous and multiphase reactions requires estimating the effects for various scenarios (*9, 19–21*). I will first describe the available condensed matter in the troposphere.

Water and ice. Vapor pressures of water are often high enough and the temperatures low enough in the troposphere for water to condense as a liquid or solid (Fig. 2). Production of unstable supercooled liquid water may also be possible. However, because of the presence of nucleating agents, the supercooled liquid water droplets will freeze. With increasing altitude and decreasing temperature, ice becomes the most likely condensed form of water. Cirrus clouds, which are formed in the mid- and upper troposphere, are made of ice crystals. Only in the lowest part of the troposphere is the situation favorable for the existence of liquid water droplets, and only in the marine boundary layer is the formation of ice clouds uncommon. The temperatures are not low enough and the partial pressures of other condensable species are not high enough in the troposphere to yield stable binary phases. In contrast, H_2O-HNO_3 ice is the first solid to appear upon cooling in the lower stratosphere [see the phase diagram for the HNO_3-H_2O system in (*22*)]. Because of its abundant vapor pressure, water is present in almost all condensed matter in the bulk or on the surface.

Clouds are the most abundant form of condensed water in the troposphere. On average, ~7% of the volume of the troposphere contains clouds (*23*). As seen from satellite pictures, Earth is a cloudy planet with more than 50% of its surface covered by clouds, which are almost exclusively in the troposphere. A moderately dense cloud contains $\sim 5 \times 10^{-7}$ cm^3 of water per cubic centimeter of air (*24*), which corresponds to a surface area of $\sim 4 \times 10^{-3}$ cm^2 per cubic centimeter of air if the particles are all 10 μm in diameter. Clouds are composed of liquid droplets that range in size from less than a micrometer to millimeters in diameter. The smallest liquid droplets stay in the atmosphere as clouds (including fog), where they evaporate or coagulate. Only the larger droplets sediment. The time scale for heterogeneous and multiphase reactions in or on the cloud droplets can be highly variable, ranging from a few minutes for falling rain drops to a few hours for cloud droplets. Because clouds are not present all the time or in all places, the gaseous atmosphere is exposed only episodically to condensed matter. The theoretical investigations of Crutzen (*20*) and Chameides and co-workers (*19, 21, 25, 26*) have shown that clouds can alter the composition of the troposphere on a global scale.

Sulfuric acid aerosols. Similar to the stratosphere, the troposphere contains a considerable amount of sulfate aerosols formed from natural and anthropogenic sulfur emissions. The anthropogenic sulfates are largely confined to the Northern Hemisphere continental regions around industrial countries. The amounts of natural sulfate aerosols are not well characterized; for example, there is very little information on the extent, composition, or temporal trends in the sulfate aerosols in the upper troposphere (*27*). It is known, however, that sulfate aerosols often act as condensation nuclei for clouds (*1, 24*), and tropospheric sulfate aerosols are dilute and often partially neutralized, depending on their location, by the presence of bases such as ammonia.

There is a great deal of interest in the tropospheric sulfate aerosols because of their effect on climate (*28, 29*), but here, I focus on their effects on the composition of the troposphere. These acid particles may induce various multiphase reactions, especially those that require an acidic medium. For example, HNO_3 in sulfate aerosols may be reduced by aldehydes and alcohols. Tolbert *et al.* (*30*) and Chatfield (*31*) have proposed that CH_2O may react with HNO_3 in sulfuric acid aerosols to release NO_x. Gas-phase pathways for methyl nitrate production are very inefficient (*32*). Therefore, conversion of CH_3OH to CH_3ONO_2 in sulfate aerosols may be the source of tropospheric CH_3ONO_2. Yet another example is waxes, the common organics emitted by trees, which may be oxidized by HNO_3 in a strongly acidic sulfate aerosol to produce NO_x.

On the basis of our understanding of multiphase processes, anthropogenic sulfate aerosols, whose abundance has greatly increased since industrialization, must have already affected the composition of the troposphere. As the emission of SO_2 into the atmosphere changes as a result of implementation of governmental regulations and industrialization of the developing world, the amount of sulfate in the troposphere will also change and hence will alter the gas-phase composition. Such changes require further scrutiny.

Dust. It has been known for a long time that dust from deserts and other terrestrial sources is ubiquitous in the troposphere (*33*). Dust particles, mostly silicates containing metals such as Al, Fe, and Mn, may play a role in multiphase chemistry. They can catalytically produce oxidants such as H_2O_2 from reactions of transition metal ions (*15*). Reactions on dust particles are discussed by Andreae and Crutzen in this issue (*34*).

Organic aerosols. Organic aerosols are emitted into the atmosphere by both natural and anthropogenic processes and are also generated in the troposphere. The number, kind, and surface coverage of these aerosols are poorly characterized. Some laboratory studies have suggested that organic aerosols may destroy atmospheric constituents such as ozone and nitrogen dioxide [see (*8*) for a list of reactions]. Others have shown that these aerosols are modified by exposure to air (*35*). It is unclear whether the aerosols containing organic chemicals exist independently of other aerosols, that is, whether they are completely organic, or whether they are embedded in other aerosols (*36*). Recent measurements by Murphy and co-workers (*37*) suggest that a large fraction of aerosols in the marine boundary layer have some organic content. Similarly, a large fraction of urban aerosols have been shown to contain organic chemicals (*38*). It is presently unclear whether the particles are solid, liquid, solid with a liquid cover, or a combination of all three.

It is imperative to know the number, composition, history, and surface coverage of these particles before their effect on the composition of the troposphere can be estimated accurately. In estimating the effects, a few general points are worth noting: (i) Organic aerosols are likely to contain oxygenated (partly oxidized) hydrocarbons. (ii) They are likely to be covered, at least partly, with water. (iii) Their surfaces are unlikely to remain the same for a long time, unless the surface is a liquid, because the atmosphere will alter the surface composition. As a consequence of the third point, hydrolysis on these particles could be an important process and could augment other water-based or water-covered particles. However, organic aerosols may also initiate unexpected reactions; for example, organic-covered aerosols may act as sinks for reactive free radicals such as Cl atoms. These aerosols may also reduce species in the generally oxidizing troposphere. One possibility that has been proposed on the basis of field observations is the conversion of HNO_3 to NO_x, (*39*). Characterization of organic content and the functionality of the organics in aerosols would be beneficial.

Sea-salt aerosols. The sea-salt aerosols present in the marine boundary layer are highly concentrated solutions of halides.

These particles, which can be quite large (up to a millimeter in diameter), are formed by bursting bubbles and generally have the composition of sea water; however, they are at times enriched in constituents from the sea surface. These particles can lose water and take up other atmospheric constituents (*40*). Depending on their age and history, they have different acidities. If the sea-salt aerosols are dry (that is, below the deliquescence point), they are likely to react differently than if they are above the deliquescence point. Very often, they are supersaturated solutions (*41*). Uptake of reactive species, such as HOBr, NO_3, or N_2O_5, can lead to the liberation of halogens (*42–44*). The release of halogens from sea salt, first suspected by Barrie *et al.* (*45*) in the case of the Arctic springtime troposphere and suggested by Finlayson-Pitts and co-workers (*42*) for the marine boundary layer, has far-reaching consequences, because halogens are potent oxidants in the troposphere (*43*). This active research area is briefly mentioned below and is also addressed by Finlayson-Pitts and Pitts (*2*) and by Andreae and Crutzen (*34*) in this issue.

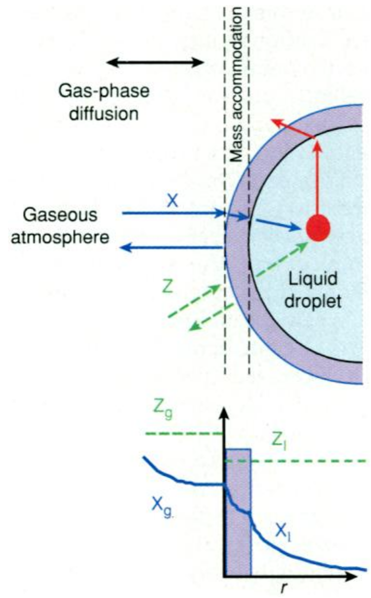

Fig. 4 (Top). Various physicochemical processes that control a multiphase reaction of a molecule X with another molecule Z in a liquid droplet. The subscripts *g* and l refer to gas and liquid phases. It is assumed that the concentration of Z in the liquid phase is controlled by the gas-phase abundance and its Henry's law solubility coefficient, *H*. The steps are described in the text and noted in the figure, except for the diffusion into and out of the liquid. **(Bottom)** The concentrations, in arbitrary units and different scales for gas and liquid phases, of species X and Z as a function of radial distance from the surface of a spherical droplet. It is assumed that there is no concentration gradient in either the gas or liquid phase for the reactant Z. The reasons for the concentration gradients of X in the liquid phase are discussed in the text.

Soot. Partially burned carbon—soot—is produced by natural and human-induced combustion. These particles can significantly affect the radiative balance of the atmosphere because, unlike most other particles, they can absorb the incoming solar radiation. These particles may also play a special role in the chemistry of the troposphere because they have the potential to reduce oxidized species. For example, on the basis of recent laboratory studies of Rogaski *et al.* (*46*), it has been suggested that HNO_3 is reduced on soot (*39, 47*). The extent to which such a special behavior is realized depends on whether soot can maintain its initial surface characteristics in the atmosphere. Its reactive surface is likely to be irreversibly affected by O_2 and other species. Furthermore, the surface is likely to be coated with various condensable species, including water. Therefore, soot's special role will be possible only if the surface remains active.

Reactions in and on Condensed Matter

The simplest way to include heterogeneous and multiphase reactions in atmospheric models that emphasize gas-phase composition changes is to represent the loss of a reactant X from the gas phase as a result of reaction on or in a condensed medium to produce a product Y as a first-order process:

$$X \xrightarrow{\text{heterogeneous/multiphase},k} Y \tag{1}$$

where *k* is the rate constant. Such a representation is often feasible because the time rate of change of the gas-phase concentration of reactant X will be first order in its concentration:

$$-\frac{d[X]}{dt} = \frac{d[Y]}{dt} = k[X] \tag{2}$$

where *t* is the time and the square brackets indicate concentration. The first-order rate constant for the removal of X from the gas phase, *k*, contains all the details of the heterogeneous and multiphase reaction and is given by

$$k = \frac{\omega A \gamma}{4} \tag{3}$$

where A is the surface area for reactions in square centimeters per cubic centimeter of air, ω is the mean molecular speed of the species X, and γ is the reactive uptake coefficient. The decomposition of γ into the basic physicochemical parameters, the determination of these parameters, and the calculation of *k* for any given atmospheric condition, is one of the central efforts in current atmospheric heterogeneous and multiphase chemistry research.

As mentioned earlier, it is convenient to differentiate between heterogeneous chemistry, which involves reactions of species coming from the gas phase on a surface, and multiphase chemistry, which involves reactions in a liquid (Fig. 1). Because diffusion in solids is slower than in liquids, to a first approximation, the reactions involving solids are confined to the surface, whereas in a multiphase reaction a gas-phase reactant is likely to enter a liquid and then react with one or more of its constituents. Such a conceptual separation suggests that the surface area is important for reactions on solids, whereas both the surface area and volume can be important for liquids. Reactions on solids may involve the substrate molecules or another molecule from the gas phase. It is unlikely that a species from the gas phase will encounter a molecule dissolved in the solid because of slow diffusion in the solid; it is more likely to react with another reactant on the surface that also originated in the gas phase. In liquids, the reactions may also be exclusively at, or very close to, the surface, and the uptake may behave like that on a surface (*48*). Even slow reactions with water can be important. For comparison, if the concentration of a dissolved species is 10^{-3} M, it needs to react 50,000 times faster with the second reactant for its reaction to compete with that of water present at a concentration of ~55 M. Therefore, hydrolysis is the first multiphase reaction to consider when assessing tropospheric loss processes. If hydrolysis is very slow, then reactions with other solutes must also be considered.

Reactions on and in droplets. Danckwerts (*49, 50*) presented the equations needed to derive the rates of multiphase reactions in terms of diffusion, liquid-phase reaction, and solubility of a molecule. Schwartz (*51*) described how to view and calculate the rates of multiphase reactions by considering the mass transport and correcting, if necessary, the rates of liquid-phase reactions to make them applicable to small atmospheric droplets. In general, atmospheric modeling calculations deal with gas-phase reactions and look at the effect of multiphase reactions on the gas-phase composition. With this in mind, Hanson *et al.* (*52*) described a framework for dealing with multiphase reactions on sulfuric acid droplets that has found widespread acceptance among stratospheric modelers and also appears appropriate for use with the troposphere. I will briefly describe this approach here.

The tropospheric multiphase reaction can be divided into several steps (Fig. 4): (i) diffusion of one or more molecules to the surface of a droplet, at a rate determined by pressure, water content of air, and the gas-phase diffusion coefficient; (ii) incorporation of the molecule into the liquid phase, mass accommodation, with an efficiency α; (iii) diffusion in the liquid droplet, at a rate controlled by liquid-phase diffusion and the radial concentration gradient; and (iv) reaction in the liquid phase, whose rate is dictated by the rate coefficient for the reaction and the concentration of the second reactant. Upon reaction, the products can either remain in the droplet, undergo further reactions, or diffuse out to the gas phase.

The term mass accommodation coefficient, α, as used here, is the probability that a molecule striking the surface is "captured" by the liquid. The reactive uptake coefficient, γ, is for the overall process of incorporation into the liquid, diffusion in the liquid, and reaction with a species in the liquid. The term sticking coefficient, commonly used in the literature, is not used here. The basic surface phenomena that control α are unclear. I assume that α can be calculated or measured. The extent of incorporation of a molecule into the liquid depends on the solubility (Henry's law) coefficient (currently, there is no evidence to suspect that this bulk property is not applicable to atmospheric particles).

The steps listed above are "barriers" for a molecule to successfully undergo a multiphase reaction; they form a network of resistances (*22*) whose total resistance controls the overall reactive uptake coefficient. All the steps described here can be, at least in principle, calculated or measured. When multiple reactions take place in the liquid phase, a "global" liquid-phase reaction mechanism can be assembled, as for gas-phase processes, and the overall first-order rate coefficient for the loss of the species of interest in the liquid can be derived. The phenomenological reactive uptake coefficient for a species X (that is, the rate coefficient for the loss of a species from the gas phase) can be calculated with the equation

$$\gamma_{\text{calc.}} = \frac{4RT}{\omega} H \sqrt{D_l \sum_i k_i^I} \qquad (4)$$

where R is the gas constant (in units of atmospheres per molar per kelvin), H is the Henry's law solubility coefficient (in units of molar per atmosphere), D_l is the liquid-phase diffusion coefficient for reactant X, and $\Sigma_i k_i^I$ is the first-order rate coefficient for the loss of X in solution, which is related to the second-order rate coefficient for the reaction of X with the reactants Z_i in solution:

$$X + Z_i \xrightarrow{k_i^{II}} Y \qquad (5)$$

Because $\gamma_{\text{calc.}}$ depends on the square root of $\Sigma_i k_i^I$, the overall removal rate for X from the gas phase is not the sum of the individual removal rates in the absence of others. In most cases, reactant Z_i is in equilibrium with the liquid phase; therefore, its liquid-phase concentration is related to its Henry's law constant and gas-phase abundance (Fig. 4). The gas-phase concentration of the reactant X near the surface will vary during the multiphase reaction because of its removal in the liquid phase and because diffusion limits it from reaching the surface. The concentration of X will vary across the surface of the droplet because of the accommodation limitation and will have a radial gradient in the droplet as a result of a combination of diffusion and reaction.

Equation 4 is only valid when the constraints due to gas-phase diffusion and mass accommodation can be neglected. The gas-phase diffusion constraint can be evaluated by using the expressions of Fuchs and Sutugin (*53*, *54*). In many situations, the rate of multiphase reactions is completely controlled by gas-phase mass transport. For example, mass transport in the gas phase will limit the processing rate to an equivalent reactive uptake coefficient, γ, of $\sim 10^{-2}$ in 1 atmosphere of air for 10-μm droplets. However, if the particle diameter were 1 μm, the reactive uptake coefficient would control the rate. When there is a gradient in the concentration of the reactant Z_i in the droplet, the mass transport and reactive loss have to be explicitly included. The mass accommodation coefficient, if known, can be also be included (*53*, *54*). One needs to correct the above reactive uptake coefficient for the finite size of the droplet (*51*, *52*). Such a correction factor is known (*49*, *50–52*) and has been tested by measuring reactive uptake on atmospheric-sized particles (*55*, *56*). With this method, the gas-phase loss of X can be evaluated as the concentration of Z_i changes in the atmosphere.

The approaches described here and by Schwartz (*51*) are two ways of incorporating the same steps into modeling that yield the same results. The choice of approach is based primarily on specific interest and convenience. When dealing with clouds, it may be easier to use Schwartz's formulation, whereas the approach described here is better suited for smaller particles with smaller surface area per unit volume of air.

Reactions on ice and other solids. On the basis of many studies of reactions on ice surfaces representative of the stratosphere, it is known that these reactions are generally confined to the surface (*22*), even though the surface is dynamic (*57*). If one of the reactants is condensed water, the rate of the heterogeneous reaction will depend on the uptake of the gas-phase reactant. If both reactants have to come from the gas phase, as in the cases of the reactions of HCl with $ClONO_2$ and HOCl, one of the reactants has to stay on the surface long enough for the second to be taken up. Because the longevity of a physisorbed molecule on a surface will likely decrease with increasing temperature, a reaction between two physisorbed molecules on a solid in the troposphere is less likely than in the stratosphere. On the other hand, if a molecule is chemisorbed or dissociated on the surface, its reactions may not be as temperature sensitive. If there is a barrier for the uptake of one of the reactants, the reactions may actually be more efficient at tropospheric temperatures. Note that reactions that involve water on the surface are likely to be more sensitive to the relative humidity (which determines the available amounts of water on the surface) than to the temperature.

Dissociative uptake onto solid surfaces may enhance heterogeneous reactions. Such an uptake may also involve ionic products, as in the case of HCl uptake onto ice (*58*). Ionization may be enhanced if the surface of the solid is covered by a liquid. The quasi-liquid layer, originally proposed by Faraday (*59*), is not believed to exist at stratospheric temperatures (*60*) but is possible in the troposphere. Liquidlike layers have been observed on ice down to ~250 K by using surface-sensitive techniques (*61*, *62*). The presence of fast-rotating surface water molecules at much lower temperatures has been suggested (*63*) and could indicate a semi-liquid layer. However, it is necessary to establish whether this layer is thick enough to act like a liquid in allowing dissociation and reactions. If it does, then reactions on ice at temperatures above ~250 K, which are common in the troposphere, may be treated as reactions in a liquid droplet, which would greatly simplify modeling. The availability of a liquidlike layer may also lead to the dissociative uptake of acids and other soluble species and efficient reactions between two gas-phase species. Such water layers may also exist on other tropospheric solids.

A framework for dealing with the reactions on atmospheric solids in models, similar to that for the liquid-phase reactions, is not currently available because the steps involved in the reactive uptake are not as well understood as in the case of liquids. The mechanisms for the atmospheric surface reactions, which may include surface diffusion and dissociation, are currently unclear. Awaiting further development in this area, experiments in the laboratory have to be performed under "atmospheric" conditions of partial pressures of reactants and temperatures.

Examples of Heterogeneous and Multiphase Reactions in the Troposphere

Oxidation of SO_2 to sulfuric acid. The most studied of the multiphase reactions in the troposphere is the oxidation of SO_2 to sulfuric acid in droplets by oxidants such as H_2O_2 and O_3. Such a transformation has been clearly demonstrated in various studies (*64*, *65*). Most tropospheric multiphase chemistry studies were driven by the need to assess the rate of sulfuric acid formation. This conversion, a phenomenon tied closely to the acid rain problem, has been amply described [see, for example, (*66*)].

Nitrate radical in the marine boundary layer (MBL). The uptake of nitrate radical (NO_3), an important nighttime oxidant, into water has been studied, and all the parameters necessary for calculating the rate of multiphase processing in the troposphere have been measured (*67–69*). In the troposphere, especially at lower altitudes, NO_3 will be essentially in thermal equilibrium with N_2O_5 at night. Both N_2O_5 and NO_3 can be lost through multiphase reactions. Using a box model, I and my coworkers have deduced that the lifetime of NO_3 in the MBL is significantly reduced in the presence of sea-salt aerosols (*44*). At warmer temperatures and low NO_x concentrations, the uptake of NO_3 will more effectively denitrify this region than will N_2O_5 hydrolysis. The reduction in NO_3 abundance leads to a slower rate of oxidation of MBL emissions such as dimethyl sulfide. The uptake of NO_3 and N_2O_5 will both reduce NO_x in the MBL and release salt-bound halogens, depending on the water content of the particles. However, only the reactive uptake of NO_3 leads to the formation of another liquid-phase oxidant, converts Cl^- to Cl, and initiates oxidation of SO_2 to sulfate in the droplets. These processes can lead to dehalogenation of the salt particle without high acidification. It is interesting to note that NO_3 can also react with water by means of a very endothermic reaction to generate OH radicals. This example shows that (i) oxidant concentration can be suppressed, (ii) water can be an important reactant even if its reaction with the molecule of interest is endothermic, (iii) two processes may compete for the removal of the same species, and (iv) multiphase chemistry can propagate changes.

Loss of peroxy acetyl nitrate. Depletion of a species that is in equilibrium with a second species by means of multiphase reactions changes the concentration of the second. For example, removal of peroxy acetyl nitrate (PAN)—which is not very soluble in water (*70*) and is inefficient in reacting with constituents of clouds—through multiphase reactions is often neglected. However, PAN is often essentially in equilibrium with NO_2 and the acetyl peroxy radical. Recently, Villalta *et al.* (*71*) showed that even though PAN does not react with water, acetyl peroxy radicals are efficiently taken up by liquid water, thus decreasing PAN's gas-phase concentration. Such a process will convert NO_y (defined as the sum of NO_x, HNO_3, N_2O_5, $RONO_2$, and others) species to NO_x species and lead to what is often called the renoxification in the troposphere.

Reactions on cirrus clouds. One of the most obvious substrates for heterogeneous reactions in the upper troposphere is the cirrus clouds made up of ice. Hydrolysis reactions of various upper tropospheric species, such as N_2O_5 to generate HNO_3, are likely to take place on these solids. Heterogeneous conversion of N_2O_5 to HNO_3 may irreversibly remove nitrogen oxides from the troposphere. The abundance of NO_x in this region is of crucial interest because of its role in the photochemical production of ozone, which is a very effective greenhouse gas in the upper troposphere. Other reactions on ice at temperatures of cirrus clouds that should be considered are those of partially oxidized hydrocarbons, organic nitrates such as PAN, and sulfur species. Further studies of heterogeneous reactions on ice particles at temperatures above 200 K are necessary to elucidate the chemistry of the upper troposphere. This region is of great current interest because it may be affected by aviation.

Looking Ahead

It is clear that heterogeneous and multiphase chemistry has the potential to alter the composition of the troposphere. The prime example is the oxidation of SO_2 in multiphase reactions. To go beyond a few examples and assess the global role, such as in determining the oxidative capacity of the troposphere, requires quantifying the extent of recognized reactions and investigating other possible pathways. Because the troposphere is an oxidizing medium for emissions that enter this region, any heterogeneous reaction that can reduce a species (that is, decrease the oxidation state of the atom of interest) is of particular interest. Organic aerosols may provide likely sites for such reactions, but because of a lack of information on organic aerosols and their composition, we currently cannot accurately assess their importance. Therefore, concerted efforts to characterize and determine the abundance of these aerosols is essential. In addition to organic aerosols, field data on composition, phase, number, surface characteristics, and time trends of other tropospheric particles, such as soot and sulfuric acid aerosols, are needed. This cataloging and characterization are essential in the absence of a full predictive ability to obtain the abundance and character of the condensed media in the atmosphere. At the same time, it is also necessary to improve our predictive capability so that the future state of the troposphere can be assessed. Even though the framework for including multiphase reactions in numerical models is in place, data on many other potentially important reactions and reactants are needed. Development of a similar framework for reactions on solids is essential. It is also essential to characterize ice surfaces at tropospheric temperatures and determine at what temperatures a quasi-liquid layer develops. Gas-phase reactions need to be reexamined in light of the changes in the tropospheric composition induced by heterogeneous and multiphase processes. Coupled modeling is a first step in this direction. Investigations of the chemical consequences of reducing the current atmospheric particulates, dictated by health, climate, and ecological considerations, should be examined. Lastly, further development of this field is essential if we intend to assess the effect of anthropogenic activity on Earth.

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Measurement Techniques in Gas-Phase Tropospheric Chemistry: A Selective View of the Past, Present, and Future

Howard K. Roscoe* and Kevin C. Clemitshaw

Measurements of trace gases and photolysis rates in the troposphere are essential for understanding photochemical smog and global environmental change. Chemical measurement techniques have progressed enormously since the first regular observations of tropospheric ozone in the 19th century. In contrast, by the 1940s spectroscopic measurements were already of a quality that would have allowed the use of modern analysis techniques to reduce interference between gases, although such techniques were not applied at the time. Today, chemical and spectroscopic techniques complement each other on a wide range of platforms. The boundaries between spectroscopic techniques will retreat as more Fourier transform spectrometers are used at visible wavelengths and as wide-band lidars are extended, and combining chemical techniques will allow detection of more trace gases with better sensitivity. Other future developments will focus on smaller, lighter instruments to take advantage of new platforms such as unmanned aircraft and to improve the effectiveness of urban sampling.

Modern tropospheric chemistry is the study of oxidants (O_3, OH, H_2O_2, HCHO, HO_2, and NO_3), gases that can be oxidized (hydrocarbons and sulfur compounds), oxidation products (carbonyls and organic nitrates), and the interactions of all of these with aerosols and clouds. Tropospheric chemistry is receiving particular attention today because of the widespread occurrence of photochemical smog in the Northern Hemisphere, which is often observable at considerable distances from the sources of pollutants. Effective pollution abatement strategies must be based on a detailed understanding of the causes and effects of pollution. We must be able to predict the three-dimensional evolution of the chemical composition of the troposphere, on spatial scales from the urban to the regional and eventually to the global. In order to define the initial state of the system and to validate model predictions, measurements must be made on each of these spatial scales. Tropospheric chemistry also presents different challenges and issues according to geographical location and altitude. These challenges have been met by deploying a wide range of instruments on different platforms. The limitations of these platforms have influenced sensor design in the past and will do so more vigorously in the future. There is a wide range of techniques for measuring tropospheric trace gases in ways that are appropriate to the different spatial scales. Because of their substantially different heritages, we make a broad distinction between spectroscopic absorption techniques, which observe over horizontal path lengths of 3 to 10 km or in a cell with mirrors to fold the path, and more localized chemical techniques, although this distinction is blurred in

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H. K. Roscoe, British Antarctic Survey/Natural Environment Research Council, Madingley Road, Cambridge CB3 0ET, UK.
K. C. Clemitshaw, Centre for Environmental Technology, Imperial College of Science, Technology and Medicine, Silwood Park, Ascot SL5 7PY, UK.

*To whom correspondence should be addressed.