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Models of cloud chemistry

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ABSTRACT

Clouds and precipitation systems play a very important rôle in the transformation and redistribution of chemical species in the atmosphere. Modeling of cloud chemistry is a complicated subject not only because chemistry in clouds is very complex, but also because cloud chemical processes are highly dependent on the microphysics and dynamics of clouds. A general cloud chemistry model must take into consideration the wide range of temporal and spatial scales over which cloud microphysical and dynamical processes take place. In this paper, a review of the basic cloud chemical and microphysical processes are presented. Special emphasis is given to the interactions between chemical and microphysical processes, and to considerations which may lead to model simplifications. SO_2 and NO_x chemistries are used as the main examples, a subject of interest in air pollution and acid rain research. A summary of recent modeling work is also presented.

1. Introduction

The transport of chemical species in the atmosphere is extremely complex. It involves: (1) the chemistry in free air, in particular the description of photochemical processes, (2) the air motion, (3) the dry deposition processes, and (4) the so-called wet deposition, including not only the rainout and washout processes, but also the chemical reactions occurring in clouds and rains. Only by bringing together adequately the treatment of these questions can it be expected to solve the fundamental problem: given a distribution of sources, forecast the transformation and final fate of the various chemical compounds.

The chemistry in free air has been extensively developed, partly stimulated by the need to understand the problems of highly polluted urban areas, such as the Los Angeles basin. But the understanding of wet deposition has been lagging behind until recently. The problem was earlier treated in highly parameterized, crude models (e.g., Dana, 1979). This was clearly insufficient, and completely inadequate to understand the increasingly serious problem of acid rain. Thus, during the last years, different researchers or teams of researchers have started to develop this field in a much more elaborate way.

One of the reasons for the complexity of modeling cloud chemistry lies in its dependence on the dynamics of cloud and precipitation systems and the microphysical processes occurring in clouds. Fig. 1 indicates this mutual dependence schematically. The microphysics in a cloud obviously depends on air motion and the properties of air (arrow 1); at the same time, these processes provide a feedback influencing the dynamics, through the latent heats of phase changes and the drag due to the weight of hydrometeors (arrow 2). The chemical processes are influenced by the dynamics, controlling the transport of chemicals

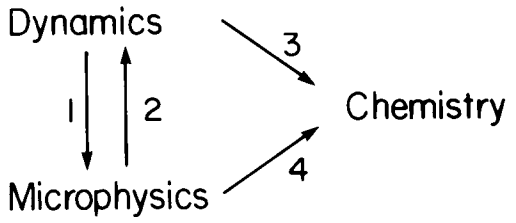

Fig. 1.

in the air (arrow 3). They are also strongly dependent on the microphysical processes (coalescence, accretion, riming, freezing, etc.) (arrow 4). While the spectrum of particles serving as cloud condensation nuclei (CCN) does have an important influence on the microphysics of the cloud, once the cloud is formed the chemical processes do not influence the microphysics or dynamics, since the masses involved and any heat released during the reactions are extremely small. It should be recognized, however, that the chemical processes of one cloud may alter significantly the CCN spectrum remaining after dissipation, thus influencing subsequent processes of condensation (Easter and Hobbs, 1974; cf. Section 5).

Clouds and cloud systems take place over a large range of temporal and spatial scales. The large stratiform cloud systems associated with midlatitude cyclones have spatial scale $\sim 10^3$ km, and last about 10^2 hours. Within these cloud systems, there are often pronounced organizations at the meso-β scale (50–100 km), e.g., rainbands. The lifetimes of these meso-β scale systems are uncertain, but typically are of the order of 10 hours. At the small end of the spectrum, there are cumulus clouds with spatial scale $\sim$1–10 km, and lifetime of the order of 1 hour. There are appreciable differences in the predominant microphysical processes taking place in these various systems, due to the difference in their temporal and spatial scales, as well as the difference in their dynamics. For chemical processes, it is also significant to consider the typical life times of cloud droplets in the cloud. This may be as long as 1 day for extended stratiform formations, or as short as a few minutes for cloud droplets in air flowing through stationary wave clouds. In convective clouds, the life time of a water drop is typically in the range of 10–50 min, measured from the moment of its formation to the time of its evaporation if carried out to free air, or the time when it reaches the ground as precipitation. These differences need to be considered when formulating a general cloud chemistry model applicable to all situations.

Another reason for the complexity of chemical models lies in the number of variables required for an adequate description of the processes. While a dynamic-thermodynamic model of the atmosphere uses only 5 variables (temperature, humidity and 3 components of the velocity), the number of variables used in microphysics depends on the complexity of the model, but usually at least 5 are required (mixing ratios of 5 species of hydrometeors: cloud droplets, ice crystals, rain, snow and graupel or hail). A proper chemical description of SO_2 and NO_x chemistry alone, on the other hand, requires 10 to 15 variables for a full chemical description of the acidity production, plus another 8 variables of diagnostic value, as will be discussed in Section 4. In view of the total number of variables involved and the complexity of the calculations, the requirements for computing time soon become onerous. Thus, a major concern of the modeler is to reach an adequate compromise between thoroughness of treatment and realistic possibilities of application. The model must take into account the main features, while remaining computationally tractable, and should avoid the requirement of detailed information that cannot be expected from field data. Obviously, strong simplifications and crude parameterization of various processes become inevitable.

In this paper, we present a brief review of the main microphysical and chemical processes which need to be considered in a cloud chemistry model. SO_2 and NO_x chemistries are used as the main examples. Special emphasis will be given to the interactions between chemical and microphysical processes. Considerations which may lead to model simplifications will be discussed. Section 5 reviews recent studies in modeling of cloud chemistry. Regarding the chemical process in aqueous phase relevant to clouds, the reader is referred to the review papers on that subject (e.g., Graedel and Weschler, 1981; Calvert et al., 1985; Hoffmann and Calvert, 1985).

2. Nucleation and dissolution of gases in liquid drops

2.1. Nucleation

Cloud chemistry begins at the formation of liquid droplets. These droplets form by the process of nucleation about hygroscopic particles, called cloud condensation nuclei (CCN). The process has been extensively studied and summarized in cloud physics monographs (Mason,

1971; Fletcher, 1962 and others). As the drop forms, all the soluble substances contained in a CCN will go into solution. Typically, a drop of 1 μm size will have concentrations of the order of 1 M. However, in about 10 s, droplets grow to the range of 5 to 10 μm. Thus the simplification can be made to treat the chemistry in the droplets as if they always constitute a dilute solution (total concentrations $\leqslant \sim 10^{-3}$ M), for which the activity coefficients are close to unity. The same simplification is also applicable to the brief periods of evaporation during the dissipation of a cloud.

Clearly, the initial chemistry of cloud droplets depends on the chemical composition of CCN. This is often taken to be the same as the chemical composition of aerosol particles in the air, a valid approximation if the fraction of mass of aerosol particles with sizes <0.1 μm, which do not act as CCN's, is rather small (cf. Prospero et al., 1983). Jensen and Charlson (1984) found that the fraction of the total mass of aerosol particles acting as CCN is very near unity for a clean continental background aerosol, while it may decrease considerably (fractions of the order of 50%) for low updraft velocities (stratiform clouds) over urban areas. Obviously, consideration of the non-active fraction in modeling chemistry would require adequate information on the aerosol activity spectrum and chemical composition of the active part.

2.2. *Scavenging of gases in the cloud and solubility equilibrium*

Once water drops form, their chemical composition is modified by absorption and reaction of gaseous chemical species (such as SO_2 and H_2O_2). Proper representation of mass transfer of gas species to liquid drops is an important component of cloud chemistry models.

The scavenging of gases by water drops is a very complex process involving diffusion of gases toward gas-water interface, transfer through the interface into the drop, the diffusion and liquid circulation within the drop, and the chemical reactions in the liquid. If the overall rate of a reaction occurring in aqueous phase is to be calculated, it is essential to ascertain which is the rate-determining step in the series of processes that bring the gases from the air to react in solution. This problem has been treated by Hales (1972), Schwartz and Freiberg (1981) and Schwartz (1986). Among the series of consecutive processes mentioned above, the transfer through the interface involves the badly known accommodation (or sticking) coefficient α. Gardner et al. (1987) report measurements of the coefficients for SO_2, indicating a value $\alpha \geqslant 0.054$ at room temperature, which is high enough to make transport across the interface fast in comparison with other steps. The overall mass transport rates are relatively insensitive to values of $\alpha \geqslant 0.01$. The assumption that α is sufficiently high to ignore the influence of transport through the interface is usually adopted (explicitly or implicitly) for all gases, although there is a subsisting uncertainty regarding this subject.

Transport within the liquid phase is generally, but not always, faster than diffusion in the gas phase. It has been shown (see for instance Schwartz, 1986) that if constant concentration of a non-reacting species is maintained at the surface of a drop of diameter D, the relaxation time τ_{aq} for diffusion towards a uniform concentration through the volume can be expressed by

$$\tau_{aq} = \frac{D^2}{8\pi D_a}, \tag{1}$$

where the diffusivity in the liquid D_a has for most gases a value of the order of 2×10^{-5} cm^2 s^{-1} at room temperature. This gives, for a 20 μm diameter drop, $\tau_{aq} = 8 \times 10^{-3}$ s; and for $D = 1$ mm (raindrop), $\tau_{aq} = 20$ s. The reactions in aqueous phase which are of interest in cloud chemistry (such as oxidation of SO_2 by H_2O_2 and O_3) generally have relaxation times >1 min (see Subsection 4.1), and thus are in general the rate-determining step, although in certain conditions there may be a mass transport limitation (cf., Martin, 1983, for the oxidation of SO_2 by O_3 at pH > 5).

For highly soluble non-reacting gases, the diffusion in gas phase (rather than in the liquid) is the rate-determining step for the absorption. It is interesting to consider the relaxation times for attaining solubility equilibrium, when the absorption is controlled by this diffusion. The rate of absorption of a gas A into a drop is given in this case by the formula (see for instance, Levine and Schwartz, 1982)

$$F = k_g(c_A - c_{A,eq}). \tag{2}$$

Here F is the density of flux of gas A (kmol m^{-2} s^{-1}) towards the drop. The concentrations within the bracket are in kmoles per m^3; c_A is the concentration in gas phase, and $c_{A,eq}$ is the value in equilibrium with the instantaneous molarity [A] in the liquid. The factor k_g is the gas-phase mass transfer coefficient. The first term within the brackets represents the diffusion towards the interface, while the second term represents the back diffusion from drop to air.

Eq. (2) together with the gas-phase mass transfer coefficient can be derived from theoretical considerations. Taking into consideration the accommodation coefficient α and the transition to a molecular regime when the drop size radius r approaches the mean free path l of molecules, Fuchs and Sutugin (1971) have derived formulae that can be taken into account by simply substituting k_g in (2) by the expression (cf. Chameides, 1984):

$$\frac{4}{3}\pi l r\left(\frac{8RT}{\pi M}\right)^{1/2}\left(1+\frac{4l}{3r\alpha}\right)^{-1},$$

where r is the drop radius, M is the molecular weight of the gas A and R is the gas constant. The last factor in this expression is ~ 1 for $\alpha = 1$ and 1/2.3 for $\alpha = 10^{-2}$. The rest of the expression gives approximately the same value as $k_g \cong D_g/r$, where D_g is the diffusivity of the chemical species considered, in the gas phase. This simple expression for k_g assumes r small enough to ignore the effect of ventilation. Since the theoretical refinement does not alter much the results, the following considerations are based on the latter simpler expression for k_g.

Formula (2) may be applied to a closed system consisting of a mass of cloudy air to determine the evolution of cloud droplets towards equilibrium. Considering, as initial conditions, $[A] = 0$, $c_A = c_{A,o}$, and introducing the gas and Henry laws and geometric relations, the differential equation

$$\frac{dc_A}{dt} + \lambda c_A = \mu \tag{3}$$

can be easily derived, where

$$\lambda = k_g\left[\pi D^2 N + \frac{6}{DH^* RT}\right],$$

$$\mu = \frac{6k_g}{DH^* RT}\, c_{A,o}.$$

N is the number concentration of drops and H^* is the effective, or pseudo, Henry coefficient. For species dissociating in aqueous solution with production of H^+ or OH^-, H^* is dependent on pH; for instance, for SO_2

$$H^* = \left(1+\frac{K_1}{[H^+]}+\frac{K_1 K_2}{[H^+]^2}\right) H,$$

where K_1 and K_2 are the first and second dissociation constants of H_2SO_3, and H is the Henry coefficient. The solution of (3) is

$$c_A = \frac{\mu}{\lambda} + \left(c_{A,o} - \frac{\mu}{\lambda}\right) e^{-\lambda t}, \tag{4}$$

with a time constant

$$\tau = 1/\lambda. \tag{5}$$

The general shape of the curves representing c_A as a function of time is shown schematically in Fig. 2 for two different values of H^*. The conditions of the initial approximately linear decay (one slope given by the dashed line) in the curves of Fig. 2 correspond to the concept of "irreversible washout", while the so-called "equilibrium washout" corresponds to the final approximately horizontal plateau. It is clear that for $H^* \to \infty$, the range of applicability of the linear part extends down to the horizontal axis.

In Table 1 the relaxation time for reaching solubility equilibrium at 25°C are given for the most relevant species in the cloud chemistry of acid rain. H^* coincides with H for the non-dissociating species (O_3, H_2O_2). For those which dissociate, the calculation has been done for the two pH values delimiting the usual range of observations (3–6). In the third column, the time constants are given, assuming $D = 20$ μm and $N = 100$ cm^{-3}.

Although the size spectrum was not taken into account in this simple consideration, the general conclusions that may be derived from these results are valid. Levine and Schwartz (1982) estimated, for typical convective cloud droplet size spectra, that τ would be ~ 5 s for highly soluble gases. Also, the previous treatment does not consider the change of droplet size by condensation growth, which will be rapid near the cloud base. Within this limitation it is clear, and this is the important conclusion from this analysis, that solubility equilibrium can be assumed for cloud droplets for all the relevant gases, since the

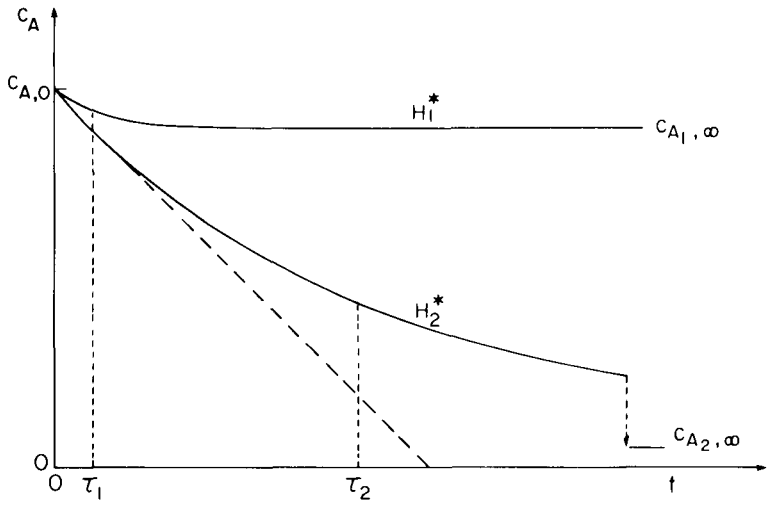

Fig. 2. Effect of scavenging on concentration in air (equation (15)) for a gas A_1 of lower H_1^* and a gas A_2 of higher H_2^*. The dashed line corresponds to "irreversible washout" applied to gas A_2.

Table 1. *Relaxation time τ for acquiring solubility equilibrium*

Species	pH	H^* (M atm^{-1})	Cloud parcel τ (s), $D = 20$ μm	Rain (local value: see text) τ (s), $D = 0.2$ mm	Rain (local value: see text) τ (s), $D = 1$ mm
O_3	--	1.0×10^{-2}	8×10^{-7}	4×10^{-5}	4×10^{-4}
CO_2	3	3.4×10^{-2}	5×10^{-7}	1×10^{-4}	1×10^{-3}
	6	4.9×10^{-2}	7×10^{-7}	2×10^{-4}	2×10^{-3}
SO_2	3	2.4×10^{1}	2×10^{-3}	1×10^{-1}	1
	6	2.3×10^{4}	1.5	9×10^{1}	9×10^{2}
NH_3	3	1.1×10^{8}	8	4×10^{5}	4×10^{6}
	6	1.1×10^{5}	4	4×10^{2}	4×10^{3}
H_2O_2		9.8×10^{4}	4	4×10^{2}	4×10^{3}
HNO_3	3	3.3×10^{9}	8	1×10^{7}	1×10^{8}
	6	3.3×10^{12}	8	1×10^{10}	1×10^{11}

relaxation times for chemical reactions are $\gg 10$ s (cf. 4.1). For the sparingly soluble O_3 and CO_2 and for SO_2 at low pH, τ becomes smaller than τ_{aq}, and diffusion in liquid phase becomes in these cases the rate-determining process in mass transport.

2.3. Scavenging by rain

Although the same basic eq. (2) can be applied in this case, the conditions are different. Raindrops have a size range from 0.2 to several mm, they fall at velocities of the order of meters per second, and the air that they cross may or may not have a constant concentration of the gas considered. In order to have an idea of the rate of approaching equilibrium at given local conditions, however, we may calculate the relaxation time for drops falling through air with a constant concentration c_A of the gas A. In this case, the variable considered is the concentration $[A]$ in the

drop, which is found to vary with time according to

$$[A] = [A]_{eq}(1 - e^{-\lambda' t}), \tag{6}$$

where $[A]_{eq}$ is the equilibrium value and

$$\lambda' = 6k_g/DH^* RT.$$

The estimated time constant $\tau = 1/\lambda'$ has been included in the last two columns of Table 1, for $D = 0.2$ mm and $k_g = 0.2$ m s^{-1} and for $D = 1$ mm and $k_g = 0.1$ m s^{-1}. The coefficient $k_g = fD_g/r$ contains in this case a correction factor f (ventilation coefficient) that represents the mass transfer enhancement produced by the relative motion of the drop and the air and by the drag-induced circulation within the liquid (cf., Baboolal et al., 1981 and Walcek et al., 1981).

These results and the previous estimates for τ_{aq} show that for rain, only very sparingly soluble gases, like O_3, may be considered in equilibrium. For highly soluble gases, the case is that of "irreversible washout". For SO_2, it depends strongly on the pH. Unless pH $\leqslant 4$, or the size of raindrops is in the lowest range, the exchange of SO_2 between raindrops and air must be calculated by the diffusion-controlled kinetic formula (2).

Two different parameters have been used to describe the effect of scavenging of air pollutants by clouds. One of them is the dimensionless *washout ratio* W defined (for gas A) as

$$W_A = \frac{[A]}{c_A}, \tag{7}$$

where the symbols have the same meaning as before. By using Henry's coefficient and making the appropriate transformation of variables, it can be seen that for equilibrium conditions,

$$W_A = RTH_A \tag{8}$$

where H must be substituted by H^* (pseudo-coefficient) if there is dissociation in the water.

The other parameter is the *scavenging coefficient* Λ, which is defined assuming that the rate of decrease of concentration in the air $-dc_A/dt$ due to scavenging is proportional to the concentration

$$-\frac{dc_A}{dt} = \Lambda c_A$$

or

$$c_A = c_{A,0}\, e^{-\Lambda t}. \tag{9}$$

This is a simplified version of (4) (with Λ identified as λ), when μ can be put $\cong 0$ (H^* very large).

The complete theory of the washout of SO_2 by rain including consideration of gas diffusion, transfer through the interface, and diffusion in the liquid, has been discussed by a number of authors: Hales (1972, 1978), Barrie (1978, 1981), Beilke and Gravenhorst (1978), Carmichael and Peters (1979). The Hales and the Beilke and Gravenhorst models do not include explicitly the liquid-side mass transfer coefficient, which the Barrie and the Carmichael and Peters models do. Altwicker and Chapman (1981) have made an experimental check of the theoretical treatments used by the previous authors. They found that the first three overestimate the SO_2 absorption (by factors between 2 and 6) while Carmichael and Peters underestimate it (factor ~ 10); they attribute the low results of the last authors to the method of calculating the mass transfer coefficient in the liquid and to the bisulfite ion/sulfur dioxide diffusivity ratios used in the calculation.

2.4. *Scavenging of particles*

The in-cloud scavenging occurs mainly through the nucleation process. Processes that could contribute to scavenging small particles of sizes below 0.1 μm, which are not active as CCN, namely Brownian motion and phoretic effects, can be generally neglected as minor contributions (see Flossman et al., 1985).

Washout by rain below the base of the cloud is an important process in the removal of atmospheric aerosol. In particular, it will contribute to the sulfate and nitrate content of the rain reaching the ground. The main mechanism for the washout of aerosols, in terms of mass, is the inertial removal by impaction. The efficiency of removal of a given aerosol particle size by a falling drop is controlled by the ratio of the falling speed to the drop radius (Twomey, 1977, Section 6). The collection efficiency depends on the aerosol size, and decreases abruptly below 1 μm (Mason, 1971, Section 2.6). The washout can be parametrically formulated as in the irre-

versible scavenging of gases, using a scavenging coefficient Λ:

$$\frac{dc}{dt} = -\Lambda c, \tag{10}$$

where c is the mass concentration of aerosol in the air at a given height (Hales, 1978). Obviously, Λ depends on the precipitation rate and on the nature of the precipitation particles, in a manner that may be approximated by empirical relations. Scavenging of aerosol in general and sulfates in particular has been the object of special attention by, among others, Hales (1978), Garland (1978) and Scott (1982). A summary has been given by Pruppacher and Klett (1978), Subsection 12.7.

3. Cloud microphysics

Since hydrometeors in clouds provide the site for aqueous phase chemical reactions, a proper model of cloud microphysics is a pre-requisite for modeling cloud chemistry. Due to the complexity of the processes, cloud microphysics models often involve gross simplifications and parameterization.

3.1. Species of hydrometeors

Besides water vapour, there is a large variety of hydrometeors in clouds, some in the form of water drops and others as ice particles. Both water and ice particles exist in a wide range of sizes: ice particles may also have a wide range of shapes and densities. Models of cloud microphysics exist which describe the time evolution of the continuous size spectra of hydrometeors, and to some extent even the complex shapes of ice particles, by considering explicitly the detailed microphysical processes and interactions (examples among others are: Cotton, 1972; Young, 1974; Scott and Hobbs, 1977; Yau and Austin, 1979; Hall, 1980; List et al., 1987). Since some chemical processes are critically dependent on the size of cloud hydrometeors, such detailed models of microphysics are desirable; but they require a large amount of computation.

A much simpler approach is to group cloud hydrometeors into several types, with a specified size distribution assumed for each type of cloud particles, and the processes responsible for the growth and the interactions between different types of particles parameterized (Ogura and Takahashi, 1971; Wisner et al., 1972; Orville and Kopp, 1977). Because of its simplicity in formulation and in computation, such a bulk approach is often used in cloud models (Rutledge and Hobbs, 1983, 1984; see also Section 5). The variety of hydrometeors can be grouped typically into five categories: cloud water drops, raindrops, cloud ice particles, snow and graupel. The grouping is by necessity somewhat crude. For example, water drops in cloud form a continuous spectrum in sizes. The smaller drops have no appreciable falling velocity with respect to air, and are moving with air parcels. These drops are commonly referred to as cloud droplets. On the other hand, the falling velocity of large drops can be quite substantial, and they are considered as raindrops. Such a grouping would be a natural approach if the water drop spectrum shows a bimodal distribution with a minimum in the spectrum separating the cloud droplets from falling raindrops. On the other hand, if there is no such a bi-modal distribution in the water drop distribution, the choice of the boundary between cloud droplets and raindrops becomes somewhat arbitrary. One possible choice is the size at which water drops survive fall to ground without complete evaporation. This corresponds usually to a drop size with diameter $D \sim 200$ μm.

Similarly, the simple grouping involves gross simplifications for ice particles as well. Small ice crystals may be in the form of hexagonal plates, prisms, needles, dendrites, etc. Snow particles also exist in many shapes and in aggregates. Graupel or ice pellets can have average densities ranging from 100 to 900 kg m^{-3}; they can be conical or spherical in shape. Hailstones, representing an extreme case of growth by accretion, are not even considered in such a grouping as a separate category, but are placed together with graupels. Again, a somewhat arbitrary choice of size is necessary to separate cloud ice particles from falling snow and graupel. A possible choice is the size at which a crystal starts falling rapidly enough to accrete water droplets by riming; this roughly corresponds to a dimension of ~ 400 μm.

To allow for some dependence of microphysical and chemical processes on the sizes of particles, a specified size distribution is often assumed in the bulk approach for each type of

precipitation particles. The exponential distribution function

$$n(D) = n_0 e^{-\lambda D} \tag{11}$$

(or Marshall–Palmer distribution) is the usual choice, where n_0 and λ are constants, D is the diameter, and $n(D)\,dD$ is the number density of particles with diameter between D and $D + dD$. The calculation of the source terms describing many of the interactions in the mass continuity equations of these hydrometeors include an integration over the size spectrum. However, all particles are assumed to fall with the same velocity—the mass-weighted average—so as to avoid the need of multiplying the independent variables by considering separately a series of size ranges. Due to the very small sizes of cloud droplets and ice crystals, many properties such as the terminal velocities and rate of dissolution of gases, are not critically dependent on their size spectra. Therefore, uniform size is usually assumed for them.

3.2. *Microphysical processes*

There are many possible mass exchange processes and interactions between hydrometeors in clouds. These include, for example, condensation–evaporation, freezing–melting, coalescence of cloud droplets to form raindrops, accretion of cloud droplets on raindrops or cloud ice particles on snow, riming, etc. These processes are illustrated in Fig. 3 and briefly considered in what follows.

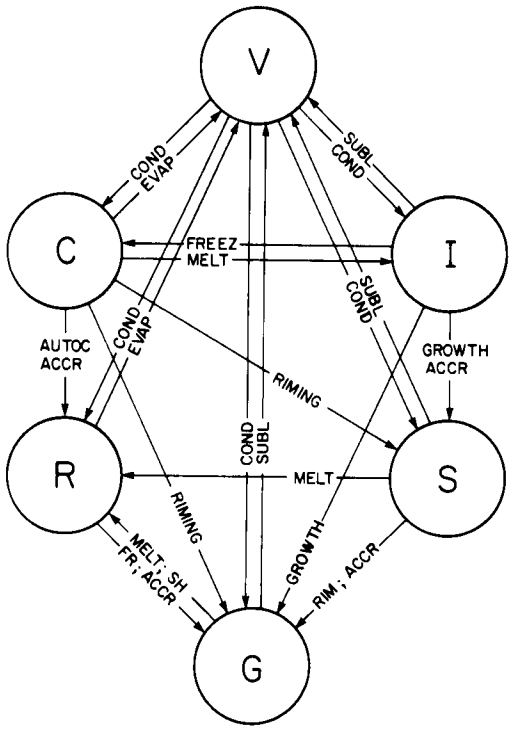

Fig. 3. Microphysical interations. V: vapour; C: cloud droplets; I: ice crystals; R: rain; S: snow; G: graupel or hail. ACCR: accretion; AUTOC: autoconversion; COND: vapour condensation; EVAP: evaporation; FR, FREEZ: freezing; MELT: melting; RIM: riming; SH: shedding; SUBL: sublimation.

There are two triggering mechanisms for the development of rain. One is the coalescence of droplets into raindrops, or "autoconversion", which initiates the so-called "warm rain" process; the raindrops continue growing by accretion of droplets, or eventually may be transferred to the category of graupel by freezing, continue growing by riming, and melting again when air temperature becomes above 0°C. The other triggering process is the appearance of ice crystals, notably by the freezing of cloud droplets, initiating the rapid growth of crystals to sizes at which the falling velocities are large enough to start actively growing by riming; this is the Bergeron–Findeisen process. Vapour deposition on, or evaporation from, drops and ice particles is governed by a diffusion-controlled kinetic equation in general. In the particular case of clouds saturated with respect to water or to ice, such kinetic calculations become unnecessary, since the thermodynamic condition of vapour saturation can be assumed. The accretion process transfers cloud water to rain in liquid phase, or to snow or graupel (riming), or ice crystals to snow, or rain to graupel. Other interactions involve changes of species: melting will change snow or graupel to rain, sublimation growth of ice crystals will transform them into snow or graupel, actively riming snow may be transformed into graupel. Some processes, like vapour deposition on raindrops or on graupel, are usually much slower than other processes that the same particles undergo (accretion, riming) and can usually be neglected.

Mathematical formulations of the various interactions are available from cloud physics

literature; readers are referred to, for example, Lin et al. (1983) and Rutledge and Hobbs (1983, 1984). These formulations obviously may differ according to the particular assumptions, simplifications and parameterizations chosen by the authors. In these bulk models of microphysics, some crude and somewhat arbitrary assumptions are necessary; for instance, the autoconversion process is usually parameterized following Kessler (1969) and the passage of the category of ice crystal to that of precipitation particle (snow or graupel) is also simply parameterized. The growth by accretion processes is usually calculated by continuous collection (rather than stochastic) equations.

4. Cloud chemistry

As previously mentioned in Subsection 2.1, cloud chemistry begins with nucleation when chemicals in cloud condensation nuclei are transferred to the liquid phase. It involves subsequently not only the chemical reactions taking place in clouds, but also the exchange of chemical compounds between two phases, and the transfer of chemicals from one hydrometeor to another. There are many possible chemical reactions in clouds involving various chemical species. In the following discussion we will consider only the chemistry of SO_2 and NO_x as examples, as they are the species of main concern in air pollution research.

4.1. Chemical reactions

Among the many possible chemical reactions in clouds, only a few seem to be really important. In order to decide which reactions should be included, the following criterion can be used. A relative reaction rate v_r can be defined as the number of equivalents of acidity produced per unit time, relative to the total number of equivalents of SO_2 present in both interstitial air and cloud droplets. For SO_2 oxidation reactions in solution,

$$v_r = \frac{1}{c_{SO_2,Cl}} \rho_w^{-1} \mu_{SO_2} r_C v, \tag{12}$$

where

$$v = -\frac{d[S(IV)]}{dt};$$

the bracket indicates molarity in solution, ρ_w = water density, $\mu_{SO_2} = SO_2$ molecular weight, r_C = mixing ratio of cloud water. For any species that becomes oxidized in air to give a product going into solution as a dissociated acid (e.g., SO_2, NO_2, NO),

$$v_r = \frac{1}{c_{SO_2,Cl}} v_i \tag{13}$$

where

$$v_i = \frac{dc_i}{dt} \quad (i = SO_2, NO_2, NO, \text{etc.}).$$

Fig. 4 shows estimated values for several reactions. The parameter $\tau = 1/v_r$ gives the time constant for the oxidation of the SO_2 present in the cloudy air, or for the production of an equivalent acidity from other precursors. It becomes obvious that there is no need to consider any reactions with $v_r \ll 10^{-6}$ s^{-1} ($\tau \gg 3$ days), or reactions that represent only a minimal fraction of a competitive pathway (such as oxidation by PAN compared with oxidation by ever present O_3). Also, in view of the large uncertainties in the knowledge of the kinetic parameters (specific reaction rates, activation energies) at the present time, there is no point in considering reactions whose contributions amount to less than the uncertainties in the main reactions.

The conditions for which the curves have been calculated in Fig. 4 are indicated in the legend. Catalytic oxidation of $S(IV)$ by O_2 in liquid containing Mn^{2+} and Fe^{3+} is expected to be significant in or close to urban areas, where the concentrations of these metals may be high. The values used in Fig. 4 (5×10^{-9} and 10^{-8} g m^{-3}, respectively, corresponding to the quoted molarities for the assumed cloud water mixing ratio) have been suggested by Chang et al. (1987) as typical background concentrations; at this level, the contribution of catalytic oxidation appears negligible. Oxidation of NO by OH and subsequent dissolution of the HNO_2 produced is of the same order as that of NO_2, depending on the concentration of NO in air. Consideration of the reactions of oxidation of NO and NO_2 by OH in gas phase requires a knowledge of the radical concentration. While the contribution of these reactions can be crudely estimated by assuming reasonable values for that parameter (eventually considered as a variable parameter depending on

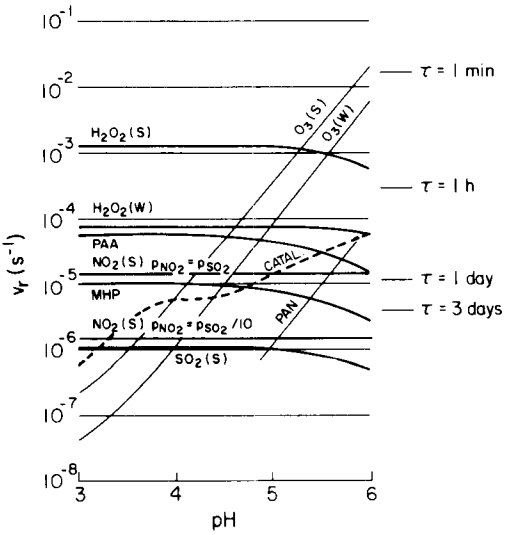

Fig. 4. Comparison of relative rates of reaction. S: typical summer conditions; W: typical winter conditions, chosen as:

Parameter	*S*	*W*
temperature	20°C	0°C
cloud water mixing ratio	2×10^{-3}	2×10^{-4}
pressure	0.8 atm	0.8 atm.
mixing ratio of SO_2 in cloudy air	5×10^{-9}	5×10^{-9}
mixing ratio of H_2O_2 in cloudy air	2×10^{-9}	0.15×10^{-9}
volume mixing ratio of O_3	40×10^{-9}	20×10^{-9}
partial pressure of OH	4×10^{-14} atm	—
volume mixing ratio of PAN, PAA, MHP	10^{-9} (each)	—
Mn^{2+}	5×10^{-8} M	—
Fe^{3+}	9×10^{-8} M	—

The lines labelled NO_2 and SO_2 correspond to oxidation by OH in gas phase. Oxidation of NO is not plotted, but it would give lines slightly lower than those for NO_2. Dashed line: catalytic oxidation.

solar radiation and on the radiation transmissivity of the cloud), a proper calculation would require the introduction of a photochemical model for the reactions occurring in the interstitial cloud air. Oxidation of NO_2 by the two successive reactions

$$NO_2 + O_3 = NO_3 + O_2$$

$$NO_2 + NO_3 = N_2O_5,$$

with subsequent dissolution of N_2O_5, producing HNO_3, has been estimated as less significant than the oxidation by OH (see Heikes and Thompson, 1983, with corrections in 1984; cf. also further discussion on the role of NO_3 in Calvert et al., 1985). Oxidation by radicals scavenged from the air includes oxidation of *S*(IV) by OH in the liquid phase and by H_2O_2 produced by reactions of HO_2 in the liquid. Estimates by Chameides and Davis (1982) suggested that these reactions might be significant. However, there is a considerable uncertainty about the kinetics and mechanisms of these reactions and more recent work suggests that radicals play only a minor role in the oxidation of *S*(IV) in liquid phase (McElroy, 1986a, 1986b; Huie and Neta, 1987). Any estimates would also be affected by the great variability of radiation transmissivity through the cloud and of droplet size spectrum, and by the lack of sufficient knowledge of the accommodation coefficient of the radicals OH on water surface (the coefficient for HO_2 has been found to be >0.2 by Mozurkewich et al., 1987). Finally, other compounds, including PAA or peroxyacetic acid (CH_3COO_2H) and MHP or methylhydroperoxide (CH_3O_2H) can contribute significantly to *S*(IV) oxidation in liquid phase, whenever they reach concentrations of the order of the ppb(v) in the air (see Calvert et al., 1985); curves have been plotted for these compounds assuming the value of 1 ppb(v).

Taking into account Fig. 4 and all the previous considerations, it may be concluded that the only chemical reactions that need to be considered (out of urban areas) are:

(a) Oxidation of SO_2 in liquid phase by H_2O_2 dissolved from the air.

(b) Oxidation of SO_2 in liquid phase by O_3 dissolved from the air.

(c) Oxidation of NO_2 by OH in gaseous phase, with subsequent dissolution of the HNO_3 formed.

(d) Oxidation of NO by OH in gaseous phase, with subsequent dissolution of the HNO_2 formed.

(e) Catalytic oxidation of SO_2 by O_2 in liquid phase containing Mn and Fe, if their concentrations are significant enough.

(f) Oxidation of SO_2 by MHP and PAA, if the atmospheric concentrations reach the order of ppb(v).

4.2. Transfer and exchange of chemical species

When water is transferred from one type of hydrometeor to another, there is the correspond-

ing transfer of part or all of the solutes contained in it. There may also be exchange of volatile solutes between the liquid and the gaseous phase. When the assumption of solubility equilibrium can be made, this exchange is of no particular concern as the partition between the two phases can always be determined from Henry's law. As seen in Subsection 2.2, this is generally the case for all the gaseous species of interest (SO_2, H_2O_2, O_3, HNO_3, NH_3, CO_2) when the drops are in the size range of cloud droplets, a fact that brings about considerable simplification in calculations. However, the assumption is no longer valid in general for raindrops, except for the slightly soluble gases. In this case, the diffusion-controlled kinetic considerations must be applied, as discussed in Subsection 2.2.

Another type of exchange between hydrometeors and air must be taken into account. When a drop freezes, solutes are rejected in greater or lesser amount by the growing ice phase at the ice–water interface. If the solute is non-volatile, it will finally remain in the frozen drop (in uneven distribution through the particle), but volatile solutes may be partially lost to the air during the process. Iribarne and Pyshnov (personal communication) have determined that there are no losses of HCl or HNO_3 from freezing droplets containing H^+ and the corresponding anion (Cl^- or NO_3^-). H_2O_2 also remains entirely in the ice. SO_2, however, is partially lost (Iribarne et al., 1983). There is uncertainty as to the fraction of S(IV) retained by the ice for the conditions prevailing in clouds during the riming process. Lamb and Blumenstein (1987) find values varying from about 5% at -5°C to 15% at -23°C, while Iribarne and Physnov (personal communication) find about 60% with little dependence on the temperature, between -10°C and -23°C.

Finally, still another exchange between ice particles and air is provided by the process of adsorption. Rutledge et al. (1986) have introduced consideration of the adsorption of HNO_3 on ice surfaces, based on a parameterization by Chang (1984).

4.3. Primary model variables

In a cloud chemistry model, there is a minimum number of variables that must be followed through integrations of the mass conservation equations in order to obtain a complete description of the development of cloud chemistry. These variables are here referred to as primary variables. Other variables which can be calculated diagnostically from primary variables are called secondary variables. The number of primary variables needed depends on the complexity of the model, and once this is established, different choices for the set of variables are possible. Consider, as an example, a model describing the chemistry of oxidation of SO_2 by H_2O_2 and O_3, and oxidation of NO and NO_2 in the gas phase. In this model, the cloud microphysics is described in terms of bulk parameters giving the mass mixing ratios of 5 hydrometeor species: cloud droplets, raindrops, cloud ice particles, snow and graupel. Assume furthermore that the concentration of O_3 in the air is taken as constant (i.e., its consumption is small, compared with the total amount) and that the concentration of solutes in ice crystals is neglected (crystals contain the solutes present in the initial frozen droplets, but greatly diluted by the growth with pure sublimated ice). In that case, an appropriate set of variables could be:

$$c_{SO_2,Cl}, [S(IV)]_R, [S(IV)]_S, [S(IV)]_G,$$

$$c_{H_2O_2,Cl}, [H_2O_2]_R, [H_2O_2]_S, [H_2O_2]_G,$$

$$c_{NO}, c_{NO_2}, n_{A,C}, n_{A,R}, n_{A,S}, n_{A,G}.$$

Here the subscripts C, R, S, G stand for cloud droplets, rain, snow and graupel, and Cl stands for total concentration in cloud droplets and interstitial air, S(IV) indicates all unoxidized species of SO_2 in solution, c_{NO} and c_{NO_2} are concentrations in the air. Square brackets mean concentration expressed in molarity. n_A is an acidity parameter defined as the number of kequivalents per kg of air of such species as will be dissolved in the liquid phase producing H^+. Substances that will neutralize acidity in solution (such as NH_3) contribute a negative value to n_A. Initially, i.e., as soon as the cloud droplets form, n_A will include the following contributions:

- acidity from the cloud condensation nuclei (CCN): mainly from NH_4HSO_4, possibly H_2SO_4, etc.;
- alkalinity (negative contribution) from the CCN: mainly $CaCO_3$, if present;

- HNO_3 from the air, that becomes totally dissolved in the aqueous phase;
- NH_3 from the air (negative contribution), that becomes totally dissolved in the aqueous phase.

The assumption is implicitly made that the dissolution of HNO_3 and NH_3 can be considered as instantaneous for modeling purposes. The justification of this assumption lies in the values of the relaxation times for acquiring solubility equilibrium (cf. Table 1). Solubility equilibrium can be assumed, say after 30 s, which in the case of these two gases means practically total scavenging by the liquid phase. During that time, an air parcel may have only ascended a distance of the order of 100 m into a convective cloud, or a few meters into a stratiform cloud.

In the subsequent evolution, n_A will be increased by the oxidation of SO_2 in liquid phase and by that of NO_2 and NO in gaseous phase, followed by the dissolution of the products. Thus n_A measures the amount of acidity (i.e., of equivalents of H^+) permanently acquired by the aqueous phase. The total acidity will still be increased by the partial dissolution of SO_2, which makes a contribution to acidity through the production of $HSO_3^- + H^+$ and of $SO_3^= + 2H^+$, but varies with the distribution of SO_2 between the liquid and gaseous phases. A very minor contribution will also come from dissolved CO_2. Notice that the concentration of acidity in solution corresponding to n_A, i.e., $[A] = \rho_w n_A / r_L$ (where ρ_w is the water density and r_L the mixing ratio of liquid), varies with the dilution, so that the corresponding pH decreases with the drops' evaporation and increases with their growth. The fact that the initial value of the parameter n_A is a combination of various terms means that different sets of initial conditions may be equivalent with respect to the production of acidity in the cloud; for instance, a high aerosol acidity and high concentration of NH_3 in air may result in the same initial value of n_A as a case of low aerosol acidity and low concentration of NH_3.

Alternatively, the contribution of aerosol and gases to the acidity of the nucleated cloud droplets has been described (Lazrus et al., 1983) by a parameter called "air pH" defined as the pH of 1 ml of water which has dissolved all the net acidity of 1 m^3 of air. This will include the effect of SO_2 and CO_2. The initial value of the parameter $n_{A,o}$ is related to the "air pH" or pH_A by

$$n_A = (10^{-pH_A} - [HSO_3^-] - 2[SO_3^=] - [HCO_3^-])/10^6 \rho, \quad (14)$$

where ρ is the air density and the concentrations in brackets are the contributions from SO_2 and CO_2, which depend on their concentration in the air and on pH_A.

Munger (1982) (see also Munger and Eisenreich, 1983) has shown that the supply of alkaline soil dust ($CaCO_3$, $MgCO_3$) and gaseous NH_3 available to neutralize acidity produced from anthropogenic sources seems to control the acidity of precipitation in north-central United States. This alkaline supply implies a large negative initial value of the parameter n_A, that requires an equivalent amount of acidity produced in the cloud to bring n_A to 0 (total neutralization), and then to positive values (actual acidity).

The set of 14 variables mentioned above assume that O_3 is present in a large enough excess over the SO_2 to consider its concentration in air as a constant. If this is not the case, new variables should be added. Again, consideration of formic acid would add further complication.

The set of variables, as stated, is sufficient to determine completely the chemical processes leading to the development of acidity. However, the networks for collecting and analyzing precipitation use most commonly the concentrations of $SO_4^=$ and NO_3^- as indicators of the oxidation processes. It should be noted that while these processes produce additional amounts of sulfate and nitrate together with the equivalent acidity, the aerosol acting as CCN contributes a background of these ions that cannot be associated arbitrarily with acidity; for instance, Na_2SO_4 and $NaNO_3$ are neutral substances that will dissolve to give $SO_4^=$ and NO_3^- ions, but no H^+; 1 mol of aerosol NH_4HSO_4 gives 1 equivalent of acidity, while 1 mol of H_2SO_4 gives 2 equivalents. Thus, statements such as "$SO_4^=$ and NO_3^- are major contributors to acid rain" are misleading, even though it is true that most of the acidity is usually associated with the $SO_4^=$ and NO_3^- present. If the concentrations of sulfate and nitrate are to be used as diagnostic variables, a knowledge of the aerosol background is necessary, and an extra set of 8 variables

should be considered for integration; for instance:

$$\Delta n_{SO_4^=,i}, \quad \Delta n_{NO_3^-,i} \qquad (i = C, R, S, G),$$

where Δn stands for the number of kmoles per kg of air, and the symbol Δ is added to emphasize that the calculation follows the amounts of sulfate and nitrate *added* to the background by the oxidation reactions.

4.4. *Secondary variables*

In a cloud chemistry model, it is often necessary to calculate a rather large number of secondary variables. These are variables whose values can be derived diagnostically from the primary ones; for instance, the concentration of SO_2 in interstitial air (alone), the concentration in solution in cloud droplets and in rain of the various unoxidized species of S(IV): H_2SO_3, HSO_3^-, $SO_3^=$, the acidity concentrations $[A]_i$ $(i = C, R, S, G)$, the H^+ concentration in cloud droplets and in rain, etc. In order to calculate these variables, a series of diagnostic equations can be set up, which can be classified as follows.

(a) Solubility equilibria (Henry's law for the various gaseous species).

(b) Ionic equilibria (dissociation constants, including the ionic product of water).

(c) Mass conservation, for different species.

(d) Electroneutrality. With the concept of acidity as defined above, this condition is expressed by

$$[H^+] = [HSO_3^-] + 2[SO_3^=] + [HCO_3^-] + [OH^-] + [A] \qquad (15)$$

to be applied to cloud water and to rain, separately. Here $[A]$ is equal to the sum of all anion concentrations not compensated by an equivalent concentration of cations other than H^+. $[OH^-]$ is usually negligible; in fact, alkaline drops cannot persist in the atmosphere, due to the rapid neutralization by absorbed CO_2, always present in a relatively massive concentration (340 ppm(v)), followed by an additional dissolution that produces some acidification.

These equations form a set of simultaneous equations which can be solved for the values of secondary variables, for example, $[H^+]_C$, $[H^+]_R$, etc.

4.6. *Modifications and simplifications*

As mentioned before, the chemical model is necessarily dependent on the microphysics model. However, once the latter is chosen, it is a trivial matter to introduce improvements or modifications without altering the framework of such a model. Thus for instance, better values of the chemical constants that may appear in the literature, or new reactions that are shown to be important, are easily introduced.

Many simplifications can and have been introduced by various researchers. A rather crude one consists in considering only SO_2 as an acidity precursor, i.e., ignoring the minor contribution of NO_x. Most workers, even in elaborate models, have ignored the presence of S(IV) in frozen particles. Variations of O_3 concentration in the interstitial air can be ignored, assuming that its consumption by SO_2 in solution can be neglected. A considerable simplification of the chemical model can be obtained, if the calculations are restricted to the range of pH most frequently found in clouds and precipitation. This has been done in most models until now. From the equilibria of solubility of SO_2 and the two dissociations of H_2SO_3, it can be readily derived that

$$[S(IV)] = H_{SO_2} p_{SO_2} \left(1 + \frac{K_{SO_2,1}}{[H^+]} + \frac{K_{SO_2,1} K_{SO_2,2}}{[H^+]^2}\right). \qquad (16)$$

(H_{SO_2}: Henry coefficient; p_{SO_2}: partial pressure; $K_{SO_2,1}$, $K_{SO_2,2}$: first and second dissociation constant) where the three terms at the right correspond to $[H_2SO_3]$, $[HSO_3^-]$ and $[SO_3^=]$, respectively. Thus, these three species are in the relative concentrations of

$$[H_2SO_3]:[HSO_3^-]:[SO_3^=] = 1 : \frac{K_{SO_2,1}}{[H^+]} : \frac{K_{SO_2,1} K_{SO_2,2}}{[H^+]^2}. \qquad (17)$$

The relative abundances depend thus on $[H^+]$. From formulas (16) and (17) the graph of Fig. 5 can be constructed, giving the fraction contributed by each species, as a function of pH. Perusal of the figure indicates that in the usual range of pH from 3 to 6, the simplification can be introduced that

$$[S(IV)] \cong [HSO_3^-]; \; [H_2SO_3] \cong 0; \; [SO_3^=] \cong 0. \qquad (18)$$

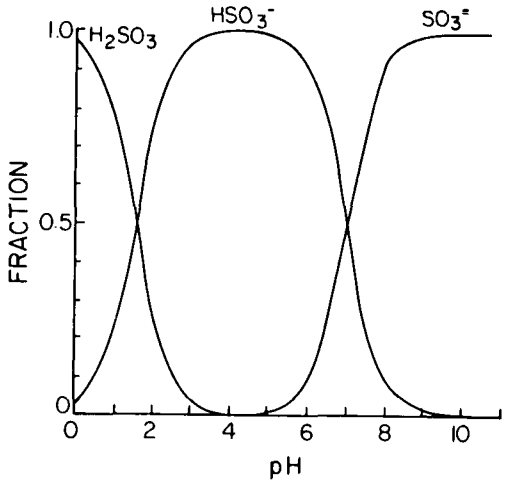

Fig. 5. Distribution of *S*(IV) in solution among the three species, as a function of pH. Calculated for −10°C.

A further simplification is obtained if the raindrops are in their low size range and pH < 6. In that case, solubility equilibrium can be assumed for SO_2 between rain and the air.

5. Cloud chemistry models

In the previous sections, an attempt has been made to discuss the main problems that a modeler has to consider, in setting up a cloud chemistry model. According to the aim of the authors, there has been a variety of approaches, differing in the range of applicability, the degree of elaboration and the particular simplifications adopted. Numerous articles have been devoted to restricted problems, treated with more or less degree of thoroughness. In Section 3, reference has already been made to some publications dealing with microphysical descriptions. Other work refers to the role of the aerosol and to aerosol scavenging. Easter and Hobbs (1974) studied the effects of the chemistry in a wave cloud on the spectrum of cloud condensation nuclei (CCN). They found that for concentrations of SO_2 and NH_3 typical of unpolluted air, chemical processes taking place in cloud droplets will produce, after evaporation of droplets emerging from the wave cloud, particles of ammonium sulfate which alter significantly the activation spectrum of CCN. For instance, the model predicted an increase of 75% in the concentration of CCN active at 0.5% supersaturation, after the air flow through the cloud in 4 min. Flossmann et al. (1985) studied the scavenging of aerosol particles by cloud and rain drops through nucleation and impaction. They found that nucleation scavenging may reduce the number concentration of aerosol particles by 48–94%, but scavenging by impaction of aerosol particles remaining in air involves a mass several orders of magnitude smaller than the mass scavenged by nucleation.

During the last few years, models have been developed by various research groups which have been used to obtain a comprehensive picture of the chemical transformation in clouds. The complexity of the cloud models in which the chemical processes have been investigated varies considerably. The simplest type is the box model or flow-through reactor. These models have been useful in obtaining insight of chemical evolutions of a system without the complication of meteorological and dynamical considerations. Hong and Carmichael (1983) used a simple flow-through reactor model to study the sulfate production in clouds. The test region inside the reactor is well mixed and contains cloud droplets of a given size. Boundary layer air containing SO_2, HNO_3, NO_x, NH_3, O_3, H_2O_2, CO_2 and sulfate aerosol flows through the reactor. Gas scavenging and chemical reactions are considered, including the oxidation of *S*(IV) by H_2O_2, O_3 and by O_2 catalyzed by Mn^{2+} but not the oxidation of NO_x in gas phase. Both precipitating and non-precipitating conditions, and the influence of drop size, rain intensity, liquid water content and updraft velocity are studied. The authors found that both the H_2O_2 and O_3 oxidation reactions can be significant, and that the results were highly dependent on the air composition. Seigneur and Saxena (1984) made calculations for a time-dependent box model containing only gas and aqueous phase. The chemical reactions include oxidation of SO_2 by O_3, H_2O_2, radicals, and O_2 catalyzed by Mn^{2+} and Fe^{3+}, the combination of HSO_3^- with formaldehyde, and the oxidation of NO and NO_2 in gas phase by OH. The presence of HNO_3, HNO_2, NH_3, NO_2, PAN and hydrocarbons is taken into account. The model was applied to four types of environment: (1) non-

precipitating clouds in the Adirondacks for summer and winter conditions; (2) raining clouds in the Ohio river valley; (3) night-time fog in the Los Angeles basin; and (4) night-time stratus clouds in the Los Angeles basin. General qualitative agreement with field data was found.

Cumulus clouds play a very important role in the transformation and redistribution of air pollutants. A number of models have been developed to study the chemical processes taking place in this type of clouds (e.g., Tremblay and Leighton, 1984; Walcek and Taylor, 1986; Lee, 1986; Niewiadomski et al., 1986; and Tremblay and Leighton, 1986). The basic chemical processes included in these models are quite similar. However, there are substantial differences in the dynamics and cloud microphysics, leading to substantial differences in simulation results.

For chemical processes, most of these models considered the contribution to the chemistry of cloud water from the soluble portion of the condensation nuclei in the form of H_2SO_4, $(NH_4)_2SO_4$, and NH_4NO_3. Solubility equilibrium is generally assumed between gas phase and liquid phase in cloud droplets for chemical species such as SO_2, NH_3, CO_2, and HNO_3. In the liquid phase, all of these models considered oxidation of sulfur dioxide by H_2O_2 and O_3. Oxidations by methylhydroperoxide (MHP), by peroxyacetic acid (PAA), and through catalytic reactions by Fe^{3+} and Mn^{2+} were included in some cases (Walcek and Taylor, 1986).

There are considerable differences in the details of treatment of microphysical processes in these cumulus models. Most of the models (Walcek and Taylor, 1986; Lee, 1986; Tremblay and Leighton, 1984, 1986) considered only water clouds; in the model developed by Niewiadomski et al. (1986) the presence of ice, including cloud ice particles, snow and graupel, was described by bulk parametric representation. Walcek and Taylor (1986) and Lee (1986) studied only non-precipitating clouds. In Walcek and Taylor (1986), a uniform cloud drop size was assumed while in Lee (1986) the evolution of cloud drop size spectrum was modeled explicitly. Precipitation processes were considered in Tremblay and Leighton (1984, 1986) and Niewiadomski et al. (1986). Tremblay and Leighton (1984, 1986) considered the warm rain processes using the Kessler (1969) parameterization while in Newiadomski et al. (1986) precipitation in both the liquid phase and the ice phase were included.

Due to its complexity, the dynamics of cumulus clouds can be modeled properly only using a three dimensional cloud, but such a model is computationally expensive, and for the purpose of modeling cloud chemistry, gross simplifications are often made. For example, in Walcek and Taylor (1986), a steady-state one-dimensional model was used in which air parcel was assumed to rise throughout the cloud depth with a uniform velocity. The interaction between the cloud air and the air in the cloud environment was modeled using an empirical formula based on Paluch's (1979) conceptual model of cloud top entrainment. While Paluch's cloud-top entrainment model has its empirical justifications, the assumption of uniform rising velocity for all air parcels is clearly unrealistic. In the study by Tremblay and Leighton (1984), a vertical profile of air rising velocity was assumed in their one-dimensional model with entrainment of environmental air and detrainment of cloud air determined through mass continuity. The model was used to study the time evolution of cloud chemistry, even though the model dynamics was a steady-state model. Complete time-dependent one-dimensional model was used in the studies by Lee (1986) and Niewiadomski et al. (1986). Lee's model was based on the formulation by Asai and Kasahara (1967): a cumulus cloud is represented by two concentric cylindric air columns with the inner column corresponding to the cloud region and the outer annular column corresponding to the surrounding clear air. The interactions between the two columns take place through buoyancy, lateral eddy mixing, and dynamic entrainment. A similar model based on the formulation by Ogura and Takahashi (1971) was used by Niewiadomski et al. (1986). In the study by Tremblay and Leighton (1986), the three dimensional model developed by Yau (1980) was used.

Although details of simulation results using these models differ, due to the differences in model formulation and the assumed environmental and initial conditions, some general model behaviour can be summarized. The model results show that aerosol particles contribute significantly to the liquid phase concentrations of various chemical species and the pH values of

liquid water, especially during the initial formation stage of the cloud, and in the lower levels of the cloud. In addition to the background meteorological conditions and the vertical distributions of chemical species in the clear air, the cloud chemistry and the vertical variation of pH values of liquid water depend strongly on cloud liquid water content and the entrainment of clear air into clouds through eddy mixing and dynamic entrainment. Generally speaking, clear air at levels above cloud base has relatively high moisture content and relatively low content in chemical species. The entrainment of clear air into clouds therefore has the effect of diluting the concentration of chemical species. At the same time, cloud liquid water content increases as air parcels accelerate upward, due to additional condensation. This results in a general increase with height in pH values of cloud water droplets. Depending on the chemical concentrations at the initial time and in the boundary layer, there are possible exceptions to this general behaviour during the formation stage and in the lower levels of a cloud.

The most important in-cloud oxidation process of SO_2 is that by H_2O_2 which is responsible for most of the in-cloud production of sulfate. However, due to its rapid reaction, in-cloud H_2O_2 is quickly depleted at lower levels of clouds. At upper levels, the rate of oxidation by O_3 could be comparable to that by H_2O_2, due to both the lower concentration of H_2O_2 and the higher pH value of cloud water at these levels. In the simulation presented in Tremblay and Leighton (1986), the environmental and initial conditions were such that the pH value of cloud water was very low throughout the entire depth of the cloud. In this case, the oxidation by O_3 was insignificant and oxidation by H_2O_2 is responsible for practically all of the in-cloud production of sulfate.

Model simulation results also show some interesting interactions between cloud microphysics and chemistry. In the study by Lee (1986), the evolution of cloud droplet spectrum, together with chemistry in the droplets, was simulated explicitly. The simulated cloud droplet spectrum showed that the modal size increases during the mature stages of the cloud development, and that a bimodal spectrum develops during the dissipation stage of the cloud, presumably due to evaporation of cloud droplets. But throughout the evolution, the pH value of cloud droplets is a decreasing function of the cloud droplet size. The pH ranges between 3.5 and 5.3 for drops larger than about 20 μm in radius. For small particles in the sub-μm range the pH could be less than 2.

The effect of washout by rain in the content of unoxidized sulfur and sulfate in cloud was examined in Tremblay and Leighton (1984). These authors showed that during the evolution toward a steady state, there was almost a complete depletion of S(IV) in the cloud column within one hour of simulation. This occurred despite the continuous upward transport of SO_2 into the cloud from below the cloud base. There was a similar depletion of secondary sulfate produced in the cloud. During the early stage of chemistry evolution, sulfate formed in cloud and there was an increase in the total sulfate content in the cloud column. The sulfate was subsequently transferred to rain as a result of microphysical processes. As soon as precipitation began, the sulfur dioxide content was diminished. This led to less production of sulfate, and eventually to almost complete depletion of sulfate content in the cloud column as well. These results, although interesting, probably overestimated the effects of washout by rain. First of all, in this one-dimensional model, rain falls through cloud updraft in which pollutants from the boundary layer are transported upward. This tends to exaggerate the effect of washout, especially when the model is integrated to a steady state situation. Secondly, the pH values of rain simulated by the model were in a high range, which increases considerably the solubility of SO_2, which is taken in their model as corresponding to the equilibrium value; this was the result of the high initial mole ratio of NH_3 to SO_2 (~ 2). In a set of time-dependent simulations of a three dimensional cloud, Tremblay and Leighton (1986) showed that the wet deposition of sulfate by rain, although very significant, was only a fraction of the secondary sulfate produced in cloud.

Despite the complexity of the models used in these studies, comparison of model results with observations remains a difficult problem. Although some qualitative agreement has been reported between general model behaviour and observations (e.g., Walcek and Taylor, 1986), very few detailed, quantitative comparisons have

been made. Simulations using these models require as input the vertical profiles of chemical species and aerosol particles, and these measurements are difficult to obtain. The work by Tremblay and Leighton (1986) is one of the few studies in which observed vertical profiles were used as initial conditions of the model, and model results were compared quantitatively with observations. Their results show that the model significantly underpredicts the concentrations of ionic species in cloud water, sometimes by a factor as large as 6.2.

Rainbands in midlatitude cyclones are mesoscale precipitation systems which occur at temporal and spatial scales distinctly different from those of individual cumulus clouds. Modeling of these systems is difficult because of the incomplete understanding of their origin and dynamics. One interesting approach, used by Hegg et al. (1984), Rutledge et al. (1986), and Hegg et al. (1986), is to describe the dynamics of these systems by the kinematic flow fields deduced from observations. In Hegg et al. (1984), the sulfur chemistry of a warm frontal rainband was studied. The microphysics of the rainband was described by a bulk representation of cloud droplets, ice crystals, rain and snow. The cloud chemistry included oxidation of S(IV) by H_2O_2, scavenging of sulfate particles by nucleation, impaction and Brownian diffusion. Their results indicated that nucleation and impact scavenging, and aqueous oxidation of S(IV) contribute significantly to the net sulfate deposition, which is in general a nonlinear function of the initial amount of sulfur species. The predicted concentrations of sulfate in rain are in general accord with observations. However, in this study the concentration of H_2O_2 in solution was held constant so that the depletion of this oxidant was ignored.

In Rutledge et al. (1986) and Hegg et al. (1986), the chemistry in a narrow cold frontal rainband was studied. This type of rainband is of particular interest because of its relatively small width, strong updraft, and very intense precipitation, all in marked contrast to the warm frontal rainband studied by Hegg et al. (1984). The microphysics and chemistry models used were improved versions of their previous study (Hegg et al., 1984). The cloud physics model was extended to include graupel, and the cloud chemistry model was generalized to include both sulfur and nitrogen scavenging. The nitrogen chemistry was treated by dissolution of gaseous HNO_3 into liquid water without explicit consideration of oxidation of NO_x in the gaseous phase. The concentrations of S(IV) and H_2O_2 in ice phase, however, were ignored in their study. Their results showed that the effects of cloud microphysics and dynamics on the distribution of chemical species and wet depositions are comparable to those of chemical processes, and chemical reactions contribute to between 20% and 50% of the sulfate deposited. The different sulfate production mechanisms (e.g., oxidation by H_2O_2 and oxidation by O_3) may dominate at different heights, and such systems should not be treated as chemically homogeneous. The relationship between input chemical concentrations and the wet deposition of sulfate and nitrate is less than linear, and the sulfate and nitrate depositions are largely independent of one another. Although no quantitative comparisons were presented, the authors noted that their results were in reasonable agreement with observations.

Most of the studies discussed so far are based on chemistry conditions in non-urban environments. It is appropriate to include here a reference to the greatly increased complication that arises when considering highly polluted regions. An appropriate comprehensive study relevant to this subject has been given by Graedel and Goldberg (1983). They have considered the chemical processes taking place in raindrops while falling through various urban or suburban polluted environments. The model included both inorganic and organic processes, totalling 94 reactions in 53 species. They conclude that photochemical processes and many of the produced radicals are important in these conditions, that many organic reactions occur—oxidation of aldehydes to acids being particularly important—that the composition in drops depends on drop size and altitude and that given initial conditions, the ion concentrations in water increase as the rain rate decreases.

In each of the investigations just mentioned, which are summarized (with the exception of Graedel and Goldberg, 1983) in Table 2 for reference, an effort was made to elucidate the main factors affecting the chemical processes in clouds. The degree of elaboration of the cloud

Table 2. *Cloud chemistry models*

Reference	Type of cloud	Dimensionality	Hydrometeor phases	Acidity precursors	Oxidants in aqueous phase
Hong and Carmichael, 1983	time-dependent flow-through reactor	0	water	SO_2	H_2O_2, O_3, O_2 (catal.)
Seigneur and Saxena, 1984	time-dependent box model	0	water	SO_2, NO, NO_2	H_2O_2, O_3, O_2 (catal.)
Hegg et al., 1984	warm-frontal rainbands	2	water, ice	SO_2	H_2O_2
Tremblay and Leighton, 1984	steady updraft column	1	water	SO_2	H_2O_2, O_3, O_2
Tremblay and Leighton, 1986	time-dependent convective cloud	3	water	SO_2	H_2O_2, O_3
Rutledge et al., 1986; Hegg et al., 1986	narrow cold-frontal rainbands	2	water, ice	SO_2	H_2O_2, O_3
Walcek and Taylor, 1986	steady state entraining cumulus	1	water	SO_2	H_2O_2, O_3, O_2 (catal.), MHP, PAA
I-Y. Lee, 1986	time-dependent cumulus, with entrainment	1	water	SO_2	H_2O_2, O_3
Niewiadomski et al., 1986	time-dependent 2-stream cumulus with entrainment	1	water, ice	SO_2, NO, NO_2	H_2O_2, O_3, radicals
Kavassalis et al., 1986	time-dependent front	2	water, ice	SO_2, NO, NO_2	H_2O_2, O_3, radicals
Carmichael et al., 1986	time-dependent unspecified type, part of a LRT model	1, 2	water	SO_2	H_2O_2, O_3, OH
Venkatram and Karamchandani, 1986	stratiform and convective, part of a LRT model	1	water, ice	SO_2	O_3, O_2 (catal.), peroxides
Chang et al., 1987	box model, part of a LRT model	0	water	SO_2	O_3, O_2 (catal.), peroxides
Cho et al., 1987	stratiform, part of a LRT model	3	water, ice	SO_2, NO, NO_2	H_2O_2, O_3

models ranges from the simple box model to a three-dimensional model. The simplest models allow an estimate of the relative importance of various chemical processes; the more elaborate ones give also indication of the importance of various meteorological parameters and dynamic and microphysical processes. Most of the papers have focused attention on SO_2 as an acidic precursor and on sulfate production; only some have also considered the contribution of NO_x. There is a general consensus that H_2O_2 is predominant in SO_2 oxidation, and the non-linearity of the relation between SO_2 input and sulfate deposition has been repeatedly mentioned. The number of independent chemical variables utilized in a model depends on both the microphysical variables and on the chemical species included; the complexity of the chemical computations is thus a compound of both the complexity of the microphysics and that of the chemical description. For instance, to follow the evolution of just one chemical species, say $SO_4^=$, its concentration in each one of the hydrometeors included has to be followed separately (cf. Rutledge et al., 1986). Some simplifications can here be introduced; variations in O_3 concentration can be ignored, concentrations of $S(IV)$ and H_2O_2 in solid particles is usually neglected (except in Niewiandomski et al., 1986 and Kavassalis et al., 1986), HNO_3 adsorbed on ice

surface has only been taken into account by Rutledge et al. (1986), etc. Separated calculation of acidity (pH) has been included only by some of the authors. The results of some of the models have been compared, within limited possibilities, with field observations, with reasonable agreements claimed in most cases.

Recently, there have been a number of major efforts in developing models of long-range transport (LRT) of air pollutants (Carmichael and Peters, 1984; Venkatran and Karamchandani, 1986; Chang et al., 1987; and Cho et al., 1987). In addition to pollutant emissions, transport and chemical reactions in free air, and dry deposition, clouds and the processes taking place in them are important components of such a model. Most of the cloud models used in the present versions of these LRT models are fairly simple and crude, partly because of the intrinsic difficulties in modeling clouds in the context of atmospheric dynamics over a spatial scale of the order 1000 km.

Carmichael and Peters (1984) developed an Eulerian LRT model for the transport and chemistry of SO_2 and sulfate. Oxidation of SO_2 in clouds is taken into account by a kinetic equation including oxidation by O_3 and by O_2, catalyzed and uncatalyzed, but not the oxidation by H_2O_2. The model is claimed to permit the parametric study of competing atmospheric processes by simulating sulfur transport. It was applied to the eastern United States, showing the influence of various factors (meteorological conditions, eddy diffusivity, dry deposition velocities) on the resulting distributions, and the need of a detailed vertical resolution. The model was further developed by Carmichael et al. (1986) to include the irreversible scavenging of aerosol, the interaction between aerosol and gas phase NH_3, HNO_3 and H_2SO_4, as well as the oxidation in aqueous phase by H_2O_2, O_3 and OH.

In the long range transport model (ADOM: Acidic Deposition and Oxidant Model) developed by Venkatram and Karamchandani (1986) (see also Venkatram et al., 1987), the treatment of cloud chemistry includes 25 reactions among 13 species, including the oxidation of *S*(IV) by O_2, O_3 and hydrogen peroxide, and incorporates a fairly complete treatment of mass transfer between air and water. The stratiform clouds are simulated by a one-dimensional steady state model, applying a parameterization of microphysics according to Kessler (1969). The microphysics for cumulus cloud models is based on the parameterization by Scott (1978). The treatment of wet scavenging is considered by the authors as the least satisfactory component of their LRT model, and considerable improvement is needed.

Chang et al. (1987) (see also Chang, 1983, 1985, 1986) have developed a three-dimensional Eulerian acid deposition model (RADM: Regional Acid Deposition Model) including gas phase chemistry, dry deposition and cloud chemistry. Cloud chemistry is studied using a one-dimensional dynamical and microphysical cloud model and a box aqueous chemistry and scavenging submodel, which calculates time-dependent chemical composition of cloud water and rainwater. In a preliminary formulation, SO_2 is oxidized by H_2O_2, O_3, methylhydroperoxide, peroxyacetic acid and by the O_2 oxidation catalyzed by Fe^{3+} and Mn^{2+}. All meteorological and chemical parameters are averaged over the vertical depth of the cloud and provided as initial conditions to an aqueous chemistry model. The cloud water composition is computed using the chemical model described by Walcek and Taylor (1986).

Cho et al. (1987) have reported the development of an Eulerian LRT model which includes a comprehensive treatment of clouds and cloud chemistry. The model, however, does not yet include the gas phase chemistry which is important in the study of long-range transport of air pollutants.

6. Conclusions

Although much work has been done during the last years in the field of modeling cloud chemistry, further development is still necessary. The modeling efforts must of course be adapted to the aim and scope of the application. For example, much more detail can be included in a study of a particular process than in a model destined to be used in LRT. This is particularly true for the microphysics description. Microphysical processes have received much attention during the past several decades, and the uncertainties

regarding such details as shape of crystals, etc., lie in the great variability of these parameters in the natural systems and the computational complexity that would result if such variabilities were to be included in the models.

The situation is rather different regarding chemistry. Truly, obtainig fairly complete information about the parameters which is necessary for an application of the model (such as concentrations in the air of the various relevant gases) must require considerable effort in any field experiment. But at the same time, the basic parameters regarding the chemical reactions (rate constants, dependency on temperature, accommodation coefficients, etc.) have large uncertainties in their values, which will reflect on the results. It is also possible that new reactions or processes (e.g., reactions of previously ignored compounds, adsorption, heterogeneous reactions) will be shown in the future to be too important to be neglected. In these aspects, future progress relies largely on laboratory studies.

Finally, even when a model appears elaborate and complete enough for its purpose, and up to date in scientific information, the critical task of verification against field data remains to be performed. A great deal of work will have to be done in this field, for instance, before cloud chemistry is introduced in a satisfactory operational model for the LRT of pollutants.

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