A THREE DIMENSIONAL CLOUD CHEMISTRY MODEL

by

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ABSTRACT

A cloud chemistry model is formulated in term of continuity equations for chemical species in the aqueous and gas phases within the cloud. The model includes scavenging of SO_2 , HNO_3 , NH_3 , H_2O_2 , and sulphate aerosol particles. Calculations have been performed within the framework of a three-dimensional convective cloud model. The results are compared with aircraft measurements of cloud water chemistry.

Our simulations show that small cumuli are able to vent the boundary layer at a rate of the order of a few percent per hour, and that most of the sulphate and nitrate deposited at the surface by rain is generated by in-cloud processes. Oxidation of SO_2 by H_2O_2 is significant in the simulated clouds, and strongly influences the sulphate mass budget and acidity of the cloud and rainwater.

RESUME

Un modèle de chimie des nuages est formulé au moyen d'équations de conservation pour les diverses espèces chimiques présentes dans les phases aqueuses et gazeuses. Ce modèle inclut le lessivage des gaz SO_2 , HNO_3 , NH_3 et H_2O_2 , ainsi que des particules de sulfate. Des calculs sont effectués dans le contexte d'un modèle tri-dimensionnel de la convection atmosphérique, et les résultats sont comparés avec des données expérimentales.

Nos simulations montrent que les petits cumulus ventilent la couche limite atmosphérique à un taux n'excédant pas quelques pourcents à l'heure, et que la majeure partie des sulfates et nitrates déposés à la surface par la précipitation est générée à l'intérieur des nuages. De plus, il a été confirmé que la réaction du dioxyde de soufre avec le peroxyde d'hydrogène affecte fortement le budget de masse des sulfates ainsi que l'acidité des nuages et de la précipitation.

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PREFACE

To analyse and interpret data collected in cloud chemistry field experiments and to estimate the importance of clouds in the transport of pollutants in the vertical, models of various complexity and scope are required. Specifically, in view of the major role of cumulus clouds in the processes of transport and transformation of pollutants in the ambient atmosphere, a cloud chemistry model is introduced in this study. In order to be as mechanistic as possible and to reduce the number of processes that need to be parameterized, a fully three dimensional numerical model is formulated. This model is able to incorporate some of the data from field measurements and some of its output can be compared with aircraft cloud water samples. The author considers these aspects of the thesis to be original contributions to knowledge.

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Chapter 1

INTRODUCTION

1.1 Overview

During the past few decades, there has been an increasing concern about the effects of man's activities on the environment. The rate at which modern society consumes fossil fuels for energy generation is likely to have some important long term consequences on the global environmental quality. Attention was first drawn to the problem of transboundary air pollution when Scandinavian scientists reported in 1972 the so-called "acid rain" phenomenon. It has been realized that atmospheric dilution not only fails to solve industrial waste problems, but also that the receiving aquatic ecosystems are strongly affected by the transport and deposition of pollutants. Since the early 1970's acid deposition has become recognized in North America as a consequence of the numerous atmospheric sources of sulphur and nitrogen oxides, all dependent on atmospheric dilution to resolve the gaseous residual problems.

Introduction of various acidic species including SO_2 and NO_x from combustion and other sources, has resulted in the acidification of precipitation in both Europe and United States (Galloway et al., 1982). Increasing amounts of strong, inorganic acids, primarily sulphuric and nitric acids, have appeared in precipitation falling over wide areas surrounding industrial regions of the world (Likens and Bormann, 1974). Analysis of precipitation samples in both Northern Europe and North

Eastern America has revealed a steady increase in the hydrogen ion concentration of rain since the mid-1950's (Likens, 1976). An individual storm with a pH as low as 2.1 has even been recorded in the north eastern part of the United States (Likens and Bormann, 1974).

Released during the combustion of fossil fuels, sulphur and nitrogen oxides are further oxidized in the atmosphere to sulphuric and nitric acids (homogeneous oxidation). A number of oxidation mechanisms are known (Calvert and Stockwell, 1984), and characteristic reactions times vary from hours to days. Many reactions pathways are quite slow and only significant in long range transport.

1.2 Aqueous Chemistry

Once produced, these acids may either be incorporated in the atmospheric hydrometeors and eventually fall to the surface with precipitation (wet deposition), or come directly in contact with the surrounding landscape (dry deposition). An alternative to this is the direct dissolution of sulphur and nitrogen oxides followed by aqueous-phase oxidation (heterogeneous oxidation), to form high oxidation state acids found in cloud water and precipitation. It is generally believed that for representative NO_x partial pressures, direct reactions to form HNO_3 in atmospheric liquid water are too slow to be of importance (Lee and Schwartz, 1981). The exact mechanism for oxidation of sulphur dioxide in aqueous solution is still a matter of discussion. The most widely accepted mechanisms are: (1) uncatalyzed oxidation by O_2 ; (2)

uncatalyzed oxidation by strong oxidizing agents and (3) oxidation in the presence of catalysts. It is well established that (1) is unimportant in the atmosphere (Beilke et al., 1978), but (2) and (3) both remain potentially important pathways for sulphate production in atmospheric liquid water (Schwartz, 1984; Hoffmann and Jacob, 1984). In particular, the oxidation of SO_2 by dissolved H_2O_2 could be an important reaction in the atmosphere, even at low pH's encountered in polluted situations (Penkett et al., 1979). However, extensive measurements of H_2O_2 concentrations in clean and polluted air masses still remain to be made before the importance of this reaction can be adequately evaluated.

1.3 Cloud Transport

Clouds are not only important from the point of view of the chemical transformations occurring within their liquid phase, but also air motions associated with their evolution are likely to redistribute the pollutants in the vertical. The cloud transport effects may be classified in three categories: (1) the detrainment of the cloud air into the cloud environment at upper levels, which acts as an apparent source of pollutants, since cloud air mainly originates from lower levels where pollutant concentrations are higher; (2) the downward transport of cleaner air from the upper levels to lower levels by compensating subsidence in the cloud environment; and (3) the recycling of air by clouds which can result in a column of air at the end of the cloud's life cycle that has a different concentration than the surrounding air. Processes (1) and (3) could have important effects on long range transport since they

transport the pollutants confined in the lower part of the atmosphere to upper levels where horizontal advection occurs at a higher rate. Experimental evidence of cloud vertical transport has been established by Isaac et al. (1982), who found from aircraft observations that the local concentration of SO_2 within clouds was significantly higher than in the cloud-free environment. Even if they are relatively simple to conceptualize, cloud transport processes are virtually ignored in the present generation of air quality models. One of the main reasons for this neglect is the high complexity of cloud dynamical processes, which make them difficult to be included in a parameterized form in numerical models. Several parameterized descriptions of these processes have been recently introduced (Cho et al., 1984; Gidel, 1983) and are currently being incorporated in long range transports models (Hong and Carmichael, 1985).

1.4 Scavenging Models

Even if field measurements provide help in improving our understanding of cloud chemical and transport mechanisms, it becomes increasingly clear that a reliable method is needed to estimate their temporal and spatial variations. A useful tool for simulating these processes is through a suitable mathematical model based on pertinent chemical and physical theories. Such a model can be designed to account for the transport and chemical transformations occurring within clouds and provide a test bed to verify hypotheses developed from laboratory

investigations and facilitate comparisons with field measurements.

Many researchers have conducted investigations using cloud chemistry, washout and scavenging models to estimate the effects of atmospheric pollutants on the chemical composition of cloud and raindrops. In general these models can be conveniently classified as : (1) aqueous chemistry models with conceptual or non-existent cloud processes; (2) below-cloud scavenging models; (3) kinematic cloud chemistry/scavenging models; (4) aerosol scavenging models; and (5) cumulus cloud microphysics/chemistry numerical models. It is in this last area that this thesis seeks to make a contribution.

(1) Aqueous Chemistry Models

Based on the experimental work of Junge and Ryan (1958), which showed that the essential features of the formation of sulphate in the atmosphere could be explained by the reaction of SO_2 and NH_3 in cloud and fog droplets, Scott and Hobbs (1967), developed a chemical model for the production of sulphate in liquid water. Their study was based on the assumption that sulphur dioxide, ammonia and carbon dioxide were in equilibrium in the liquid and gas phases. The oxidation rate of SO_2 to SO_4 was estimated from the experimental results of Van den Heuvel and Mason (1963), and the theory was found to be in qualitative agreement with the experimental results of Junge and Ryan. The Scott-Hobbs mechanism has been applied to clouds with a number of variations, involving

consideration of gas-phase depletion of reagents, a different oxidation rate of aqueous SO_2 and incorporation of sulphate aerosol into the cloud water (McKay, 1971; Miller and de Pena, 1972; and Barrie et al., 1974). These models are purely chemical models, since they ignore cloud dynamical and microphysical processes. Equivalent assumptions, regarding cloud processes have been used by Chameides and Davis (1982, 1983) and by Schwartz (1985) to study the free radical chemistry in liquid water clouds, and by Otha et al., (1981) to examine cloud water acidification over Japan.

(2) Below Cloud Scavenging Models

The washout of atmospheric gases by rain has been the subject of a number of investigations. In these studies, it is assumed that the chemical composition of a raindrop population, initially situated at a given location is known. The change in the concentration of the dissolved gas is calculated along the raindrop trajectory for each dropsize from appropriate mass transfer equations (Hales, 1972), and the air concentration of gases generally follows some specified scheme (e.g the Pasquill-Gilford bivariate normal distribution). The mathematical formulation leads to a set of non-linear first order differential equations which are numerically solved to obtain the values of dissolved species concentrations as a function of fall distance. This procedure has been shown to compare favorably with washout measurements (Dana et al., 1975) and was used by Hales et al. (1975) and by Barrie (1978) (with some modification to take into account the effects of internal drop

circulation) to study the non-reactive rain scavenging of sulphur dioxide, and by Lee and Hales (1975) to investigate the washout of organic contaminants. Hill and Adamowicz (1977), Adamowicz (1979), Overton and Aneja (1979) and Drewes and Hales (1982, 1983) also applied this scheme to study the scavenging of a mixture of gases and the production of sulphate in raindrops. It was found that the time scale of the half life of atmospheric SO_2 removal by precipitation may range from hours to days depending upon pH, rainfall rate and mixed layer height.

(3) Kinematic Models

The interactions between storm systems and air pollutants have been studied within the framework of one dimensional steady updraft columns, both analytically (Fisher, 1982) and numerically (Hales, 1982; Tremblay and Leighton, 1984). These studies are based upon sets of continuity equations, appropriate for the specification of pollution distribution within rain systems, and involve parameterized descriptions of cloud and precipitation chemistry, and the microphysical interactions between aerosols and water droplets. They were aimed at determining the efficiency of removal of SO_2 by storms, sulphate wet deposition characteristics, sulphate budget, vertical distribution of chemical concentration within the cloud and rainwater, and sensitivity of these parameters to the aqueous SO_2 oxidation mechanisms. For example, Fisher (1982) found that the overall fraction of SO_2 removed by the storm is a strong function of the oxidation rate of aqueous SO_2 and the acidity of cloud and rainwater. The results of Tremblay and Leighton (1984) indicate

that the acidity of the rainfall reaching the ground is sensitive to oxidation rate and to the presence of ammonia. However, it would not be justified to draw general conclusions from these studies, due to the simple and somewhat unrealistic dynamics considered. A similar formulation has also been adopted by Hegg et al. (1984) to study the sulphur chemistry in warm frontal rainbands within the framework of a two dimensional kinematic model of warm frontal precipitation (Rutledge and Hobbs, 1983). It was found that nucleation scavenging, aqueous oxidation of SO_2 and washout of sulphate particles, all contribute significantly to wet sulphate deposition with nucleation scavenging generally the most important process.

^T
Easter and Hobbs (1974) used the mechanism proposed by Scott and Hobbs to study the aqueous phase oxidation of sulphur dioxide by molecular oxygen in the presence of ammonia. In this work they consider a parcel containing fixed amounts of sulphur dioxide, carbon dioxide and ammonia, and the chemical reactions were allowed to take place in growing and evaporating cloud droplets. This framework has been used with a hypothetical air motion field to simulate the relatively simple wave cloud situation, and it was found that a significant increase in the concentration of cloud condensation nuclei can be produced by SO_2 oxidation within the clouds (see also Hegg and Hobbs, 1979; 1981) with subsequent cloud evaporation.

(4) Aerosol Scavenging Models

The study of aerosol scavenging was started in the early 1950's as a consequence of the beginning of the nuclear era. Today, an additional interest lies in the potential role of atmospheric particles on the chemical composition of cloud and precipitation. Pioneering investigations in this area were performed by Chamberlain (1953) who introduced the washout coefficient approach to scavenging modelling. The work of Greenfield (1957) seems particularly important in improving our understanding of the scavenging of particulates. Based on the theory of Brownian diffusion, inertial impaction and turbulence, he found that there exists a gap in the aerosol radius distribution, ranging from about $0.1 \mu\text{m}$ to $1.0 \mu\text{m}$, in which neither aerodynamics impaction nor Brownian capture can remove particles with appreciable efficiency. Later investigations by Slinn and Hales (1971), Pilat and Prem (1976) and Wang and Pruppacher (1977) yielded to the same conclusion. McDonald (1964) first pointed out that soluble particulates are removed from the gap region via cloud-nucleation, providing a bridging mechanism. In the light of the works of Dingle and Lee (1973), Slinn (1974) and more recently Flossmann et al. (1985), the removal of atmospheric particles by clouds may be regarded as a process where all scavenging mechanisms, especially nucleation, transfer the aerosol particles to the cloud water, followed by the capture of the cloud droplets by the relatively large precipitating hydrometeors; this later mechanism being the rate limiting stage of the overall process (Slinn, 1974).

Several aerosol scavenging models have been developed. For example, Molenkamp (1974) utilized the one dimensional time dependant cumulus cloud model of Wisner et al. (1972) as a framework to do scavenging calculations. He considered that the aerosol was incorporated in the cloud water by nucleation, and conversion of cloud droplets into raindrops accounted for the incorporation of pollutants into falling rain. Dingle and Lee (1974) used a trajectory method and prescribed air velocity fields, to infer the concentration of pollutant observed in the rainfall. To help in the interpretation of experimental measurements (Hales and Dana, 1979), Hane (1978) used a two dimensional time dependant squall line model (Hane, 1974) to simulate the interaction between the St. Louis (USA) urban plume and storms. He found that the trends and order of magnitude of the wet deposition compared favourably with observations. More recently, Chaumerliac et al. (1983) apply a three-dimensional numerical mesoscale model including orographically forced clouds, and precipitation to the aerosol scavenging problem. They found that vertical profiles of aerosol concentration are strongly affected by precipitation scavenging.

(5) Cumulus Cloud Microphysics/Chemistry Numerical Models

Only few studies have been published that include chemistry as part of numerical cloud models. Sarma (1983) modified the two dimensional cloud model of Orville (1965) to investigate the transport of sulphur dioxide in convective clouds and its subsequent oxidation to sulphate in the aqueous phase. He found that the acidity of cloud water is a

function of its location within the cloud and that the rain from a cloud close to a ground level source of SO_2 representative of emissions from a large coal-fired power plant, was 2.5 times more acidic than the rain from a cloud away from the source. To examine the time history of cloud water pH and sulphate production in a cumulus cloud, Lee and Shannon (1985) coupled a cloud chemistry model (Otha et al. 1981) and a one dimensional cloud model (Asai and Kasahara, 1967). Their calculations have also shown that the acidity of the cloud water is a strong function of the location and time.

Niewiadomski (1984) used Clark's (1977) cloud model to study the vertical transport of a passive pollutant by a field of cumulus clouds. His simulations were performed with a domain size comparable with one cell of an Eulerian long range transport model, and he found that the pollutant concentration within clouds was typical of the value found in the boundary layer, suggesting that cumuli are relatively effective in venting the polluted mixed layer.

1.5 The Present Model

From the above considerations, it is apparent that most of the previous cloud chemistry/transport/scavenging models either consider detailed chemical and microphysical processes, but over-simplified cloud dynamics, or more complex cloud dynamical framework but with only chemically inert pollutants. To fill this gap, and to gain insight into some of the questions regarding the transport and transformation processes

In cumulus clouds, and to help in the interpretation of field measurements, a three dimensional cumulus cloud transport/chemistry model has been developed. Calculations are based on continuity equations for chemical species in the gaseous and aqueous phases within clouds and, ideally the model is initialized with data obtained from field measurements. In its present version the model includes sulphur dioxide, nitric acid vapour, hydrogen peroxide, ammonia and sulphate aerosol.

This model uses as input the output of a three dimensional convective cloud model (Yau, 1980), which provides as functions of time and location, fields of three dimensional air velocity, turbulence, water substance and pertinent microphysical parameters. Results of the cloud chemistry model are the three dimensional distributions of the chemical species, their wet deposition and detailed description of their budgets.

Simulations are discussed for a case where some measurements of the chemistry of the cloud water and ambient air are available, and comparisons between simulated and measured concentrations of some ions are presented. Specifically, our simulations indicate that small cumulus clouds could vent the boundary layer at a rate of the order of few percents per hour. It is also shown that 60-70% of the sulphate and nitrate deposited at the surface in rain is generated by in-cloud processes, and that both nucleation and oxidation by H_2O_2 may strongly influence the sulphate budget and acidity of the cloud and rainwater.

In presence of few ppbv of H_2O_2 , it has also been found that small non-precipitating cumuli could process SO_2 in their aqueous phase at a rate of $8\% \text{ h}^{-1}$, emphasizing the potential importance of this oxidation pathway.

Chapter 2

A MODEL FOR CLOUD CHEMICAL PROCESSES AND SCAVENGING

Physical and chemical processes within clouds are in general extremely complex and occur on a wide variety of scales. Cloud microphysics and chemistry deal with particles and water droplets ranging in dimensions from micrometers to millimeters, while air motion related to cloud evolution ranges from the scale of turbulent eddies to mesoscale features.

On the small scale, soluble aerosols may be activated as condensation nuclei, grow by diffusion, stochastic collection, and breakup. The chemical content of the aerosols will be carried along as the water substance is transformed from one category of hydrometeor to another. Partial evaporation will increase the concentration in the hydrometeors, but total evaporation will return the aerosol to the atmosphere. Simultaneously, a variety of chemical reactions occur in both the gaseous and aqueous phases which may involve a large number of reactants. Mass transfer of atmospheric trace gases to the cloud and precipitation also takes place, all these processes spanning a large range of time scales. These mechanisms depend on the physical and chemical properties of the local atmosphere and the distribution of pollutants in atmospheric hydrometeors is a function of drop size, spacial location within the cloud and time. This function is not necessarily single-valued with respect to drop size since drops of the same dimension found in a given neighbourhood may have had different histories.

On a larger scale, pollutants are transported by the turbulent air motion in and around clouds, leading to substantial redistribution of mass.

Even if an adequate description of all the processes pertinent to cloud - pollutant interactions were available, it would not be feasible to include them in detail in a three dimensional cloud chemistry model because such a model would tax the capacity of even the largest and fastest computers available. Therefore, simplifications must be made in the formulation of a cloud chemistry model that are consistent with the goal of the study. ^a

For simplicity, and for consistency with the resolution of aircraft sampling of air chemistry and cloud microphysics parameters, equations used here to model the evolution of pollutants within and around clouds are averaged over an appropriate geometric volume. Thus, we are interested in the calculation of the average physical and chemical properties and the average pollutant concentrations within elementary volumes of this size. Processes occurring on smaller scales are parameterized in term of these average properties and will be described in this chapter. This procedure, common in numerical cloud modelling, is often referred in the literature as "bulk parameterization" and has been shown to simulate atmospheric convection with a fair degree of realism (e.g., Turpeinen and Yau, 1981).

Due to the sparsity of data regarding the influence of the ice phase on in-cloud chemistry, we restrict our analysis to warm clouds. Also, as atmospheric pollutants are not likely to influence the cloud dynamics, we assume that the cloud dynamics and cloud chemistry are uncoupled. This

introduces an important simplification, since cloud properties and air motion are calculated independently of the chemistry.

2.1 Continuity equations

Our objective is to study how atmospheric trace pollutants interact with clouds. This is done by formulating and solving continuity equations for pollutants in the gaseous and liquid phases within the storm. Such equations are obtained using the traditional procedure of expressing the rate of gain of material in an arbitrary volume of space in terms of the divergence of this material and the contributions of source-sink terms. By denoting $Q_{1,a}$, $Q_{1,c}$ and $Q_{1,r}$ as the molar densities of pollutant species 1 associated with air, cloud water and precipitation water, respectively, the local change of each within a precipitating cloud is given by:

$$\frac{\partial}{\partial t} Q_{1,a} = - \nabla \cdot Q_{1,a} \mathbf{V} + \nabla \cdot v_h \nabla Q_{1,a} + S_{1,a} \quad (2.1)$$

$$\frac{\partial}{\partial t} Q_{1,c} = - \nabla \cdot Q_{1,c} \mathbf{V} + \nabla \cdot v_h \nabla Q_{1,c} + S_{1,c} \quad (2.2)$$

$$\frac{\partial}{\partial t} Q_{1,r} = - \nabla \cdot Q_{1,r} \mathbf{V} + \delta \nabla \cdot v_h \nabla Q_{1,r} + \frac{\partial}{\partial z} Q_{1,r} V_F + S_{1,r} \quad (2.3)$$

Here we follow a procedure first suggested by Kessler (1969) and assume partition of all liquid water substance into cloud and precipitation. The former is assumed to fully share air motion and the latter to fall with a single effective velocity which depends only on the rain water content and altitude.

In the above equations, V represents the three dimensional wind velocity, V_f the fallspeed of $Q_{i,r}$ relative to the moving air, v_h an eddy diffusivity coefficient and $S_{i,a}$, $S_{i,c}$ and $S_{i,r}$ the microphysical and chemical processes which act as sources and sinks; they are illustrated schematically in figure 2.1 and will be discussed subsequently in the text. The symbol δ is a flag ($\delta = 0$ or 1) which allows one to turn off the diffusion of rain.

Fig. 2.1. Schematic of microphysical and chemical processes.

2.2 Cloud and precipitation chemistry

There is no doubt that the liquid phase chemistry of atmospheric aerosols is complex. An important process in cloud and precipitation chemistry is the dissolution of soluble atmospheric trace gases in cloud and rainwater. Table 2.1, taken from Graedel and Weschler (1981), gives typical concentrations of various gaseous species of importance and their dissolved counterpart within atmospheric liquid water. From this table, we see that molecular oxygen is predominant in solution followed by nitric acid and carbon dioxide. The next most abundant species of chemical interest are hydrogen peroxide, ammonia, hydrochloric acid and sulphur dioxide. With the exception of ozone, the concentrations and reactivities of the other species suggest that they are not of chemical importance in aqueous atmospheric aerosols and raindrops (Graedel and Weschler, 1981). It is well known that oxygen, ozone and hydrogen peroxide are active oxidizing agents and sulphur dioxide is an active reducing agent. Carbon dioxide, nitric acid, ammonia and hydrochloric acid influence the pH and indirectly the chemistry of the solution.

Another important process influencing the chemistry of cloud and raindrops is the scavenging of aerosol particles. Since the work of Junge (1954, 1963), sulphur has been recognized as an important constituent of the atmospheric aerosol. In these studies, it has been found that sulphur is predominant in submicron sized aerosols and that NH_4^+ and SO_4^{2-} coexist in these particles as a mixture of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . In their review of the chemical properties of tropospheric sulphur aerosols, Charlson et al. (1978) state that the chemistry of the accumulation mode

Species	Urban			Rural		
	Gas Concentration, ppb	Reference	Aqueous Concentration, M	Gas Concentration, ppb	Reference	Aqueous Concentration, M
O ₂	2 × 10 ⁸		3 × 10 ⁻⁴	2 × 10 ⁸		3 × 10 ⁻⁴
O ₃	70	1	2 × 10 ⁻¹³	30	1	9 × 10 ⁻¹²
H ₂	2 × 10 ³	1	2 × 10 ⁻⁹	600	1	5 × 10 ⁻¹¹
H ₂ O ₂	20	2, 3	3 × 10 ⁻⁶	1	4, 5	3 × 10 ⁻⁷
CO	8 × 10 ³	1	7 × 10 ⁻⁹	120	1	1 × 10 ⁻¹⁰
CO ₂	5 × 10 ⁶	6	2 × 10 ⁻⁵	3.3 × 10 ⁵	7	1 × 10 ⁻⁵
NO	10	1	2 × 10 ⁻¹¹	0.1	1	2 × 10 ⁻¹³
HNO ₃	1	1, 8	5 × 10 ⁻⁵	0.3	1, 8	1 × 10 ⁻⁶
NH ₃	25	1	2 × 10 ⁻⁶	1.5	1	1 × 10 ⁻⁷
H ₂ S	2	1	2 × 10 ⁻¹⁰	0.1	1	1 × 10 ⁻¹¹
CS ₂	0.15	9	3 × 10 ⁻¹²	0.04	9	9 × 10 ⁻¹³
OCS	0.6	10	1 × 10 ⁻¹¹	0.6	10	1 × 10 ⁻¹¹
SO ₂	50	1	7 × 10 ⁻⁸	1	1	2 × 10 ⁻⁹
HCl	6	1	1 × 10 ⁻⁷	0.7	1	1 × 10 ⁻⁸
HClO	6	11	5 × 10 ⁻⁸	0.2	11	2 × 10 ⁻⁹

References are to the gas phase concentration except for H₂O₂ and HNO₃, where references to both gas phase and aqueous phase concentrations are given: (1) Graedel [1980], (2) Kok et al. [1978], (3) Kok [1980], (4) Kelly et al. [1979], (5) Bufalini et al. [1979], (6) McRae and Graedel [1979], (7) Woodwell [1978], (8) Likens et al. [1979], (9) Maroulis and Bandy [1980], (10) Torres et al. [1980], (11) Platt et al. [1979].

Table 2.1. Typical concentration of selected gases in the atmosphere and in the aqueous phase of atmospheric aerosols. (After Graedel and Weschler, 1981)

aerosol in North Eastern United States can be described semi-quantitatively as a collection of particles composed of impure sulphate compounds ranging from H_2SO_4 to $(\text{NH}_4)_2\text{SO}_4$. Sulphate particles are generally hydrophilic and should be effective as cloud condensation nuclei. It has been argued by Scott (1978) that airborne sulphate aerosol could be responsible for nearly all of the cloud droplets appearing in continental clouds.

As an objective of this work is to model the spatial and temporal distributions of the concentration of pollutants within storms, it is imperative to have an adequate but simple representation of the chemistry of cloud and rain. A suitable parameterized description of chemical processes occurring within clouds should have the capability of forecasting the major chemical species of importance in clouds and should be capable of being used within the framework of a dynamical cloud model. A description of modelled chemical processes and reactions is given below.

(a) Sulphur Chemistry

Sulphur exists in the atmosphere in a number of different compounds and oxidation states. Insofar as cloud and precipitation chemistry is concerned, the most important sulphur species are sulphur dioxide (S(IV)) and sulphate (S(VI)); other sulphur compounds being only of marginal interest (see table 2.1). Sulphur dioxide exists in aqueous solutions as physically dissolved SO_2 , bisulphite (HSO_3^-) and sulphite (SO_3^{2-}). The equilibrium between gaseous SO_2 and total dissolved S(IV) is represented as:

Chemical transitions involving the conversion of aqueous SO_2 to sulphate in the atmosphere have received a considerable attention (for reviews see Beilke and Cravenhorst, 1978; Hegg and Hobbs, 1978; Moller, 1980; Seinfeld, 1980; Middleton *et al.*, 1980; Graedel and Weschler, 1981; Martin, 1984; Hoffmann and Jacob, 1984). It is currently believed that two important oxidation mechanisms of atmospheric S(IV) in clouds are oxidation by O_3 and H_2O_2 (Schwartz, 1984):

The kinetics of the reaction of S(IV) with O_3 has been experimentally studied by Erickson et al. (1977), Penkett et al. (1979) and Larson et al. (1979). From values given in Moller (1980), the rate of reaction (2.7) can be written as:

$$R_{O_3} = \frac{d}{dt} [S(VI)] = 1.78 \times 10^4 [H^+]^{-0.4} [O_3] [S(IV)] \quad (2.9)$$

Where the square brackets represent concentration and where $[S(IV)] = [SO_2(aq)] + [HSO_3^-] + [SO_3^{2-}]$ depends upon the pH.

The reaction of S(IV) with H_2O_2 has also been the subject of a number of investigations (Martin and Damschen, 1981; Penkett et al., 1979; Hoffmann and Edwards, 1975). According to Martin and Damschen (1981) the rate of reaction (2.8) is:

$$R_{H_2O_2} = \frac{d}{dt} [S(VI)] = 8 \times 10^4 [H_2O_2] [SO_2(aq)] (0.1 + [H^+])^{-1} \quad (2.10)$$

Here the units of R_{O_3} and of $R_{H_2O_2}$ are expressed in $M s^{-1}$. These reactions rates can also be referred to the gas-phase reagent Schwartz (1984):

$$\rho_{O_3} = R^* T Q_L (\rho_L)^{-1} R_{O_3} \quad (2.11)$$

And a similar expression can be written for H_2O_2 . Here ρ represents the gas phase depletion of O_3 or H_2O_2 ($ppb h^{-1}$), Q_L is the amount of water present per unit volume of space, R^* is the universal gas constant, T is the absolute temperature and ρ_L is the density of liquid water.

In figure 2.2, we display as functions of pH, the oxidation rates R_{O_3} and $R_{H_2O_2}$ per part per billion of SO_2 partial pressure (left ordinate) and on the right ordinate these rate referred to the gas phase per $g\ m^{-3}$ of liquid water content. The former quantities would scale linearly with SO_2 partial pressure and the latter with Q_L .

Examination of this figure shows the strong dependance upon pH of the reaction of S(IV) with ozone. This reflects the variation of [S(IV)] with pH (this matter will be discussed subsequently in the text) as well as the explicit dependance of R_{O_3} on $[H^+]$. It is also apparent that this rate becomes quite important for pH ≥ 6 ($\rho = 10\% h^{-1}$; $R = 4 \times 10^{-5} M h^{-1}$) and negligible for pH ≤ 5 (on the time scale of convective cloud life times). An important consequence of this is that the reaction of S(IV) with O_3 is strongly self limiting due to the production of aqueous H_2SO_4 , unless the acid is neutralized by a continuous supply of an alkaline material. Thus, it is rather unlikely that oxidation by ozone alone could produce solution droplets with a low pH. We also see from this figure that the oxidation rate of S(IV) with H_2O_2 is quite high ($\rho = 800\% h^{-1}$; $R = 2.5 \times 10^{-4} M h^{-1}$) and independent of the pH of the solution. Consequently, oxidation by H_2O_2 remains important for sulphate production even if the solution becomes acidified during the reaction.

The catalysed oxidation of S(IV) by the transitions metal ions Mn (III), Fe(III) and Co(II) can be potentially important in heavily polluted atmospheric droplets (Hoffmann and Jacob, 1984) but the distribution of these catalysts in aqueous particles and droplets is unknown and likely to be small in moderately polluted or remote air masses. The catalysed

Fig. 2.2. Rate of oxidation of $S(IV)$ by ozone and hydrogen peroxide as a function of the pH. Gas-aqueous equilibrium assumed for all reagents. Temperature = 25 C.

oxidation of S(IV) by Cu(II), V(IV), V(V), Ni(II), Zn(II) or Pb(II) is too slow for any of these reactions to be effective (Brock and Durham, 1984).

It has also been proposed by Chameides and Davis (1982, 1983) that oxidizing free radicals may be scavenged by aqueous particles and react directly with S(IV) and other species to acidify the solution. This oxidation mechanism requires a knowledge of the distribution of free radicals, data which is not easily available from atmospheric measurements, and an understanding of the scavenging processes of free radicals by water droplets which has yet to be experimentally investigated.

Another potentially important transformation mechanism for S(IV) is oxidation by nitrogen dioxide. NO_2 is moderately soluble in water (Schwartz, 1980) and is known as a fairly strong oxidizing agent. A number of studies indicate a possible significant reaction (Nash, 1979; Lee and Schwartz, 1982) but the details of the stoichiometry and the pH dependence of the rate remain unknown.

(b) Nitrogen Chemistry

Nitrogen occurs principally in cloud and precipitation water as nitrate and ammonium ions which, with hydrogen and sulphate ions characterize the inorganic chemistry of cloud and precipitation in north eastern America (Semonin and Bowersox, 1982). Although nitrate may be present in atmospheric aerosols as sodium nitrate or potassium nitrate (Graedel and Weschler, 1981) it is thought that most NO_3^- in rainwater arises from the direct dissolution of gaseous HNO_3 in cloud and raindrops (Altwicker, 1982), i.e.:

Reaction of dissolved nitrogen oxides (NO_x) has been thought to be an important mechanism for the formation of HNO_3 in cloud and rainwater (Martin et al., 1981). However, it has been found that for representative NO_x partial pressures, direct reactions to form HNO_3 in atmospheric liquid water are too slow to be of importance (Lee and Schwartz, 1981; Schwartz, 1984).

Ammonium salts are very common in atmospheric aerosols and the scavenging of these particles by water droplets may constitute a source of ammonium ions found in atmospheric liquid water. Another source of NH_4^+ in atmospheric water droplets is the dissolution of NH_3 :

Ammonia is the most important alkaline compound commonly found in the atmosphere and its influence on the pH of the aqueous aerosol may be critical.

(c) Carbon Dioxide, Ozone, Hydrogen Peroxide and Water

Carbon dioxide is the most concentrated natural trace substance in the air of significance to the chemistry of cloud and precipitation (Junge, 1963). It dissolves readily in water to form carbonic acid, which is in equilibrium with both the bicarbonata and carbonate ions:

At atmospheric concentration, CO_2 establishes equilibrium with pure water at a pH of about 5.6.

The role of ozone and hydrogen peroxide as oxidizing agents for S(IV) have already been discussed above. These substances establish an equilibrium between their aqueous and gaseous phases:

Although there is experimental evidence for H_2O_2 production within the aqueous phase (Heikes et al., 1982), precursor species, aqueous intermediates and mechanisms remain to be identified. Theoretical calculations of Chameides and Davis (1982) show that sulphate production

due to aqueous phase synthesis of H_2O_2 within cloud water is typically one order of magnitude less than for the direct dissolution of H_2O_2 .

Obviously, water is the most abundant compound in cloud and raindrops and makes up nearly all their mass. Water molecules establish an equilibrium relationship with H^+ and OH^- ions;

(2.22)

(d) Summary and Equilibrium Constants of Chemical Reactions

Atmospheric hydrometeors can be regarded as aqueous solutions of very complex chemical composition. These aqueous particles may typically contain over 100 species of both organic and inorganic compounds (see Graedel and Weschler, 1981). Even if organic acids may significantly contribute to the acidification of rainwater in some remote regions of the globe (Galloway et al., 1982), it is generally believed that HNO_3 and H_2SO_4 are primarily responsible for lowering the pH of rain below 5.6 the value water attains in equilibrium with atmospheric CO_2 (Granat, 1972). Consequently, we pay particular attention in this work to chemical mechanism related to sulphate and nitrate. A summary of the chemical reactions and their equilibrium constants or rates used here can be seen in table 2.2. We expect these mechanisms to provide an adequate parameterized description of the chemistry of clouds typical of air masses over north eastern America.

CHEMICAL REACTIONS	EQUILIBRIUM CONSTANT OR RATE EXPRESSION	REFERENCE
$\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{SO}_2(\text{aq})$	$K_{\text{HS}} = [\text{SO}_2(\text{aq})]/[\text{SO}_2(\text{g})] = 1.6 \times 10^{-3} \exp(2967/T)$	1
$\text{SO}_2(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$K_{1\text{S}} = [\text{H}^+][\text{HSO}_3^-]/[\text{SO}_2(\text{aq})] = 1.9 \times 10^{-5} \exp(2022/T), M$	2
$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$K_{2\text{S}} = [\text{H}^+][\text{SO}_3^{2-}]/[\text{HSO}_3^-] = 2.3 \times 10^{-10} \exp(1671/T), M$	2
$\text{O}_3 + \text{S}(\text{IV}) \rightleftharpoons \text{S}(\text{VI}) + \text{O}_2$	$R_{\text{O}_3} = 1.8 \times 10^4 [\text{H}^+]^{-0.4} [\text{S}(\text{IV})][\text{O}_3], M \text{ s}^{-1}$	3
$\text{H}_2\text{O}_2 + \text{S}(\text{IV}) \rightleftharpoons \text{S}(\text{VI}) + \text{H}_2\text{O}$	$R_{\text{H}_2\text{O}_2} = 6 \times 10^4 [\text{H}_2\text{O}_2][\text{SO}_2(\text{aq})]/(0.1 + [\text{H}^+]), M \text{ s}^{-1}$	4
$\text{HNO}_3(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{HNO}_3(\text{aq})$	$K_{\text{HN}} = [\text{HNO}_3(\text{aq})]/[\text{HNO}_3(\text{g})] = 5 \times 10^6 (25^\circ \text{C})$	5
$\text{HNO}_3(\text{aq}) \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	$K_{1\text{N}} = [\text{H}^+][\text{NO}_3^-]/[\text{HNO}_3(\text{aq})] > 1 M (25^\circ \text{C})$	1
$\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{NH}_4\text{OH}(\text{aq})$	$K_{\text{HA}} = [\text{NH}_4\text{OH}]/[\text{NH}_3(\text{g})] = 2 \times 10^{-2} \exp(3402/T)$	1
$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$K_{1\text{A}} = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_4\text{OH}] = 1.8 \times 10^{-5} M$	6
$\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$	$K_{\text{HC}} = [\text{H}_2\text{CO}_3(\text{aq})]/[\text{CO}_2(\text{g})] = 8.6 \times 10^{-5} M$	-1
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$K_{1\text{C}} = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 4.8 \times 10^{-7} M$	6
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$K_{2\text{C}} = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 4.8 \times 10^{-11} M$	6
$\text{O}_3(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{O}_3(\text{aq})$	$K_{\text{HO}} = [\text{O}_3(\text{aq})]/[\text{O}_3(\text{g})] = 1.4 \times 10^{-8} \exp(3877/T)$	1
$\text{H}_2\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_2\text{O}_2(\text{aq})$	$K_{\text{HP}} = [\text{H}_2\text{O}_2(\text{aq})]/[\text{H}_2\text{O}_2(\text{g})] = 3 \times 10^{-4} \exp(6697/T)$	7
$\text{H}_2\text{O}_2(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HO}_2^-$	$K_{1\text{P}} = [\text{H}^+][\text{HO}_2^-]/[\text{H}_2\text{O}_2] = 1.5 \times 10^{-12} M$	1
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$K_{\text{W}} = [\text{H}^+][\text{OH}^-] = 10^{-14} M^2$	6

(1) derived from values given in Graedel and Weschler (1981); (2) Gravenhorst et al. (1978); (3) Møller (1980); (4) Martin and Damshen (1981); (5) Derived from a value given in Schwartz et al. (1982); (6) Robinson and Stokes (1959); (7) derived from values given in Martin and Damshen (1981).

Table 2.2. Chemical reactions, equilibrium constants and rates used for the parametrization of the cloud chemistry.

2.3 Gas-aqueous equilibrium chemistry.

An essential consideration in cloud chemistry is the study of the equilibrium between aqueous and gas phases. The processes discussed in the remaining parts of this chapter apply to the same arbitrary well-mixed volume of space implicit to the formulation of the continuity equations of section 2.1. According to equations (2.1)-(2.3), this volume can be subjected to advection, turbulent mixing and chemical transformations which act as sources or sinks. Because we consider equilibrium, we implicitly assume here that the liquid water remains within this volume for a sufficiently long time. The time scales implied in our formulation will be discussed subsequently in the text. For dilute solutions, the equilibrium concentration of a gas dissolved in a liquid is proportional to the concentration in the gas-phase (Henry's law):

$$[i' (aq)] = H_i [i (g)] \quad (2.23)$$

Here the prime means that we consider the totality of the dissolved species. H_i is an effective Henry's law coefficient that encompasses the totality of dissociation products and can be seen as the equilibrium constant of the overall reaction:

Using the equilibrium constant expressions given in table 2.2 we get:

$$H_{SO_2} = [S(IV)] [SO_2(g)]^{-1} = A + B[H^+]^{-1} + C[H^+]^{-2} \quad (2.25)$$

$$H_{CO_2} = [C] [CO_2(g)]^{-1} = A' + B'[H^+]^{-1} + C'[H^+]^{-2} \quad (2.26)$$

$$H_{NH_3} = [N(-III)] [NH_3(g)]^{-1} = D + E[H^+] \quad (2.27)$$

$$H_{HNO_3} = [N(V)] [HNO_3(g)]^{-1} = F + G[H^+]^{-1} \quad (2.28)$$

$$H_{H_2O_2} = [H_2O_2'] [H_2O_2(g)]^{-1} = F' + G'[H^+]^{-1} \quad (2.29)$$

$$H_{O_3} = [O_3(aq)] [O_3(g)]^{-1} = K_{HO} \quad (2.30)$$

Where we have introduced the notation:

$$A = K_{HS} = 1.6 \times 10^{-3} \exp (2967/T) \quad (2.31)$$

$$B = K_1 S K_{HS} = 3 \times 10^{-8} \exp (4989/T) \quad (2.32)$$

$$C = K_1 S K_2 S K_{HS} = 7.3 \times 10^{-8} \exp (6660/T) \quad (2.33)$$

$$A' = K_{HC} = 8.6 \times 10^{-5} \exp (2700/T) \quad (2.34)$$

$$B' = K_1CK_{HC} = 3.9 \times 10^{-11} \exp (2700/T) \quad (2.35)$$

$$C' = K_1CK_2CK_{HC} = 1.9 \times 10^{-21} \exp (2700/T) \quad (2.36)$$

$$D = K_{HA} = 2 \times 10^{-2} \exp (3402/T) \quad (2.37)$$

$$E = K_1AK_{HA}K_W^{-1} = 3.6 \times 10^7 \exp (3402/T) \quad (2.38)$$

$$F = K_{HN} = 5 \times 10^6 \quad (2.39)$$

$$G = K_1NK_{HN} = 1.05 \times 10^{21} \exp (-8995/T)^{(*)} \quad (2.40)$$

$$F' = K_{HP} = 3 \times 10^{-4} \exp (6697/T) \quad (2.41)$$

$$G' = K_1pK_{HP} = 4.5 \times 10^{-16} \exp (6697/T) \quad (2.42)$$

$$[S(IV)] = [SO_2(aq)] + [HSO_3^-] + [SO_3^{=}] \quad (2.43)$$

$$[C] = [CO_2(aq)] + [HCO_3^-] + [CO_3^{=}] \quad (2.44)$$

$$[N(-111)] = [NH_4OH] + [NH_4^+] \quad (2.45)$$

$$[N(V)] = [HNO_3(aq)] + [NO_3^-] \quad (2.46)$$

$$[H_2O_2'] = [H_2O_2(aq)] + [H_2O^-] \quad (2.47)$$

(*) Derived from an expression given in Levine and Schwartz (1982)

Figure 2.3 shows these effective Henry's law coefficients as functions of the pH, for gases of interest in this work.

The partition of a solute i between the gaseous and aqueous phases within a cloud is evaluated as the ratio of the amount of material in the gas phase (or liquid phase) to the total amount within a given volume of the cloud. For the fraction in the gas phase we have:

$$f_{i,a} = (V_a [i(g)]) / (V_a [i(g)] + V_L [i'])^{-1} \quad (2.48)$$

Here V_a is the volume occupied by the air and V_L the volume of the liquid water. When equilibrium exists between gas and aqueous phase we have:

$$f_{i,a} = (1 + \gamma H_i)^{-1} \quad (2.49)$$

Where γ is the dimensionless volume fraction of the liquid water. Thus we see that the partition between gas and liquid is described by the non-dimensional argument γH_i . When $\gamma H_i \ll 1$ gases are expected to be mainly in the liquid phase, and when $\gamma H_i \gg 1$ the gas phase predominates. For a typical atmospheric liquid water content of 1 g m^{-3} ($\gamma = 10^{-6}$) we see, from figure 2.3 that HNO_3 and NH_3 will be present essentially entirely in solution at low pH, while CO_2 and O_3 will remain in the gas phase. It is also seen, that the partition of SO_2 between liquid and gas phase changes appreciably over the pH range 3-6 and that H_2O_2 is partitioned almost evenly between aqueous and gas phases.

It is also of interest to know how the different species resulting from the dissolution of the gases are distributed as a function of pH.

Fig. 2.3. Effective Henry's law coefficients for gases of interest.
Temperature = 25 C.

Again using the expressions for the equilibrium constants given in table 2.2 we get:

$$[\text{SO}_2(\text{aq})] [\text{S(IV)}]^{-1} = A (\text{HSO}_2)^{-1} \quad (2.50)$$

$$[\text{HSO}_3^-] [\text{S(IV)}]^{-1} = B [\text{H}^+]^{-1} (\text{HSO}_2)^{-1} \quad (2.51)$$

$$[\text{SO}_3^{2-}] [\text{S(IV)}]^{-1} = C [\text{H}^+]^{-2} (\text{HSO}_2)^{-1} \quad (2.52)$$

$$[\text{CO}_2(\text{aq})] [\text{C}]^{-1} = A' (\text{HCO}_2)^{-1} \quad (2.53)$$

$$[\text{HCO}_3^-] [\text{C}]^{-1} = B' [\text{H}^+]^{-1} (\text{HCO}_2)^{-1} \quad (2.54)$$

$$[\text{CO}_3^{2-}] [\text{C}]^{-1} = C' [\text{H}^+]^{-2} (\text{HCO}_2)^{-1} \quad (2.55)$$

$$[\text{NH}_4\text{OH}] [\text{N(-III)}]^{-1} = D (\text{HNNH}_3)^{-1} \quad (2.56)$$

$$[\text{NH}_4^+] [\text{N(-III)}]^{-1} = E [\text{H}^+] (\text{HNNH}_3)^{-1} \quad (2.57)$$

$$[\text{HNO}_3(\text{aq})] [\text{N(V)}]^{-1} = F (\text{HNNH}_3)^{-1} \quad (2.58)$$

$$[\text{NO}_3^-] [\text{N(V)}]^{-1} = G [\text{H}^+]^{-1} (\text{HNNH}_3)^{-1} \quad (2.59)$$

$$[\text{H}_2\text{O}_2(\text{aq})] [\text{H}_2\text{O}_2']^{-1} = F' (\text{HH}_2\text{O}_2)^{-1} \quad (2.60)$$

$$[\text{H}_2\text{O}^-] [\text{H}_2\text{O}_2']^{-1} = G' [\text{H}^+]^{-1} (\text{HH}_2\text{O}_2)^{-1} \quad (2.61)$$

Figure 2.4 shows the relative abundance of dissolved species of SO_2 and CO_2 . Between pH 3 and 6, the precipitation pH range, these species will exist in solution mainly as HSO_3^- , $\text{CO}_2(\text{aq})$ and HCO_3^- . Numerical evaluation of (2.56) - (2.61) shows that over the same pH range HNO_3 , NH_3

Fig. 2.4 Relative abundance of dissolved species of sulphur dioxide and carbon dioxide as functions of pH.

and H_2O_2 are present in solution entirely as NO_3^- , NH_4^+ and $H_2O_2(aq)$.

The ionic species in solution must satisfy the following electroneutrality equation:

$$[H^+] + [NH_4^+] + [B^+] = [OH^-] + [NO_3^-] + [HSO_3^-] + 2[SO_3^{=}] + [HCO_3^-] + 2[CO_3^{=}] + [A^-] \quad (2.62)$$

Here $[B^+]$ and $[A^-]$ represent additional unspecified alkaline and acidic ions. Using table 2.2 and equations (2.25) - (2.49) we can show that:

$$[NH_4^+] = E [H^+] f_{NH_3,a} (NH_3)_T \quad (2.63)$$

$$[NO_3^-] = G [H^+]^{-1} f_{HNO_3,a} (HNO_3)_T \quad (2.64)$$

$$[HSO_3^-] = B [H^+]^{-1} f_{SO_2,a} (SO_2)_T \quad (2.65)$$

$$[SO_3^{=}] = C [H^+]^{-2} f_{SO_2,a} (SO_2)_T \quad (2.66)$$

$$[HCO_3^-] = B' [H^+]^{-1} f_{CO_2,a} (CO_2)_T \quad (2.67)$$

$$[CO_3^{=}] = C' [H^+]^{-2} f_{CO_2,a} (CO_2)_T \quad (2.68)$$

Where the f 's are defined by (2.49) and where $(i)_T$ is the total concentration of i in an arbitrary volume of space (1) . Inserting (2.63) - (2.68) in (2.62) we can obtain a complex equation relating

(1) $(i)_T$ is the total number of moles of i per unit volume of space, and is equivalent to $Q_{i,T}$

$[H^+]$ in terms of the total amount of NH_3 , HNO_3 , SO_2 and CO_2 within a given volume of space. Some pertinent simplifications to this equation are given below.

In acidic situations, when the pH is below 5, which is the region of interest in this work, it follows that $[OH^-] \ll [H^+]$, $[SO_3^{=}] \ll [HSO_3^-]$ and $[CO_3^{=}] \ll [HCO_3^-]$. Also, there is no doubt that for HNO_3 , $\gamma_{HNO_3} \gg 1$ for all representative values of γ . This implies that all HNO_3 can be considered dissolved and we get:

$$[NO_3^-] \approx 1/\gamma (HNO_3)_T \quad (2.69)$$

A similar approximation is valid for NH_3 provided that $pH < 5$ and that $\gamma > 10^{-7}$. We then have:

$$[NH_4^+] \approx 1/\gamma (NH_3)_T \quad (2.70)$$

Again, from figure 2.3, we see that we always can consider $\gamma_{HCO_2} \ll 1$ so for all practical purposes:

$$f_{CO_2,a} \approx 1 \quad (2.71)$$

With these approximations, the electrical neutrality equation can be written as:

$$[H^+]^2 - \Delta [H^+] - [B f_{SO_2,a} (SO_2)_T + B' (CO_2)_T] = 0 \quad (2.73)$$

where:

$$\Delta = \{[A^-] + 1/\gamma (HNO_3)_T\} - \{[B^+] + 1/\gamma (NH_3)_T\} \quad (2.73)$$

Equation (2.72) can be used to calculate the equilibrium pH of the solution provided $pH < 5$. Application of this equation to the modelling of cloud chemistry will be discussed later. For the general case where there is no restriction on the pH range, the calculation of the pH of a solution would require the simultaneous solution of (2.62) - (2.68).

2.4 Gas Scavenging.

The absorption and desorption of gaseous pollutants by cloud and raindrops is a key step in the removal and redistribution processes for many atmospheric trace gases. This absorption-desorption mechanism involves the transport of gases to the air-water interface, absorption, diffusion, convection, hydrolysis and chemical transformations of the gas into the liquid phase, while water droplets may undergo either evaporation or condensation.

The limiting concepts of irreversible ("total solubility") and equilibrium scavenging have been fully discussed by Hales (1972). The former is promoted by high solubilities and large drop sizes, and implies that the partial pressure of the species in the gas phase is much larger than the equilibrium pressure over the liquid. On the other hand, the notion of equilibrium scavenging is understood as the case in which solubility equilibrium between the two phases can be assumed. This limiting case is favoured by small drops sizes and low solubility.

Criteria for determining the applicability of these limiting conditions to rain scavenging have been suggested by Hales (1972) and Hill and Adamowicz (1977). In particular, it is straightforward

to generalize the results of the later study to get (in our notation)(*):

$$3K_{l,g} h (rUH_l)^{-1} > 1 \text{ for equilibrium washout} \quad (2.74)$$

$$3K_{l,g} h (rUH_l)^{-1} < 1 \text{ for irreversible washout} \quad (2.75)$$

Here $K_{l,g}$ is an overall mass transfer coefficient based on the gas driving force, h the height of the well mixed layer where washout occurs, r the equivalent radius of the drop (defined as the radius of the sphere of the same volume as a deformed falling drop), U the speed of the drop relative to the air, and H_l the effective Henry's law coefficient. For all cases of practical interest, the drops may be considered well mixed (Levine and Schwartz, 1982) and the mass transfer coefficient can be estimated from the semi-empirical expression (Pruppacher and Klett, 1978):

$$K_{l,g} = \begin{cases} \frac{D_{l,g}}{2r} \{2.56 + 0.616 \text{Re}^{1/2} \text{Sc}^{1/3}\}; & \text{Re}^{1/2} \text{Sc}^{1/3} \geq 1.4 \\ \frac{D_{l,g}}{2r} \{2.00 + 0.216 \text{Re}^{1/2} \text{Sc}^{1/3}\}; & \text{Re}^{1/2} \text{Sc}^{1/3} < 1.4 \end{cases} \quad (2.76)$$

where $\text{Re} = 2rUv^{-1}$ is the Reynolds number, $\text{Sc} = \nu (D_{l,g})^{-1}$ is the

(*) see Hill and Adamowicz, equation (25)

Schmidt number and ν is the kinematic viscosity of the air.

Diffusivities used here were either deduced from the literature or from the theory of molecular diffusion (Skelland, 1974).

Table 2.3 lists the values of $3K_{i,g} h (r U H_i)^{-1}$ at pH of 3 and 5, for a typical raindrop size of $r = 500 \mu m$ and for $h = 10^2 m$ (the figures given in this table would scale linearly with h). It is seen, for all cases of practical interest, that irreversible washout is a satisfactory approximation for HNO_3 , NH_3 and H_2O_2 , while rain scavenging of SO_2 , CO_2 and O_3 fulfill the criterion of equilibrium washout.

The gas aqueous equilibrium chemistry has been fully described above. For irreversible rain scavenging, the rate of increase of the concentration of a species i in a raindrop is given by (Levine and Schwartz, 1981):

$$\frac{d}{dt} [i'] = (3/r) K_{i,g} [i(g)] \quad (2.77)$$

Expressing this in a manner consistent with the formulation of section 2.1 we get:

$$\frac{d}{dt} Q_{i,r} = \Lambda_{i,ar} Q_{i,a} \quad (2.78)$$

where $Q_{i,a} = [i(g)]$ is the gas phase concentration of the species i and where;

$$Q_{i,r} = (4/3)\pi \int r^3 [i'] N(r) dr \quad (2.79)$$

	$3K_{i,g}h(rUH_i)^{-1}$	
	pH = 3	pH = 5
HNO_3	3×10^{-7}	3×10^{-9}
NH_3	3×10^{-6}	3×10^{-4}
H_2O_2	3×10^{-2}	3×10^{-2}
SO_2	3×10^2	3×10^0
CO_2	3×10^4	3×10^4
O_3	3×10^6	3×10^6

Table 2.3. $3K_{i,g}h(rUH_i)^{-1}$ at pH of 3 and 5, for gases of interest.

Here $Q_{1,r}$ is the molar density of pollutant species 1 associated with rain and $N(r) dr$ is the number of raindrops per unit volume within the range r and $r+dr$. The washout coefficient $\Lambda_{1,ar}$ is defined as:

$$\Lambda_{1,ar} = \int 4\pi r^2 K_{1,g} N(r) dr \quad (2.80)$$

has dimension of time^{-1} and is seen to be dependent upon the gas diffusivity (through $K_{1,g}$) and raindrop size spectrum. In their study of the scavenging of nitric acid vapor, Levine and Schwartz (1982) recommended values for $\Lambda_{\text{HNO}_3,ar}$ of 0.65, 1.8, 4.2 and $5.6 \times 10^{-4} \text{ s}^{-1}$ for rainfall rates of 1, 5, 15 and 25 mm h^{-1} . These values are well represented by

$$\Lambda_{\text{HNO}_3,ar} = 6.84 \times 10^{-5} + 2.07 \times 10^{-5} I \quad (2.81)$$

Here Λ is expressed in s^{-1} and I is the rainfall rate in mm h^{-1} . For a rainfall rate of 10 mm h^{-1} , $\Lambda = 1 \text{ h}^{-1}$. The washout coefficients for H_2O_2 and NH_3 are related to $\Lambda_{\text{HNO}_3,ar}$ through their respective diffusivities in air:

$$\Lambda_{\text{H}_2\text{O}_2,ar} = 1.1 \Lambda_{\text{HNO}_3,ar} \quad (2.82)$$

$$\Lambda_{\text{NH}_3,ar} = 1.6 \Lambda_{\text{HNO}_3,ar} \quad (2.83)$$

A different situation prevails for the rainout of gases by cloud droplets. Due to the negligible fall velocity of cloud droplets relative to the air, one can assume that they fully share the air motion and the system to be considered is an air parcel containing cloud droplets and gases. From calculations based on this situation, Iribarne (see Cho and Iribarne, 1983; Vol. I) has shown that the characteristic time constants for scavenging of O_3 , CO_2 , SO_2 , NH_3 , H_2O_2 and HNO_3 are typically less than 10 s, with the consequence that solubility equilibrium can be assumed inside the cloud. It has also been estimated by Levine and Schwartz (1982), that the characteristic time of dissolution for highly soluble gases such as HNO_3 is about 5 s, for typical convective cloud droplet spectra.

Based on these results we consider here that the cloud water is in equilibrium with the gaseous phase for all gases of interest.

Thus from the above considerations and the discussion of section 2.3, we see that independent of the pH, HNO_3 and NH_3 are instantly scrubbed by the cloud water and that their interstitial concentrations are zero. In acidic solutions, these gases exist essentially as NO_3^- and NH_4^+ ions. For hydrogen peroxide, comparable amounts are found in the gaseous and aqueous phases and the partition is not significantly dependent upon the acidity of solution. For SO_2 , the fraction of the gas dissolved in the liquid is a strong function of pH and due to the abundance of carbon dioxide and low solubility of ozone, gas phase depletion of these two species can be neglected. We assume that the concentrations of these two gases are constant and uniform in the domain during the integration.

2.5 Aerosol scavenging

(a) Rainout of sulphate aerosol particles.

The study of the scavenging of particulates by atmospheric hydrometeors involves attachment by (1) convective diffusion, (2) thermophoresis and diffusiophoresis, (3) turbulent shear and turbulent inertial capture and (4) gravitational or inertial capture. These processes are discussed in detail in Pruppacher and Klett (1978, section 12.7) and have been combined in a number of studies to obtain overall scavenging effects (Greenfield, 1957; Sparks and Pilat, 1970; Slinn and Hales, 1971; Dingle and Lee, 1973; Beard and Grover, 1974; Pilat and Prem, 1976; Wang and Pruppacher, 1977; Grover et al., 1977; Wang et al., 1978; Lai et al., 1978). It is found that the overall scavenging coefficient exhibits a broad minimum for aerosol particle radii between about $0.1 \mu\text{m}$ and $1.0 \mu\text{m}$. This is usually termed in the literature as the "Greenfield Gap" (after Greenfield, 1957) and is the result of the fact the Brownian motion dominates the capture of the smallest particles while inertial impaction dominates the capture of the largest ones. In this gap, neither aerodynamic impaction nor Brownian capture can remove particles with appreciable efficiency. It has been pointed out by McDonald (1964) that soluble particulates are removed from the gap region via nucleation, providing a bridging mechanism to the gap. As the major fraction of the sulphate aerosol mass lies within the gap size range (Whitby, 1978), we regard in-cloud

scavenging of sulphate aerosol as being dominated by nucleation and neglect other mechanisms (this is consistent with the approach of: Junge, 1963; Slinn, 1974; Garland, 1978).

When sulphate aerosols enter a super-saturated region of the atmosphere, some fraction of the particles serve as condensation nuclei. The fraction activated depends in a complex way on the particle size distribution and supersaturation. For simplicity, we assume here that a fixed fraction of sulphate mass flux at cloud base is transferred to the bulk cloud water by nucleation, provided condensation occurs and that there is an updraft. This nucleated mass is assumed to increase the average molar density of cloud-dissolved sulphate within the grid box. This idea is summarized by:

$$(d/dt)Q_{SO_4,c} = \Lambda_{SO_4,ac} Q_{SO_4,a} \quad (2.84)$$

$$\Lambda_{SO_4,ac} \delta t = \epsilon w \delta t (\delta z)^{-1} \quad (2.85)$$

where w is the updraft speed, δt the time step, and δz the vertical extent of a grid box.

It can be seen, that this procedure does not lead to a consistent partition of sulphate between air and cloud within the grid box when the vertical resolution $\delta z > w \delta t$. To resolve this difficulty, we assume here that when condensation occurs for the first time in an

elementary volume of space, the fixed fraction ϵ of the sulphate aerosol present in the air enters cloud water by nucleation. Thus we have:

$$Q'SO_{4,a} = (1 - \epsilon)QSO_{4,a} \quad (2.86)$$

$$Q'SO_{4,c} = \epsilon QSO_{4,a}$$

where the primes denote the sulphate molar density within a grid box after nucleation capture.

The undesirable dependence of Λ on δz in (2.85) is the consequence of a too coarse resolution ($\delta z > w\delta t$) and if for a given situation, one desires to change the vertical resolution, special care should be taken to select appropriate values of $\epsilon(\delta z)^{-1}$. If computer resources had allowed a selection of $\delta z \leq w\delta t$ a formulation similar to (2.86) could have been used at cloud base for each time step. Above the cloud base, we neglect additional nucleation and we interpret an increase in the cloud water content as condensation of water vapor on existing cloud droplets. It is useful to note that for a typical updraft speed of 1 m s^{-1} , for $\epsilon = 0.5$ and for $\delta z = 300 \text{ m}$, $\Lambda = 6 \text{ h}^{-1}$.

(b) Cloud to rain transport of cloud-dissolved species.

Another important step in the sequence of processes involved in the scavenging of atmospheric pollutants by clouds is the transport of cloud-dissolved species to rain. This occurs as the result of the conversion of pollutant-laden cloud droplets to precipitation sized particles and by accretion of the cloud water by falling raindrops. The microphysics involved in the transformation of cloud into rain has been parameterized by Kessler (1969), in terms of an autoconversion rate of cloud to rain (α_1) and an accretion rate of cloud by rain (α_2). Details of the formulation and values of the parameters pertinent to our study are given by Kessler. We have:

$$\frac{d}{dt} Q_{1,r} = \Lambda_{1,cr} Q_{1,c} \quad (2.87)$$

Where the scavenging coefficient $\Lambda_{1,cr}$ applies to any species subjected to an irreversible process and is given by:

$$\Lambda_{1,cr} = (\alpha_1 + \alpha_2) (\gamma_{cpl})^{-1} \quad (2.88)$$

Here we implicitly assume that the concentration of pollutant in the cloud water converted into rain is given by:

$$[i']_c = \int r^3 [i'] N(r) dr \left\{ \int r^3 N(r) dr \right\}^{-1} = Q_{1,c} (\gamma_c)^{-1} \quad (2.89)$$

which is the concentration that would exist in the bulk cloud water.

For $\gamma_c = 10^{-6}$, $\gamma_r = 6 \times 10^{-7}$, (10 mm h⁻¹) we have $\alpha_1 = 0$ and $\alpha_2 = 2.8 \times 10^{-3}$ g m⁻³ s⁻¹, so $\Lambda_{1,cr} \approx 10$ h⁻¹.

(c) Washout of particulate matter by rain.

The washout of sulphate aerosols in the air by precipitation particles is a pathway by which the atmosphere is cleansed and may significantly contribute to the chemical composition of rainwater. Following Scott (1978), when a raindrop population is assumed to be distributed in size according to the Marshall-Palmer (1948) distribution and to fall through air containing $Q_{SO_4,a}$ units of mass of sulphate per unit volume, the raindrops accumulate sulphate at a rate given by:

$$\frac{d}{dt} Q_{SO_4,r} = \Lambda_{SO_4,ar} Q_{SO_4,a} \quad (2.90)$$

where

$$\Lambda_{SO_4,ar} = 5.2 \times 10^{-3} E_s Q_r^{7/8} \quad (2.91)$$

and E_s is an average collection efficiency. In this work, we assume that the aerosol is washed out with a collection efficiency equal to that for the mean volume particle. In the next chapter, we will see that the mean volume diameter of the aerosol distribution involved here is $0.2 \mu m$. This implies a collection efficiency of about 0.1 (Radke et al., 1980). This gives, with $Q_r = 0.6 g m^{-3}$, $\Lambda = 1.25 h^{-1}$.

(d) Redistribution of pollutant mass due to evaporation of liquid water.

Evaporation, which is the fate of most clouds is thought to be an important process for redistributing cloud-dissolved species in the atmosphere (Cho et al., 1984; Gidel, 1983). Redistribution occurs when a substance which has been collected by cloud droplets is deposited in clear air upon complete evaporation of the droplets. This mechanism is a complicated function of the properties of the cloudy air, the environmental air, and the turbulence of the flow field and is therefore too complex to be described in terms of the simple Λ parameterization. As our calculations are done within the framework of a dynamical and microphysical cloud model, where these fields are calculated (for details see Yau, 1980) we simply keep track of grid points where the bulk cloud water evaporates totally and redistribute the mass of pollutant accordingly. For the purpose of formulating the theory, we symbolize this mechanism by $E_{1,ca}$.

When the bulk cloud water evaporates only partially, it is possible that a fraction of the mass of the evaporated water arises from droplets which evaporate completely. This may contribute to redeposition of the cloud-dissolved species in the interstitial air. However, a detailed analysis of cloud water evaporation involved in our calculations shows that this mechanism can be neglected.

When a raindrops population falls through a subsaturated atmosphere, evaporation increases the aqueous concentration of

rain-dissolved species subjected to irreversible washout but redistributes species subjected to reversible scavenging. The only way for substances experiencing an irreversible process to return to the gas phase, is the total evaporation of a fraction of their "host" droplets. However, under typical atmospheric conditions, it is unlikely for drops with radii larger than 200 μm to evaporate completely. As the most significant contribution to the mass of the rainwater is from dropsizes larger than 200 μm , redeposition of highly soluble gases and particulate matter due to the total evaporation of a fraction of raindrops is neglected here. For completeness (even if in practice its importance is limited) and because it is relatively inexpensive in computer time, we also keep track of grid points where the bulk rainwater evaporates completely (virga) and redistribute the pollutant in the air as we do for cloud. We denote this process by $E_{1,ra}$.

2.6 Calculation of pH.

Since they are subjected to different microphysical mechanisms and since they have a relative velocity with respect to each other, cloud drops and raindrops within a given volume at a particular time, must have different histories and hence their intrinsic chemical composition may be significantly different. On the other hand, it has been previously demonstrated that cloud and raindrops can be considered in equilibrium with sulphur dioxide and therefore are coupled through the gas phase (see Tremblay and Leighton, 1984). When we consider different concentrations of nitrate, sulphate and ammonium ions in the bulk cloud and rainwater, we have:

$$\Delta_C = [\text{NO}_3^-]_C + 2[\text{SO}_4^{2-}]_C - [\text{NH}_4^+]_C \quad (2.92)$$

and a similar equation can be written for rain. The bulk concentrations are calculated from (2.89). If both cloud and rain coexist within a given volume of space, their respective hydrogen ions concentrations must be calculated from the two coupled electro neutrality equations:

$$[\text{H}^+]^2_C - \Delta_C [\text{H}^+]_C - \{B^f \text{SO}_{2,a} (\text{SO}_2)_T + B^i (\text{CO}_2)_T\} = 0 \quad (2.93)$$

$$[\text{H}^+]^2_R - \Delta_R [\text{H}^+]_R - \{B^f \text{SO}_{2,a} (\text{SO}_2)_T + B^i (\text{CO}_2)_T\} = 0 \quad (2.94)$$

where:

$$f_{SO_2,a} = \{1 + \gamma_c H_{SO_2,c} + \gamma_r H_{SO_2,r}\}^{-1} \quad (2.95)$$

The dependence of $H_{SO_2,c}$ and $H_{SO_2,r}$ upon $[H^+]_c$ and $[H^+]_r$ has been previously noted and the following relationships emerge:

$$f_{SO_2,c} = \gamma_c H_{SO_2,c} f_{SO_2,a} \quad (2.96)$$

$$f_{SO_2,r} = \gamma_r H_{SO_2,r} f_{SO_2,a} \quad (2.97)$$

$$f_{SO_2,a} + f_{SO_2,c} + f_{SO_2,r} = 1 \quad (2.98)$$

In tables 2.4 and 2.5 we display numerical solutions of (2.93) and (2.94) for a wide range of values of Δ ($\Delta = -10^{-4}$ would give a pH of 10 in the absence of SO_2 and CO_2 , while $\Delta = 10^{-2}$ a pH of 2) for $\gamma_c = 10^{-6}$, $\gamma_r = 5 \times 10^{-7}$, $T = 298^\circ K$, $p = 1 \text{ atm}$, $(SO_2)_T = 10 \text{ ppbv}$ and $(CO_2)_T = 3.3 \times 10^{-5} \text{ ppbv}$, which are typical of atmospheric conditions. From this table, we see that the pH of cloud water is almost independent of Δ_r (except in very alkaline situations) but is a strong function of Δ_c . Similar conclusions hold for rainwater acidity. This implies that unless Δ is exceptionally negative, coupling via the gas depletion of SO_2 can be neglected and that we can simply assume, for calculating the pH that $f_{SO_2,a} = 1$. This

PH OF CLOUD

$+10^{-2}$	5.76	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
$+10^{-3}$	5.76	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
$+10^{-4}$	5.76	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
$+10^{-5}$	5.76	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
$+10^{-6}$	5.77	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
0	5.77	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
-10^{-6}	5.77	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
-10^{-5}	5.77	4.96	4.83	4.82	4.80	4.68	3.99	3.00	2.00
-10^{-4}	5.83	5.01	4.87	4.85	4.84	4.70	3.99	3.00	2.00
Δ_r Δ_c	-10^{-4}	-10^{-5}	-10^{-6}	0	$+10^{-6}$	$+10^{-5}$	$+10^{-4}$	$+10^{-3}$	$+10^{-2}$

Table 2.4. pH of the cloud water as a function of Δ_c and Δ_r .

PH OF RAIN

$+10^{-2}$	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
$+10^{-3}$	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
$+10^{-4}$	3.99	3.99	3.99	3.99	3.99	3.99	3.99	3.99	3.99
$+10^{-5}$	4.72	4.68	4.68	4.68	4.68	4.68	4.68	4.68	4.68
$+10^{-6}$	4.86	4.80	4.80	4.80	4.80	4.80	4.80	4.80	4.80
0	4.88	4.82	4.82	4.82	4.82	4.82	4.82	4.82	4.82
-10^{-6}	4.90	4.83	4.83	4.83	4.83	4.83	4.83	4.83	4.83
-10^{-5}	5.04	4.96	4.96	4.96	4.96	4.96	4.96	4.96	4.96
-10^{-4}	5.83	5.72	5.71	5.71	5.71	5.71	5.70	5.70	5.70
$\Delta_r \backslash \Delta_c$	-10^{-4}	-10^{-5}	-10^{-6}	0	$+10^{-6}$	$+10^{-5}$	$+10^{-4}$	$+10^{-3}$	$+10^{-2}$

Table 2.5. pH of the rain water as a function of Δ_c and Δ_r .

decouples the electroneutrality equations and we have:

$$[H^+]_C = 1/2 \{ \Delta_C + [\Delta_C^2 + 4(B(SO_2)_T + B'(CO_2)_T)]^{0.5} \} \quad (2.99)$$

$$[H^+]_R = 1/2 \{ \Delta_R + [\Delta_R^2 + 4(B(SO_2)_T + B^1(CO_2)_T)]^{0.5} \} \quad (2.100)$$

We can also show by differentiation of (2.93) and (2.94) that $[H^+]_C$ and $[H^+]_R$ are weak functions of $f_{SO_2,a}$. Table 2.6 shows uncoupled pH's calculated from (2.99) and (2.100) for the same parameter values used for the calculation of table 2.4. A comparison shows how well these calculations agree. Other calculations performed with different parameters yield the same conclusion.

Δ_c or Δ_r pH of cloud or rain

-10^{-4}	5.64
-10^{-5}	4.96
-10^{-6}	4.83
0	4.82
$+10^{-6}$	4.80
$+10^{-5}$	4.68
$+10^{-4}$	3.99
$+10^{-3}$	3.00
$+10^{-2}$	2.00

Table 2.6. Uncoupled pH of cloud and rain.

2.7 Gas phase chemistry and parameterization of the chemical composition of aerosol particulates.

Gas phase generation of sulphuric acid and nitric acid is the result of a variety of chemical reactions and compounds and is of primary importance in long range transport studies (Eliassen et al., 1982). However, for life times typical of convective clouds (one hour or less) this can be neglected (see Calvert and Stockwell, 1984).

Consistent with the discussion of section 2.2, we simply assume here that the sulphate aerosol is composed of ammonium sulphate and sulphuric acid. Therefore, the chemical composition of sulphate can be simply characterized by a single parameter which is the fraction of sulphuric acid present.

2.8 Summary and model equations.

A simple bulk parameterized description of cloud and precipitation chemistry and of scavenging of pollutants by warm clouds has been introduced. It has been assumed that the rainout of gases occurs in equilibrium, while the washout of highly soluble gases is better approximated as an irreversible process. For sulphur dioxide, both rainout and washout can be treated on an equilibrium basis. We also described the scavenging of sulphate particulate matter and suggested a scheme for calculating the acidity of the bulk cloud and rainwater. The techniques described here are simple and should require relatively low computing time and therefore are feasible for adaptation to a complex three dimensional dynamical cloud model. This is expected to provide new insight into the interaction of gases and aerosols with clouds.

As the scavenging of SO_2 occurs in equilibrium, we only need to keep track of $Q_{\text{SO}_2, \text{T}} = Q_{\text{SO}_2, \text{a}} + Q_{\text{SO}_2, \text{c}} + Q_{\text{SO}_2, \text{r}}$ because each individual term on the R.H.S. can be expressed in term of $Q_{\text{SO}_2, \text{T}}$. Adding (2.1) - (2.3) together, all terms representative of interphase transports vanish and we get:

$$\begin{aligned} \frac{\partial}{\partial t} Q_{\text{SO}_2, \text{T}} = & - \nabla \cdot Q_{\text{SO}_2, \text{T}} \mathbf{V} + \nabla \cdot v_h \nabla \{1 + (\delta-1)f_{\text{SO}_2, \text{r}}\} Q_{\text{SO}_2, \text{T}} \\ & + \frac{\partial}{\partial z} f_{\text{SO}_2, \text{r}} Q_{\text{SO}_2, \text{T}} V_F - \gamma_c \{R_{\text{O}_3, \text{c}} + R_{\text{H}_2\text{O}_2, \text{c}}\} \\ & - \gamma_r \{R_{\text{O}_3, \text{r}} + R_{\text{H}_2\text{O}_2, \text{r}}\} \end{aligned} \quad (2.101)$$

Calculations can also be simplified for HNO_3 , NH_3 and H_2O_2 since within the cloud, $f_{\text{HNO}_3,a} = f_{\text{NH}_3,a} = 0$; $f_{\text{HNO}_3,c} = f_{\text{NH}_3,c} = 1$, and since $f_{\text{H}_2\text{O}_2,a}$ and $f_{\text{H}_2\text{O}_2,c}$ are independent of the pH. We obtain on addition of (2.1) and (2.2)

$$\frac{\partial}{\partial t} Q_{l,v} = - \nabla \cdot Q_{l,v} V + \nabla \cdot v_h \nabla Q_{l,v} - \Lambda_{l,cr} Q_{l,c} - \Lambda_{l,ar} Q_{l,a} + E_{l,ra} \quad (2.102)$$

where

$$Q_{l,v} = Q_{l,a} + Q_{l,c} \quad (2.103)$$

$$Q_{l,a} = \begin{cases} f_{l,a} Q_{l,v}; & \gamma_c > 0 \\ Q_{l,v}; & \gamma_c = 0 \end{cases} \quad (2.104)$$

$$Q_{l,c} = \begin{cases} f_{l,c} Q_{l,v}; & \gamma_c > 0 \\ 0; & \gamma_c = 0 \end{cases} \quad (2.105)$$

For the part of these substances dissolved in rain, we consider:

$$\frac{\partial}{\partial t} Q_{l,r} = - \nabla \cdot Q_{l,r} V + \delta \nabla \cdot v_h \nabla Q_{l,r} + \frac{\partial}{\partial z} Q_{l,r} V_F + \Lambda_{l,cr} Q_{l,c} + \Lambda_{l,ar} Q_{l,a} - E_{l,ra} \quad (2.106)$$

when (2.102) or (2.106) are applied to H_2O_2 we must subtract from the right hand side $\gamma_c R_{\text{H}_2\text{O}_2,c}$ or $\gamma_r R_{\text{H}_2\text{O}_2,r}$ respectively, to take into account the local depletion of this gas due to oxidation of SO_2 .

Finally, for sulphate particulate matter we must consider the following equations:

$$\begin{aligned} \frac{\partial}{\partial t} Q_{SO_4,a} = & - \nabla \cdot Q_{SO_4,a} \nabla + \nabla v_h \nabla Q_{SO_4,a} \\ & - \Lambda_{SO_4,ac} Q_{SO_4,a} - \Lambda_{SO_4,ar} Q_{SO_4,a} \\ & + E_{SO_4,ra} + E_{SO_4,ca} \end{aligned} \quad (2.116)$$

$$\begin{aligned} \frac{\partial}{\partial t} Q_{SO_4,c} = & - \nabla \cdot Q_{SO_4,c} \nabla + \nabla v_n \nabla Q_{SO_4,c} \\ & + \Lambda_{SO_4,ac} Q_{SO_4,a} - \Lambda_{SO_4,cr} Q_{SO_4,c} \\ & - E_{SO_4,ca} + \gamma_c \{R_{O_3,c} + R_{H_3O_2,c}\} \end{aligned} \quad (2.117)$$

$$\begin{aligned} \frac{\partial}{\partial t} Q_{SO_4,r} = & - \nabla \cdot Q_{SO_4,r} \nabla + \delta \cdot \nabla \cdot v_n \nabla Q_{SO_4,r} \\ & + \frac{\partial}{\partial z} Q_{SO_4,r} V_F + \Lambda_{SO_4,cr} Q_{SO_4,c} \\ & + \Lambda_{SO_4,ar} Q_{SO_4,a} - E_{SO_4,ra} \\ & + \gamma_r \{R_{O_3,r} + R_{H_2O_2,r}\} \end{aligned} \quad (2.118)$$

Equations (2.101) - (2.118) constitute the core of the model and when applied to the entire range of substances of interest provide a set of 10 coupled, non linear, partial differential equations, for modelling cloud chemistry and the interactions between clouds and atmospheric gaseous and particulate pollutants. The solution of these equations requires a knowledge, as functions of space and time of V , V_F , γ_c , γ_r , v_h , as well as of the water vapour distribution and selected

microphysical fields such as evaporation, autoconversion of cloud into rain, or accretion of cloud by rain. This is achieved by linking our prognostic equations to an existing cloud model (Yau, 1980) where these fields are calculated everywhere in the domain of integration at each time step.

Initial and boundary conditions are also needed; the former may follow from aircraft measurements of vertical profiles of pollutants in the air (we will discuss this in the next chapter) and the latter from the assumption that at the lower and upper boundaries of the domain, the vertical velocity of the air is zero. The lateral boundary conditions are assumed to be periodic. The same boundary conditions are used in the cloud model for water vapor, cloud and rain water.

Following Yau, our model equations are solved numerically using a staggered grid arrangement, the second order non-diffusive leapfrog method in time and the centered difference method in space. Details are given in Yau (1980).

Chapter 3

THREE DIMENSIONAL SIMULATIONS OF CLOUD CHEMISTRY

In this chapter numerical experiments based on the solution of the equations developed in chapter 2 are discussed. As previously mentioned, our cloud chemistry model needs, as a function of time, input fields of wind velocity and of selected microphysical parameters. This information is obtained from the Steiner-Yau cloud model (for details, see Steiner, 1973; Yau, 1980; Turpeinen and Yau, 1981) and is processed by the cloud chemistry program.

Our basic approach is to use aircraft observations taken in the clear air (assumed to be representative of the cloud environment) to initialize both the cloud dynamics and chemistry simulations, and to compare the results of the cloud chemistry model with the measured chemical composition of the cloud water. For the calculation of the cloud dynamics, we need a detailed clear air sounding of temperature, humidity and horizontal wind. For the cloud chemistry model, we require as initial data clear air profiles of nitric acid vapour, ammonia, hydrogen peroxide, sulphur dioxide and sulphate aerosol. Initially, these fields are assumed to be horizontally uniform in the domain of integration.

(3.1) Cloud chemistry measurements.

We have selected as the data base for our numerical simulations, measurements from a cloud chemistry field study undertaken at North Bay, Ontario, Canada, during July 1982 (for details, see Isaac et al., 1983; Leitch et al., 1982). During this experiment, data were collected from a special ground sampling station in a remote area to the southeast of North Bay and from two aircraft specially instrumented for cloud microphysics and chemistry measurements. One of these aircraft was used to collect cloud and rainwater samples, to expose air filters (to collect aerosol, HNO_3 and SO_2), and to record sulphur dioxide concentrations in the air, cloud and precipitation drop size spectra, aerosol size distributions, air temperature, humidity and wind. A second aircraft was mainly employed to collect filter samples (aerosol, SO_2 , HNO_3 , NH_3) below cloud base.

The basic assumptions in the formulation of the cloud model, require that simulations be for days with isolated shower activity and little large scale organized motion (Yau and Michaud, 1982). An examination of the synoptic situations prevailing during July 1982 and of available cloud chemistry measurements from the field study, suggests that the clouds occurring on 15 July were suitable for simulation. The 00 GMT surface analysis of the 16 July, 1982 (which is only a few hours after the aircraft cloud penetrations) is displayed in Fig. 3.1. The triangle east of Georgian Bay indicates the approximate location of the experimental site. The only major synoptic feature on this map is a low pressure

Fig. 3.1. Surface synoptic map at 0000 GMT, 16 July 1982.

centered over Wyoming and therefore the use of the cloud model for the environmental conditions representative of the experimental area is justified.

In Fig. 3.2, we depict vertical profiles (obtained from an aircraft clear air sounding taken between 2012 and 2053 GMT) of temperature and humidity plotted on a skew T - $\log p$ diagram. It is seen that the convective condensation level is at 830 mb (1350 m) with a well mixed, nearly dry adiabatic layer below. At this level, the ambient relative humidity is 95% and above the moisture content decreases steadily, reaching 24% at 500 mb. Between 750 and 500 mb, the atmosphere is slightly unstable to moist adiabatic ascent.

Based on visual reports by aircraft crew, clouds present on this day extended approximately from a cloud base height of 1 km to a cloud top height of 3 km where the ambient temperature was 3°C; justifying the omission of the ice phase in the models. Aircraft traverses showed that the horizontal extent of those clouds was about 3 km. Surface weather observations recorded at North Bay during the same period, indicated that the cloud coverage was about 20% and radar echoes revealed that weak scattered showers were present on that day.

The three dimensional structure of the environmental wind field measured from the aircraft is displayed on a hodograph in Fig. 3.3. This

Fig. 3.2. Environmental temperature and humidity profiles plotted on a skew T - log p diagram, obtained from a clear air aircraft sounding between 2012-2053 GMT.

Fig. 3.3. Aircraft observation of horizontal wind, displayed on a hodograph, for the same period of time.

shows that at low levels the wind is from the west. Above the 2 km level, the wind veers gradually with height and increases to be from the west north west at 15 m s^{-1} at an altitude of 6 km (450 mb).

Fig. 3.4a shows vertical profiles of the particles number concentration and mean volume diameter as measured during the aircraft ascent. The dots indicate measurements points, the curve was fitted by eye and is used as the initial condition for modelling cloud chemistry. The depth of the mixing layer (1350 m) deduced from the aerosol concentration profile is consistent with that deduced from the temperature and humidity profiles (see Fig. 3.2).

The aerosol was also collected on teflon filters exposed from the aircraft flying at 670 m and analyzed by ion chromatography for soluble species (for details see Anlauf et al., 1985). Particulate sulphate and ammonium ions were present in concentrations of 4.2 and $0.6 \text{ } \mu\text{g m}^{-3}$ respectively, with an equivalence ratio of $2[\text{SO}_4^{2-}]/[\text{NH}_4^+] = 2.6$, which is assumed to remain constant and uniform in the domain of integration. Also, as the mean volume diameter of the particles does not change with height (Fig. 3.4a), we assume for simplicity that variations in number concentration are equivalent to variation in mass concentration. It is seen from Fig. 3.4a that this procedure gives a uniform aerosol mass concentration of $4.8 \text{ } \mu\text{g m}^{-3}$ in the sub cloud layer, decreasing rapidly to zero above the cloud base level.

Fig. 3.4. Vertical profiles of (a) aerosol number concentration and mean volume diameter; (b) clear air sulphur dioxide concentration; (c) nitric acid vapor; and (d) gaseous ammonia. The dots indicate measurements points while the curves which are fitted by eye are used as initial conditions in the model

The vertical distribution of sulphur dioxide in the clear air is shown in Fig. 3.4b. Above 1 km, the ambient SO_2 concentration is below the detection limit (2 ppbv) and we assume that its vertical profile is similar to that of sulphate as indicated by the solid curve.

It is also apparent from Figs. 3.4c and 3.4d that measurements of HNO_3 and NH_3 are rather restricted; only data from the surface and the second aircraft (at 670 m) are available. As for sulphur dioxide, we also assume that the concentrations of these gases are distributed in the vertical in the same way as the sulphate aerosol.

(3.2) Simulations of cloud dynamics and microphysics.

As discussed above, we are interested in simulating clouds with bases at about 1 km, top at about 3 km and horizontal extent of approximately 3 km. Thus, to keep boundary effects minimal, we consider a domain size of 12 km x 12 km in the horizontal and 6.9 km in the vertical. This gives with a $32 \times 32 \times 23$ grid mesh, a resolution of 375 m horizontally and of 300 m vertically. The same domain is used for both cloud dynamics and cloud chemistry simulations. Numerical stability required time steps not larger than 20 s for all simulations.

Because of uncertainty about subcloud forcing mechanisms and because of its computational simplicity, convection is commonly initiated in three dimensional cloud simulations by a saturated humidity impulse

(see Turpeinen and Yau, 1981). For this work, we found that an impulse with a radius of about 2 km in the horizontal and with a depth of 900 m resulted in the formation of a suitable cloud.

To prevent the simulated cloud from drifting out of the computational domain, the 740 mb (2 km) wind was subtracted out from the wind profile. To facilitate the interpretation of the results, the x - axis is aligned in the direction of the mean wind.

The time evolution of vertical sections of cloud water content and rain water content are depicted in Figs. 3.5 and 3.6 (cloud A). All xz sections presented in this work, are located at $y = 5.81$ km, which is roughly the center of the domain in the y direction. The cloud boundary is taken to be the 0.01 g m^{-3} contour. It is seen that the simulated cloud agrees fairly well with observations in terms of both horizontal and vertical dimensions and, as will be discussed subsequently in the text, that the liquid water is reasonably consistent with observed values. The bulk of the cloud dissipated quickly after 1440 s of simulation time with only a patch of cloud persisting at cloud base. This accounted for less than 10% of the cloud mass at 800 s. It is also seen from Fig. 3.6 that the cloud produced a light rain shower; the maximum equivalent rainfall rate was about 3 mm h^{-1} , which is consistent with the radar observations of the showers formed on that day.

Due to the fact that in this simulation the diffusion of rain was turned on ($\delta = 1$), the rain volume has slightly diffused in altitude

Fig. 3.5. Time evolution of the cloud water content in the xz plane at $y = 5.81$ km. Cloud A.

Fig. 3.6. Time evolution of the rain water content in the xz plane at $y = 5.81$ km. Cloud A.

beyond the cloud boundary. To insure that this is not influencing our results, we repeated this simulation with $\delta = 0$, and no significant changes were detected either in the dynamics or in the rain and cloud water distributions.

As an example of the air circulation associated with cloud A, we display in Fig. 3.7 vertical and horizontal sections of the wind velocity at $t = 1040$ s, which corresponds to the mature stage of the cloud. We see that the three dimensional wind field has a complex structure with vortices along both y and z axis. A maximum updraft speed of about 5 m s^{-1} can be detected at an altitude of 2.4 km, which corresponds roughly to the mid-cloud level. At cloud base maximum updrafts of 1.0 m s^{-1} are typical, but their horizontal extent and persistence account only for several percent of the cloud base surface and life time; downdrafts covered most of the cloud base surface during the dissipation stage. Outside the cloud, a maximum downdraft of -3.5 m s^{-1} is observed at $z = 2.5$ km. The wind field is calculated at each time step and is used in the cloud chemistry model to calculate the advection terms.

Because non-precipitating clouds were also present on the day under study, we performed an additional cloud dynamics simulation (cloud B) with precipitation formation processes turned off. As the dynamics and cloud liquid water distribution does not differ greatly from cloud A, these results are not presented. Data from the cloud B simulation were used to

Fig. 3.7. (a) vertical cross section showing the wind field at $y = 5.81$ km and $t = 1040$ s. The scale of the longest arrow is 10 m/s and (b) horizontal cross section of the wind velocity at $z = 2250$ m and $t = 1040$ s. Here, the scale of the longest arrow is 3.6 m/s.

drive the cloud chemistry model in our run V (to be discussed below).

(3.3) Description of numerical cloud chemistry experiments

The objectives of the numerical experiments undertaken here, is to provide insights into the following topics. Firstly, because of their potential influence on the long range transport of atmospheric pollutants, it is desirable to study the effects of clouds in redistributing pollutants in the vertical. Secondly, it is also of interest to ascertain qualitatively processes by which acidic species are incorporated into precipitation. Thirdly, we will investigate the capability of convective clouds for transforming the gaseous acidic precursor SO_2 into the strong acid H_2SO_4 found in precipitation. Finally, the three dimensional distribution of the concentration of the chemical species in and around clouds will be discussed.

Table 3.1 lists the parameters that distinguish the five simulations performed here. The first experiment is chosen as a standard which serves as a basis for comparison with other experiments. For this run, we have selected a nucleation efficiency ϵ of 0.5, which can be considered as minimal (Isaac et al., 1983) and, since no H_2O_2 measurements were available, we consider oxidation of sulphur dioxide by ozone only. In run II, to study the effects of increasing the nucleation efficiency, we set $\epsilon = 0.9$ which is probably appropriate for convective clouds (Jensen

EXPERIMENT		OXIDATION MECHANISM	PRECIPITATION
I	0.5	O_3	yes
II	0.9	O_3	yes
III	0.5	$O_3 + H_2O_2^{(1)}$	yes
IV	0.9	$O_3 + H_2O_2^{(2)}$	yes
V	0.9	$O_3 + H_2O_2^{(2)}$	no

50 ppbv of O_3 . (1) 1 ppbv of H_2O_2 . (2) 3 ppbv of H_2O_2 .

Table 31. Parameters of numerical experiments.

and Charlson, 1984). The importance of oxidation of SO_2 by hydrogen peroxide is explored in Simulation III, while in run IV we examine the consequences of both high nucleation efficiency and the presence of hydrogen peroxide. Finally, since the particular cloud for which the cloud water sample was collected did not precipitate, in run V we repeat the simulation of run IV but for a cloud in which the formation of precipitation is artificially suppressed.

Model output consists of vertical and horizontal sections at selected levels, of nitric acid vapour, sulphur dioxide, ammonia, hydrogen peroxide and sulphate aerosols. The concentration of each of these species associated with air, cloud water and rain water, are presented using the concept of potential partial pressure (see Daum et al., 1983). We also display the concentration in cloud and rain water, of hydrogen, ammonium, nitrate and sulphate ions. In addition to these, to facilitate the interpretation of the results, various budget parameters, average horizontal fluxes, mass distribution in the vertical and wet deposition at the surface are available at each time step.

(3.4) Results

The time evolution of the sulphur dioxide air concentration is depicted in Fig. 3.8, for run I. The dashed curve delineates the cloud boundary, while the solid curves represent isopleths of SO_2 in the air, expressed in ppbv. Because for all runs, the pH of both cloud and rain

Fig. 3.8. Time evolution of sulphur dioxide air concentration in the xz plane at $y = 5.81$ km. Run I.

water were rather low, the dissolved SO_2 is only a small fraction of the concentration found in the gas phase, and the isopleths in Fig. 3.8 are representative of total SO_2 (air + cloud + rain). Since the dynamics of the precipitating and non-precipitating clouds do not differ greatly, Fig. 3.8 is appropriate for all runs. It is also seen from this figure that the SO_2 is transported upward in response to the updrafts associated with cloud formation. It is pertinent to mention that the downdrafts on the right hand side of the cloud do not significantly reduce the concentration at low levels below pre-cloud values. This is currently included in parameterization schemes describing the effects of cumulus clouds in redistributing atmospheric pollutants vertically (Cho et al., 1984; Gidel, 1983). Our results suggest that this is not a dominant mechanism. On the other hand, it can be easily seen from the same figure, that at the end of its life cycle, the cloud leaves a column of air with a significantly higher SO_2 concentration than that in the surrounding air. This mechanism, termed as "the recycling of atmospheric air by cumulus clouds" (Cho et al., 1984) appears to be here a more important process.

A more quantitative description of the cumulus transport of SO_2 can be obtained from Fig. 3.9. In this figure, we display the horizontally averaged SO_2 vertical flux over the whole domain, as a function of altitude, at five minute intervals. One sees, that the flux increases during the cloud formation stage (up to 900 s) and decreases during the dissipation stage when downdrafts even generate a negative (downward) SO_2

Fig. 3.9. Horizontally averaged sulphur dioxide vertical flux at 5 minutes intervals. Run I.

flux. It is also seen that during the early stages of its lifetime, the cloud behaves like a device which pumps polluted air from the lower atmospheric layers to upper levels, as illustrated by the parabolic shape of the curves in Fig. 3.9. We note that the flux does not reach its maximum value at cloud base (1350 m), but at a level which roughly corresponds to the middle of the cloud. The efficiency of this mechanism can be estimated by calculating the fraction of SO_2 mass which is transported from the lower part of the atmosphere to higher levels. Thus, we have calculated the fraction of the total amount of SO_2 in the domain, below the 2450 m level, which is transported upward across this level during the life time of the cloud (32 minutes of simulation time). We found that this fraction is about 1%. This suggests, depending on their frequency of occurrence and fractional coverage, that this type of cloud may contribute significantly to the vertical transport of SO_2 . The above figure does depend on the size of the domain, but we note that the fractional horizontal area occupied by the simulated cloud was about 10% of the domain, while observed cloud coverage at North Bay was about 20% suggesting an overall upward transport by clouds of about $4\% \text{ h}^{-1}$.

Isaac et al. (1983) described the vertical transport of pollutants by clouds by mean of a "cloud vertical transport ratio (VTR)". This parameter is defined as the ratio of the volume of air pumped through the cloud base, to the volume of the sub-cloud air. Based on hourly weather records and on simplifying assumptions concerning the vertical motion

field and cloud lifetime, they calculated a VTR of about $30\% \text{ h}^{-1}$ for summer cumulus clouds occurring at North Bay. In this work, we found that the fraction of sub-cloud SO_2 pumped through cloud base during the 32 minutes of simulation time is 0.1%. This difference occurs because in their calculations, these authors have selected a constant and uniform average updraft speed of 1 m s^{-1} at cloud base, which is too large to be representative of the cloud simulated here, where most of the cloud base surface was subject to downdrafts. This emphasizes that the description of the active updraft area for a given cloud type is critical (Ritter, 1984).

Fig. 3.10 shows vertical cross sections of the nitric acid vapour concentration at different times. As we did not vary parameters related to nitric acid vapour scavenging, the distribution of HNO_3 is identical for runs I - IV. Because HNO_3 is assumed to be instantly scrubbed by the cloud water, its interstitial concentration is zero, and the isopleths within the cloud boundary represent cloud-dissolved HNO_3 . Outside the cloud, these curves are isolines of the gas phase concentration. We see that like SO_2 , nitric acid is advected and diffused upward mainly within the cloud volume, during the early stages of the cloud. However, subsequent to the formation of precipitation, rain scavenging becomes sufficiently important that nitrate is transported back down. This is illustrated by the descent of the 1 ppbv isopleth after 1040 s.

Fig. 3.10. Time evolution of of nitric acid vapour concentration (ppbv) in the xz plane at $y = 5.81$ km. Run I. Within the cloud boundary the nitric acid is dissolved in the cloud water and the isopleths represent the equivalent air concentration.

The distribution of nitrate in the rainwater is depicted in Fig. 3.11 for the same vertical plane but for different times. It is evident that nitric acid is mostly scavenged by rain within the cloudy air as indicated by the shape of the contour lines of the rain-dissolved HNO_3 , which closely resemble those of rainwater content. The equivalent air concentration of nitrate in the precipitation near the surface is comparable to the concentration in the air; for example, at 1680 s, the ground level precipitation content is 0.4 ppbv of dissolved HNO_3 , which is about 40% of the concentration found in the air at this level.

Following the same technique as above, we have calculated an overall upward transport of HNO_3 across the 2250 m level of $2.4\% \text{ h}^{-1}$. The downward transport of rain-dissolved HNO_3 accounts for the difference with what we previously found for SO_2 ($4\% \text{ h}^{-1}$); the wet deposition of nitrate is equivalent to a downward transport of $1.6\% \text{ h}^{-1}$.

An important question in the study of acidic precipitation is the relative importance of the various mechanisms by which acidity is generated in rain. In order to gain a quantitative understanding of this, we have calculated the percentage of HNO_3 incorporated into the precipitation which is the result of in-cloud scavenging and the fraction which is the result of below-cloud scavenging. After 32 minutes of simulation time, we found that roughly 70% of the nitrate was incorporated into rain by in-cloud scavenging while the remaining 30% was due to

Fig. 3.11. Time evolution of nitric acid concentration (ppbv) dissolved in the rain water, in the xz plane at $y = 5.81 \text{ km}$. Run I.

below-cloud scavenging of gaseous HNO_3 . This emphasizes the importance of in-cloud processes.

Vertical sections of sulphate aerosol concentration in the air for run I are presented in Fig. 3.12. The strong vertical gradient at cloud base is the result of the mass transfer by nucleation of the sulphate particulate matter in the air to the cloud water. As air enters cloud base, a fraction of its sulphate mass is assumed to be nucleated by cloud droplets, while the other portion remains in the interstitial air. Subsequently, the air is advected and diffused within the cloud by the turbulent flow field. It is clear that the sulphate mass in the air has a minimum value within the cloud. The effects of horizontal mixing and convergence are apparent if we consider the time evolution of the 0.8 ppbv isopleth in the same figure. During the cloud formation stage, the interstitial concentration of sulphate increases at higher levels within the cloud, as a result of horizontal entrainment. Subsequently, when the updrafts at cloud base become negligible ($t > 1040$ s), the sulphate is gradually mixed with the environmental air, leading to a more uniform distribution of aerosol mass in the horizontal.

Fig. 3.13 illustrates how the sulphate particles dissolved in the cloud water are propagated and distributed within the cloud, for run I. The aerosols are incorporated in the cloud water at cloud base by nucleation and are transported vertically by the airflow. This process

Fig. 3.12. Time evolution of sulphate concentration in the air (ppbv) in the xz plane at $y = 5.81$ km. Run 1.

Fig. 3.13. Time evolution of sulphate concentration dissolved in the cloud water (ppbv) in the xz plane at $y = 5.81$ km. Run I.

takes place mainly during the cloud formation stage (about 800 s). After this, the updraft is no longer sufficient to maintain the required mass flux at cloud base and scavenging by rain gradually reduces the mass of the cloud-dissolved sulphate. The importance of this mechanism is indicated in Fig. 3.14 where up to 0.2 ppbv of sulphate associated with rain can be detected. Due to the low pH of the water substance, oxidation does not contribute significantly to the sulphate mass in run I (here we only consider oxidation of S(IV) by O_3).

In run II the nucleation efficiency was increased from 0.5 to 0.9. The sulphate concentration in the cloud water (Fig. 3.15) simply increased in the same proportion. In run III, it is assumed that H_2O_2 is initially distributed in the vertical in the same way as HNO_3 and NH_3 (see Fig. 3.4) with a surface concentration of 1 ppbv. Comparing the sulphate concentration in cloud in this run (Fig. 3.16) with that from run I (Fig. 3.13) it is seen that as the cloud develops the importance of oxidation by H_2O_2 increases. By about 1040 s the sulphate concentration is about 0.6 ppbv higher throughout most of the cloud and maximum concentrations are in excess of 1.2 ppbv compared to 0.6 ppbv in run I, suggesting that at least under these conditions in-cloud oxidation may be important. In run IV a nucleation efficiency of 0.9 has been selected, and we have assumed an initial H_2O_2 distribution having the same shape than that of run III but with a ground level concentration of 3 ppbv. This value may also be considered representative of a remote air mass (Graedel and Weschler,

Fig. 3.14. Time evolution of sulphate concentration dissolved in the rain water (ppbv) in the xz plane at $y = 5.81 \text{ km}$. Run 1.

Fig. 3.15. As Fig. 3.13 but for Run II.

Fig. 3.16. As Fig. 3.13 but for Run III.

1981). Not surprisingly, we see in Fig. 3.17 much higher sulphate concentrations with maximum values exceeding 2.5 ppbv at 800 s. This value exceeds by a factor 5 the concentration of sulphate in the environmental air at this level. Comparing the values in Fig. 3.17 with those from run II we again see that the sulphate produced by oxidation in the cloud is greater than that resulting from nucleation throughout much of the cloud and for a significant portion of the cloud lifetime.

Fig. 3.18, taken from run V, shows how non-precipitating small cumulus clouds may act as an important source of sulphate in the air, as illustrated by the evolution of the shaded area. This sulphate has been nucleated at cloud base and generated within the aqueous phase by the oxidation of S(IV) by H_2O_2 and released in the air by evaporation of the cloud water. It is also seen from the same figure that this simulation leaves the environment significantly modified after cloud dissipation.

The influence of the various microphysical processes on the sulphate budget of the cloud is shown in Fig. 3.19 for run I. In this figure, the symbol T denotes the cumulative amount of mass transferred in a given direction; for example, T_{ac} is the cumulative mass of sulphate transported from air to cloud by the nucleation mechanism. The letters M_c and M_r represent the instantaneous mass of sulphate dissolved in the cloud or in the rainwater respectively. Thus, we have at any time, $M_c = T_{ac} - T_{ca} - T_{cr} + O_c$ and $M_r = T_{ar} + T_{cr} - T_{ra} - T_{rg} + O_r$.

Fig. 3.17. As Fig. 3.13 but for Run IV.

Fig. 3.18. As Fig. 3.12 but for Run V.

Fig. 3.19. Budget parameters for sulphate within the cloud.

Here T_{rg} is the cumulative mass of sulphate wet deposited at the ground by rain. O_c and O_r are the cumulative productions of sulphate in cloud and rain water by aqueous phase oxidation of SO_2 . The meaning of the other symbols is evident. It is of interest to note that during the first minutes of the simulation, nucleation accounts for nearly all of the mass of sulphate found in the cloud water. However, as time elapses, evaporation becomes so important that the major fraction of the cloud dissolved sulphate returns back to the air. For example, we have calculated that after 32 minutes of simulation time, 80% of the nucleated sulphate has been redeposited in the atmosphere by evaporation of cloudwater. Subsequent to the onset of precipitation, sulphate becomes attached to the rain via the cloud microphysical processes of autoconversion and accretion (T_{cr}). This contributes to the decrease of M_c and increase of M_r . After 18 minutes, the process of washout (T_{ar}) becomes effective and also contributes positively to M_r . We found that after 32 minutes of simulation time, washout accounted for 40% of the mass of sulphate found in precipitation, while in-cloud scavenging accounted for 60%. These values are similar to those found previously for nitrate. It is also seen that rain-laden sulphate reaches the ground after 24 minute, leading to wet deposition at the surface. We note that in run I, oxidation is not sufficiently important to appear in Fig. 3.19.

Fig. 3.20 shows the sulphate budget in relative units ($T_{ac} = 100$ for run I) after 32 minutes of simulation time, for runs I - V. For

Fig. 3.20. Schematics of sulphate budget parameters values (relative units) after 32 minutes of simulation time. Runs I-V; (a)-(e).

Fig. 3.20 (cont'd).

example, it is seen from Fig. 3.20a that for 100 units of sulphate nucleated in run I, 78 were returned to the air by evaporation of cloud, 11 were transferred to precipitation by microphysical processes, 8 were washed out and 11 were deposited at the ground by the rain. As mentioned above, in this run, oxidation does not contribute significantly to the mass of sulphate found in the cloud and in the rainwater. Fig. 3.20b shows that in-cloud processes in run II are simply increased by a factor 9/5 but the washout and oxidation processes remain unaffected. Results from run III (Fig. 3.20c) demonstrate the importance of hydrogen peroxide in producing sulphate within the cloud. It is seen in this case, that oxidation contributes more importantly to the mass of the cloud-dissolved sulphate than nucleation, with the consequence that the cloud now acts as a source of sulphate to the air. Net transfer of sulphate of cloud to air is even more important in run IV where both the nucleation efficiency and the initial concentration of H_2O_2 were increased (see Table 3.2). Here 179 units are transferred from the air to cloud but 340 are transferred from the cloud to air.

As during most of the cloud lifetime, liquid water exists mainly as cloud, and because the rainout of H_2O_2 occurs at equilibrium while its washout is irreversible, most of the dissolved H_2O_2 mass is associated with the cloud water. Consequently, in runs III and IV, the production of sulphate within the cloud is about a factor 10 greater than the production in the rainwater. For example, in run III, we have $O_C = 109$ and $O_R =$

11, while in run IV, $O_C = 265$ and $O_T = 33$. This shows that most of the aqueous phase oxidation of S(IV) in the presence of H_2O_2 occurs within the cloud, while the precipitation simply transports the sulphate downward. This demonstrates the importance of in-cloud oxidation processes. It is also seen in run V that oxidation provides a large input of 248 units of sulphate to the cloud water. It is noteworthy that this represents 2% of the total amount of SO_2 initially present in the computational domain, suggesting an overall in-cloud production rate of $8\% h^{-1}$.

The relative contribution of nucleation and oxidation to the amount of sulphate deposited at the surface by the rainfall, has received some attention in the past. For example, based on a simplified mesoscale kinematic storm model, Scott (1982) found that for a summer situation; in-cloud conversion processes accounted for 55-70% of the wet deposited sulphate. For the cloud simulated here, it is clear, from a comparison between runs I₀ and III (Fig. 3.20), that in-cloud oxidation of S(IV) by H_2O_2 can account for 56% of the total sulphate deposited at the surface by the rain, also demonstrating the potential importance of oxidation on the chemical composition of the rain.

Time evolution of the pH of the cloud water in run I is displayed in Fig. 3.21. The main features of these diagrams are the strong vertical gradients of cloud water acidity during the early stages of cloud

Fig. 3.21. Time evolution of the pH of cloud water in the xz plane at $y = 5.81$ km. Run I.

Fig. 3.22. Time evolution of the pH of rain water in the xz plane at $y = 5.81 \text{ km}$. Run I.

RUN	$\langle Q_c \rangle$ (g m ⁻³)	pH	[NH ₄ ⁺] (x10 ⁵ M)	[NO ₃ ⁻] (x10 ⁵ M)	[SO ₄ ⁼] (x10 ⁵ M)
I	0.42	4.27	5.01	3.87	1.56
II	0.42	4.18	5.96	3.87	2.77
III	0.42	4.16	5.01	3.87	3.00
IV	0.42	3.99	5.96	3.87	6.34
V	0.43	3.98	6.00	3.94	6.44
OBS	0.61	3.6	9.80	12.50	12.50

Table 3.2. Time averages of horizontally averaged concentrations of ionic species found in the cloud water at an altitude of 2250 m for the five numerical experiments and from chemical analysis of the cloud water sample collected at an altitude of 2073 m.

development due to dissolution of pollutants dissolved in the cloud drops near cloud base, followed by a steady weakening of the gradient. Since typical aircraft cloud penetrations are likely to fail to sample the initial stage of cloud formation, the concentrations of chemical species in a collected cloud water sample are likely to be more representative of the mature and dissipating stages of the cloud life cycle. However, since the initial stage of cloud formation is characterized by low liquid water contents, this probably does not introduce a significant bias in aircraft samples. Moreover, the weak gradients imply that the aircraft samples will not be highly sensitive to location and timing, making comparison with theory more reliable. Since rain first forms at about 800 s, the pH of rain is uniform within the cloud and decreases below cloud base due to washout and partial evaporation (Fig. 3.22). In the simulation, the rain at the surface had a pH as low as 3.6. This value decreased to 3.5, 3.3 and 3.1 for runs II, III and IV respectively, demonstrating the influence of increased nucleation and oxidation on the acidity of the rain.

Table 3.2 shows time averages of horizontally averaged cloud water content and concentrations of ionic species found in the cloud water, at an altitude of 2250 m, for runs I-V. An intercomparison between runs I, II, III and IV shows quantitatively how nucleation and oxidation processes influence the acidity and the sulphate concentration in the cloud water. For example, in run IV, concentrations of H^+ and SO_4^{2-} are

about a factor 2-4 greater than in run I. The difference in the average concentration of ammonium ion between these runs is simply due to variations of ϵ . We note that the concentration of nitrate does not change in runs I - IV since we did not vary parameters related to nitric acid vapor scavenging. As mentioned before, from a comparison of run IV and V it is evident that the occurrence of precipitation has relatively little influence on the cloud water chemistry.

The same table also shows the measured cloud water content and the chemical analysis of the cloud water sample collected on this day at an altitude of 2073 m. The simulated cloud water content agrees within 30% with the observed value and the pH of cloud water collected was 3.6, which is rather low and probably the signature of a polluted air mass. The concentration of ammonium, nitrate and sulphate ions are of the order of 10^{-4} M and the charges are balanced within 10%, which may be caused by errors in measurements or in the analysis.

Since several aircraft traverses were required to collect this sample, we consider it as corresponding to both time and horizontal average cloud water at this level, and the comparison with calculated concentrations given in Table 4 is appropriate. In all cases, the model underpredicts the concentrations of ionic species in the cloud water. In particular, in run I, the concentrations of ammonium nitrate and sulphate ions are underestimated by factors 1.9, 3.2 and 8.0 respectively. There is some experimental evidence that the aerosol aircraft filter

measurements may have underestimated the sulphate and ammonium concentrations below cloud base and that nitrate may have been present in the aerosol. To the extent that this is so this would tend to improve the agreement between the observations and the simulation.

Chapter 4

SUMMARY AND CONCLUDING REMARKS

To study the interactions between clouds and aerosol and gases which influence the acidity of cloud and rain, a model was formulated in terms of continuity equations for chemical species in the aqueous and gaseous phases. These equations were assumed to be representative of the average microphysical and chemical properties of the cloud and cloud environment within elementary well-mixed volumes. Processes occurring on smaller scales were parameterized in terms of these average properties. Our study was restricted to clouds where the ice phase is not present so the chemical processes within both cloud droplets and raindrops were treated with the methods and data of the chemistry of aqueous solutions. Since the chemical species of interest in this work are likely not to influence the dynamical and microphysical properties of the clouds, the cloud dynamics and chemistry were assumed to be uncoupled and the continuity equations for different pollutant species were solved separately from the equations of the cloud dynamics.

A simplified description of cloud chemical processes and scavenging has been given. We have considered the detailed solution chemistry of SO_2 , HNO_3 , NH_3 , CO_2 , O_3 and H_2O_2 gases and the oxidation of S(IV) by O_3 and H_2O_2 . It is currently believed that these two oxidation mechanisms are important pathways for aqueous production of S(VI) in clouds (Schwartz, 1984). Other oxidation mechanisms of atmospheric S(IV) such as: catalysed oxidation by transition metal ions (Hoffmann and Jacob,

1984; Martin, 1984); direct reactions of S(IV) with oxidizing free radicals (Chameides and Davis, 1982) and oxidation by oxides of nitrogen (Nash, 1979; Lee and Schwartz, 1982; Martin et al., 1981; Chang et al., 1981) may be important but are not well understood and were omitted from this study.

Other chemical reactions such as the aqueous production of HNO_3 due to catalysed reactions of NO_x in cloud and rain water (Lee and Schwartz, 1981) or in-cloud generation of H_2O_2 (Heikes et al., 1982) are also possibly important. Basically for the same reasons as above, these mechanisms were not considered here.

Based on gas solubilities, mass transfer coefficients, drop sizes and terminal fallspeeds relative to the air, we have shown that the simplifying concept of equilibrium scavenging can be applied to the rainout of gases of interest in our study. Due to large drop sizes involved, the washout of highly soluble gases such as nitric acid vapour, ammonia and hydrogen peroxide was assumed irreversible. Because of their relatively low solubilities, the washout of sulphur dioxide, carbon dioxide and ozone, was described in term of the concept of equilibrium scavenging.

We also suggested a scheme for calculating the nucleation scavenging of aerosol particulate matter and proposed a simple but appropriate

formula for calculating the pH of both cloud water and rainwater within the cloud.

In order to understand the transport and transformation processes in both precipitating and non-precipitating cumulus clouds, and to investigate the modification of pollutant concentration in the local cloud environment, fully three dimensional simulations of the chemistry of clouds have been undertaken. Information regarding the wind field, cloud and rain water distribution and cloud microphysics, was obtained from a three-dimensional, dynamic convective cloud model (Yau, 1980) and was processed by the cloud chemistry model.

As a first application, the model was used to simulate the chemistry of a cloud for which some cloud environment and cloud water chemistry measurements were available (Isaac et al., 1983; Leitch et al. 1983). We found that the cloud being simulated left an air column with a significant higher SO_2 concentration than the surrounding air at the end of its life cycle. We also noted in this case that the transport of clean air to the polluted sub-cloud layer by downdrafts was not particularly significant. Our calculations also showed that about 1% of the sulphur dioxide in the computational domain below 2 km was transported above this level during the lifetime of the simulated cloud. Taking into account the spacing of clouds on that day results in an average upward transport across the 2 km level of about $4\% \text{ h}^{-1}$. Calculation of the SO_2 transport across the cloud base level (1350 m), showed that less than 1% of the SO_2 in the

sub-cloud layer is transported above. This is considerably less than values suggested by other investigators (Isaac et al., 1983), demonstrating that the correct specification of the active updraft area is critical. Due to the downward transport of nitric acid by the falling rain, the average upward transport of HNO_3 across the 2 km level was reduced to $2.4\% \text{ h}^{-1}$. It has been shown that the downward transport of rain-dissolved HNO_3 ($1.6\% \text{ h}^{-1}$) could account for the difference with SO_2 . Detailed budget calculations of nitrate and sulphate lead to the conclusion that 60-70% of the mass of the sulphate and nitrate deposited at the surface in rain is generated by in-cloud processes, the remaining amount being washed out below cloud base. It was also shown that both nucleation and oxidation by H_2O_2 may strongly influence the sulphate budget and acidity of the cloud and rain water. For example, we found that in the presence of 1 ppbv of hydrogen peroxide in the sub-cloud layer, nucleation and oxidation each account for about 50% of the sulphate in the rainfall. The sulphate concentration in the air had a minimum within the cloud boundary because of nucleation scavenging, and during the dissipating stage of the cloud the sulphate concentration in the cloud environment may be significantly modified.

Comparisons between predicted and measured ionic concentrations in the cloud water indicated that the model underpredicted the cloud water sulphate concentration by factors ranging from 1.5 to 6 depending on the assumptions of nucleation efficiency and H_2O_2 concentration. However, it

still remains to be shown by more extensive comparisons between observations and simulations for several cases that the model is an effective tool to aid in the interpretation of the observed results.

There are a number of appropriate modifications and revisions of this work that may be considered. Thus, even though we believe the aqueous-phase chemical processes modelled here are of primary importance in cloud and precipitation chemistry, other interesting alternatives such as free radical aqueous-phase chemistry remain to be investigated (e.g. Chameides and Davis 1982, 1983; Schwartz, 1985) and our cloud dynamics/chemistry framework could eventually be modified to study these processes. It is also well known that the ice-phase can play an important role in both precipitating and non-precipitating clouds at mid-latitudes. Thus, it should be possible to apply the experimental results of Iribarne et al. (1983) to simulate the effects of the ice-phase on the chemistry of clouds. In this case, an existing version of the cloud model including the ice phase (MacPherson, 1981) would be used to provide the additional fields related to the presence of ice. By driving the chemistry model with the output from a modified version of the dynamical cloud model (Yau and Michaud, 1982), the model may be easily extended to simulate the influence of a cumulus ensemble.

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