A Modeling Study of the Effects of Ice-Phase Microphysical Processes on Trace Chemical Removal Efficiencies

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ABSTRACT


A simple cloud-chemistry model has been developed to study the effects of specific microphysical processes of precipitation formation and scavenging on the efficiency with which clouds remove trace chemicals from the atmosphere. The model is designed to let an isolated precipitation particle fall through the mixed-phase zone of a steady-state background cloud derived from the ascent of a Lagrangian parcel in which given mixing ratios of SO₂, CO₂ and NH₃ are in equilibrium with the aqueous phase. The precipitation particle is allowed to acquire water mass by both vapor deposition and accretion of supercooled cloud water and solute content by gaseous entrapment in rime ice, as parameterized from prior laboratory experiments.

The concept of a relative removal efficiency has been employed to identify the important microphysical fractionation processes within the cloud. The model calculations show that the removal efficiencies of the chemical constituents in the cloud nuclei and soluble trace gases are controlled largely by the accretional growth process. Even with modest solubilities, a trace gas such as SO₂ is estimated to be removed much more efficiently than is water vapor via cold-cloud precipitation because of substantial entrapment of the gas during rime ice formation.

RESUME

Un module simple de la chimie des nuages a été développé pour étudier les effets des processus spécifiques de la précipitation (son déclenchement et la collecte de ses composants). Le module porte sur l'efficacité avec laquelle les nuages lessivent les composants chimiques rares de l'atmosphère. Le modèle est construit pour permettre une chute de gouttelettes isolées à travers la zone à phases mélangées d'un nuage stationnaire. Le nuage est créé par les parcelles d'air qui s'élèvent dans un mode Lagrangien, les rapports de mélange des composants (SO₂, CO₂, NH₃) restant en équilibre avec la phase de l'eau.

Selon la paramétrisation avec les mesures expérimentales, les gouttelettes peuvent s'accroître par dépôt de la vapeur d'eau, et par combinaison avec l'eau surfondu et les contenus de soluté en interceptant le gaz dans le givre.

L'efficacité de collecte des composants chimiques est un concept employé pour identifier les
processus microphysiques importants dans les nuages. Les calculs montrent que l'efficacité des composants chimiques dans les germes et dans les gaz rares de soluté est presque complètement contrôlée par le processus d'agglomération. Même avec des solubilités qui ne sont pas très grandes, on estime que le gaz SO$_2$ est collecté beaucoup plus rapidement que la vapeur d'eau par la précipitation dans le nuage surfondu, parce que la plupart des gaz sont interceptés pendant le givrage.

INTRODUCTION

Clouds are instrumental in removing both water and other trace substances from the atmosphere. Clouds are the places in the atmosphere where the phase transitions of water take place, where water vapor is converted into precipitable water, and where a variety of physical and chemical transformations occur that are not possible through gas-phase processes alone (Hegg, 1985; Lamb et al., 1987). Thus, clouds can be thought of as macroscopic entities which “process” atmospheric air, filtering out certain portions of the microscopic components (water and trace chemicals) contained in the air and depositing them on the ground in precipitation (Engelmann, 1971, 1988).

The effectiveness with which clouds perform this removal function depends both on the amount of air processed and on the particular set of microphysical processes responsible for cloud and precipitation formation. Determination of absolute removal efficiencies, as when trying to estimate precipitation efficiency, is particularly difficult because of the large uncertainties associated with measuring the fluxes of air through storm systems (Marwitz, 1974; Scott, 1982; Lesins and Lin, 1986; Rutledge et al., 1986). However, no matter how complicated or uncertain the kinematic structure of a storm may be, the air being processed simultaneously carries both the water vapor, from which the cloud particles and precipitation form, and the other trace substances in given proportions. To a reasonable first approximation, ratios of the fluxes of the various trace substances through the storm are relatively insensitive to the amount of air processed. Thus, with some sacrifice of information content, ratios of absolute removal efficiencies can be determined more readily and with less ambiguity than can the absolute efficiencies themselves. With the ambiguous macroscopic part of the problem virtually eliminated, the removal efficiency ratio serves as a direct measure of chemical fractionation resulting from the microphysical and chemical processes active in the storm.

The efficiencies with which various trace chemicals are removed from the atmosphere by any particular storm are related to each other and to the precipitation of water vapor removal efficiency (Dingle and Lee, 1973; Engelmann, 1988; Hegg and Hobbs, 1988). Such relationships are often expressed in terms of enrichment factors, which are defined as the ratio of the concentrations of two compounds in one phase (typically precipitation) to their ratio in another phase (pre-storm air). An example is the study of Meszaros and
Szentimrei (1985) to distinguish the in-cloud processing of sulfate and lead. Engelmann (1988) has used water vapor as the reference compound to show that the natural variability of the scavenging ratio, a crude measure of absolute removal efficiency, is thereby reduced. As shown in the next section, enrichment factors based on water vapor as the reference compound are identical to Engelmann’s “normalized scavenging ratios” and therefore to the ratios of the absolute removal efficiency of the compound in question to that of water vapor. We prefer to call this particular type of enrichment factor a “relative removal efficiency” since it measures the effectiveness of the cloud in processing the specified chemical species relative to that in processing water vapor into precipitation, the carrier of the trace chemical to the surface.

The overall relative removal efficiency of a storm is comprised of several mechanistic steps that parallel the evolution of precipitation. As we conceptually follow a parcel of air through a storm, we note that the relative concentrations of the specified compound and water will change as cloud drops and precipitation form and grow. If the trace compound existed originally in the particulate phase, perhaps in a cloud condensation nucleus, for instance, dilution will result in a time-dependent concentration ratio. If it originally existed as a gaseous component in Henry’s law equilibrium with the aqueous phase, the aqueous phase concentration (and therefore enrichment factor) will vary with temperature and drop pH (Lamb and Chen, 1988). Subsequently, as precipitation develops, additional possibilities for fractionation exist, particularly within mixed-phase regions of the cloud, where precipitation is often initiated. The Bergeron process, an effective mechanism for converting cloud water mass to large precipitable ice particles is a low-temperature distillation process which tends to block the interphase transfer of cloud water solute (Borys et al., 1983). On the other hand, the hydrodynamic collection of cloud water by the sedimenting precipitation elements is an effective interphase transfer mechanism which tends to preserve the concentration ratios. Overall, precipitation microphysics generates a “bottleneck” to the removal of water and trace substances (Greenfield, 1957; Slinn, 1974; Pruppacher, 1986; Lamb et al., 1987). Under ideal conditions such microphysical limitations to trace chemical removal are evident in field data (Borys et al., 1983; Hegg and Hobbs, 1988; Mitchell and Lamb, 1989).

In this paper, we formulate a cloud-chemistry model that allows us to assess the impacts of various microphysical processes on the overall removal of trace substances by precipitating clouds. Emphasis is placed on precipitation formation by vapor deposition and cloud water accretion in supercooled, mixed-phase cloud and on specific scavenging mechanisms which have not been explored previously in a cloud-scale context. In particular, we take into account laboratory findings of the partial expulsion of dissolved trace gases during the riming process (Iribarne et al., 1983; Lamb and Blumenstein, 1987; Iribarne and Physhnov, 1988). The overall goal is to quantify the mechanistic links
that exist between the microphysics of precipitation formation and the removal efficiencies of specific trace chemicals from the air. In the next section we provide a historical basis for our use of the relative removal efficiency. Then, we describe the model and use it to show that the accretional sweepout of supercooled cloud water can be an effective process by which soluble trace gases are removed from the atmosphere.

MEASURES OF REMOVAL EFFECTIVENESS

Various concepts have been employed in the past for estimating the wet deposition flux of specific atmospheric constituents given their concentrations or mixing ratios in pre-storm air. The utility of any single-parameter relationship between storm input and output parameters lies in the simplification made of inherently complicated systems. However, as pointed out by Barrie (1985), caution must be exercised to ensure that the air in which the predictor value is determined is representative of the air processed by the storm.

The cloud system may be portrayed to first approximation as a steady-state macroscopic processor which draws in air through the base and expels it near the top, as depicted in Fig. 1. In general, the air passes through three distinct zones characterized by all-liquid cloud particles, a mixture of liquid and solid particles, and all-solid particles. Due to the microphysical processes active during cloud and precipitation formation, a certain fraction of each trace chemical constituent $i$ contained in the inflow becomes incorporated into the precipitation elements. This fraction contributes simultaneously to the wet deposition flux, shown by the arrow pointing toward the surface, and to the removal of species $i$ from the air.

The scavenging ratio, earlier termed a washout ratio (Engelmann, 1971), is one measure of the overall processing ability of the storm. It has been used in a variety of contexts by a number of workers (e.g., Engelmann, 1971, 1988; Gatz, 1977; Scott, 1981; Barrie, 1985; Davidson et al., 1987; Wolff et al., 1987). If $C$ represents the concentration of a substance in the condensed phase (precipitation) and $n$ the concentration of the substance in the cloud-free air, then the volumetric or concentration-based scavenging ratio is simply

$$W = \frac{C}{n} \quad (1)$$

It is often more convenient to work with mixing ratios, so a mass-based scavenging ratio $w$ may also be defined, which Barrie (1985) has shown to be related to the volumetric scavenging ratio through:

$$w = \frac{\rho_A}{\rho_L} W \quad (2)$$
where $\rho_A$ and $\rho_L$ are the densities of air and liquid water (precipitation), respectively. While both $w$ and $W$ are claimed to be dimensionless (Slinn, 1977; Scott, 1981), it must be realized that different phases are being considered. Thus, the units of $w$ may be grams of air per gram of water, for instance.

While, the scavenging ratio is a first-order measure of the effectiveness with which a precipitating cloud or cloud system removes a substance from the air, a true removal efficiency would have to take pollutant mass fluxes and storm flow fields into account (Scott, 1982). This may be seen by considering an idealized storm, which processed a total of $N_{\text{air}}$ moles of air over its lifetime. If the mean mole fraction (a molar mixing ratio) of substance $i$ in the air was $y_i$, then the total influx of the substance was
Given some estimate of the deposition magnitude \( N_{i,\text{dep}} \), the removal efficiency may be defined as the ratio of the deposition and influx magnitudes:

\[
E_i = \frac{N_{i,\text{dep}}}{N_{i,\text{in}}} = \frac{y_i N_{\text{air}}}{N_{i,\text{in}}} \tag{4}
\]

Since the compound is carried to the surface in precipitation, the deposition magnitude, \( N_{i,\text{dep}} \), may be expressed in terms of condensed-phase parameters. Thus, if \( x_i \) is the average mole fraction of \( i \) in the precipitation that fell from the storm, then:

\[
N_{i,\text{dep}} = x_i N_{\text{H_2O,dep}} \tag{5}
\]

Therefore, the removal efficiency may also be expressed as:

\[
E_i = \frac{x_i N_{\text{H_2O,dep}}}{y_i N_{\text{air}}} \tag{6}
\]

While this expression contains information related to the input and output of the storm, as does the scavenging ratio, it also contains the generally inaccessible quantities, \( N_{\text{H_2O,dep}} \) and \( N_{\text{air}} \).

However, a second compound \( j \) may be similarly considered, leading to an expression which is identical in form to eq. 6. Moreover, essentially the same values for \( N_{\text{H_2O,dep}} \) and \( N_{\text{air}} \) can be used, since each constituent is borne by the same air processed by the storm. The ratio of the two removal efficiencies:

\[
\frac{E_i}{E_j} = \frac{x_i/y_i}{x_j/y_j} \tag{7}
\]

is thus independent of, or at least insensitive to the precipitation amount and the flux of air through the system.

A slight rearrangement of eq. 7 shows that the ratio of removal efficiencies can also be identified with chemical fractionation. As written, eq. 7 is based on the ratio of a given compound existing in two different phases (precipitation and air). Since this expression may also be written as:

\[
\frac{E_i}{E_j} = \frac{x_i/x_j}{y_i/y_j} \equiv EF_{ij} \tag{8}
\]

it is clear that the ratio of removal efficiencies is also identical in concept to an enrichment factor \( EF_{ij} \), which provides a measure of how much substance \( i \) is enriched relative to substance \( j \) during a phase transition. This measure of fractionation is a direct reflection of the microphysical and chemical process occurring within the cloud, since the uncertain macroscopic features of the system, the mass fluxes, have already been cancelled out. The usefulness of the
concept of chemical fractionation during cloud and precipitation formation has been demonstrated by Meszaros and Szentimrei (1985) and Tanaka et al. (1980), among others.

We now identify the reference substance $j$ in the expression for enrichment factor (eq. 8) with the most important constituent in any storm, namely $H_2O$. Water is the trace substance in greatest abundance and the primary ingredient of the cloud elements and precipitation particles. Without it there would be no phase transformations and no fractionation. Early links between the wet scavenging of pollutants and the removal of atmospheric water were made by Engelmann (1971) and Dingle and Lee (1973). Most recently, Engelmann (1988) developed the concept further by referring to the ratio of trace chemical removal efficiency to water removal efficiency as a “normalized scavenging ratio”. In our nomenclature, this same concept can be obtained from eq. 8 by setting $j=H_2O$. Since to good approximation $x_{H_2O}=1$ (precipitation is primarily $H_2O$), and $x_i=C_i/C_L$, we therefore make the operational definition:

$$\epsilon_i \equiv \frac{E_i}{E_{H_2O}} = \frac{x_i/x_{H_2O}}{y_i/y_{H_2O}} = \frac{y_{H_2O}}{y_i} \cdot \frac{C_i}{C_L}$$

where $C_L=55.6$ mol $1^{-1}$ is the concentration of water in aqueous solution. Here we have identified the ratio of removal efficiencies, when water vapor is the reference substance, with a new parameter, $\epsilon_i$, which we call the “relative removal efficiency”. Each of the variables in eq. 9 is readily measurable in the field or obtainable through model calculations, as done in this paper.

MODEL DEVELOPMENT

The approach taken here is to develop a conceptually simple precipitation scavenging model which connects the microphysics of precipitation growth with the acquisition of trace chemicals by the precipitation elements. A “background” cloud is created through which individual precipitation particles are allowed to fall and simultaneously acquire water mass and various trace chemicals. Since the effects of a population of precipitation particles on the microstructure of the background cloud are parameterized, this model is inherently non-interactive. Nevertheless, the key processes which control the relative removal efficiencies can be identified with this approach. Moreover, such modeling provides an initial vehicle for carrying new laboratory findings into an atmospheric context.

Background cloud

The background cloud is represented by steady-state vertical profiles of various properties, the magnitudes of which were calculated by letting a Lagrangian air parcel ascend adiabatically from near the surface to about 6 km. En-
ergy and mass are conserved throughout the depth, and chemical equilibria are maintained between the gaseous species and the liquid drops, in accordance with Henry's law, as well as within the aqueous phase. Table I shows the various equilibria employed, along with data used in the van't Hoff equation to calculate the temperature dependencies of the equilibrium constants (Seinfeld, 1986, p. 200). Equilibria in the aqueous phase are constrained in the usual way throughout the use of the electroneutrality relation.

The specific set of conditions used for the calculations presented in this paper is shown in Table II. The air parcel starts its ascent near the surface.

**TABLE I**

Equilibria and thermodynamic data used in the background cloud model; $\Delta H$ is the enthalpy change of the reaction which is used in the van't Hoff equation (except for reaction 2) to calculate the temperature dependence to the equilibrium constant $K$

<table>
<thead>
<tr>
<th>Equilibrium reaction</th>
<th>$\Delta H$ (J mol$^{-1}$)</th>
<th>$K_{298 K}$ (M or M atm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$</td>
<td>$5.587 \cdot 10^4$</td>
<td>$1.068 \cdot 10^{-14}$</td>
<td>$^*$2</td>
</tr>
<tr>
<td>2. $\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2\cdot \text{H}_2\text{O}$</td>
<td></td>
<td>$3.436 \cdot 10^{-2}$</td>
<td>Harned and Davis (1943)</td>
</tr>
<tr>
<td>3. $\text{CO}_2\cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$</td>
<td></td>
<td>$7.641 \cdot 10^3$</td>
<td>$^*$2</td>
</tr>
<tr>
<td>4. $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$</td>
<td></td>
<td>$1.486 \cdot 10^4$</td>
<td>$^*$2</td>
</tr>
<tr>
<td>5. $\text{NH}_3(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\cdot \text{H}_2\text{O}$</td>
<td>$-3.402 \cdot 10^4$</td>
<td>$5.635 \cdot 10^1$</td>
<td>Dasgupta and Dong (1986)</td>
</tr>
<tr>
<td>6. $\text{NH}_3\cdot \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$</td>
<td></td>
<td>$3.662 \cdot 10^4$</td>
<td>$^*$2</td>
</tr>
<tr>
<td>7. $\text{SO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{SO}_2\cdot \text{H}_2\text{O}$</td>
<td>$-2.634 \cdot 10^4$</td>
<td>$1.250$</td>
<td>Maahs (1982)</td>
</tr>
<tr>
<td>8. $\text{SO}_2\cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$</td>
<td>$-1.633 \cdot 10^4$</td>
<td>$1.33 \cdot 10^{-2}$</td>
<td>Maahs (1982)</td>
</tr>
<tr>
<td>9. $\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$</td>
<td>$-1.191 \cdot 10^4$</td>
<td>$6.463 \cdot 10^{-8}$</td>
<td>Maahs (1982)</td>
</tr>
</tbody>
</table>

*1 Use $K \text{ (in M atm}^{-1}) = \exp \left( \frac{5493.0}{T} - 32.28 + 0.03515 \times T \right)$ (Harned and Davis, 1943).

*2 Values and original references are listed in Seinfeld (1986).

**TABLE II**

Model conditions in the background cloud

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Surface</th>
<th>Cloud base</th>
<th>Mixed-phase zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (mb)</td>
<td>1000</td>
<td>910</td>
<td>870</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>10</td>
<td>2.2</td>
<td>0</td>
</tr>
<tr>
<td>CCN concentration (m$^{-3}$)</td>
<td>$10^9$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$O mixing ratio (g kg$^{-1}$)</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ mixing ratio (ppmv)</td>
<td>332</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_2$ mixing ratio (ppbv)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$ mixing ratio (ppbv)</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
with a relative humidity of about 65% and continues dry adiabatically to cloud base, where the temperature is about 2.2°C and the pressure is 910 mb. The cloud drops form on $10^9$ m$^{-3}$ cloud condensation nuclei (CCN), each having a dry radius of 0.1 µm and composed of ammonium sulfate. This monodisperse population is immediately incorporated into and dissociated by the cloud water (nucleation scavenged). The use of more realistic specifications of aerosol size spectra might affect the results in quantitative detail, but not in substance. During the subsequent growth of the cloud drops, heterogeneous equilibria and mass balances are maintained with the given trace gases CO$_2$, SO$_2$ and NH$_3$.

Above the 0°C isotherm, the ice phase is allowed to develop in a way that generically accounts for the glaciation of the cloud and the formation of precipitation. The fraction of the total condensate that exists as ice is made to vary linearly from zero at 0°C to unity at -40°C, the top of the mixed-phase zone. The liquid-water mass mixing ratio is computed as the difference between that of the total condensate and that of the ice, yielding a maximum near the -15°C level. The vertical profiles of these condensate forms in the background cloud are shown in Fig. 2. The partial vapor pressure of water was

![Fig. 2. Vertical profiles of condensate mass mixing ratios used in the background cloud.](image)
relaxed linearly with temperature, from being equal to the saturation value with respect to liquid at 0°C to being equal to the saturation value with respect to ice at −40°C. This parameterization of the mixed-phase zone permits an ice hydrometer to grow by both vapor deposition and hydrodynamic collection of supercooled cloud water (riming).

*Precipitation growth and scavenging*

Individual ice particles, which serve as representative precipitation embryos, are “introduced” into the background cloud and allowed to fall at their terminal velocity. Along the fall trajectory, each particle is allowed to interact with its local environment; it acquires additional water mass by vapor deposition (ventilation adjusted) and hydrodynamic collection of supercooled cloud drops, and it gathers non-aqueous compounds by specific scavenging mechanisms.

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**Fig. 3.** Microphysical processes conceivably acting on an ice precipitation particle during its fall through a supercooled cloud.
Throughout the journey of the precipitation particle in the cloud, the amount and concentration of "solute" (whether soluble or not) is calculated both differentially and cumulatively. The relative removal efficiency for a particular chemical species is calculated from eq. 9.

The various microscale processes acting on the representative precipitation particle are schematically summarized in Fig. 3. As suggested by the broad arrow on the right-hand side, the ice particle grows in mass by water vapor deposition to the extent that the ambient vapor density of water, $\rho_{v,\infty}$, exceeds the saturation value, $\rho_{v,\text{ice}}(T_s)$, at the surface temperature $T_s$ of the ice particle. The value of $T_s$ is calculated from consideration of the total energy balance of the particle (a modification of the procedure given by Pellett and Dennis, 1974) and is generally greater than the ambient temperature $T_{\infty}$ because of the release of latent heat during vapor deposition and riming. Ventilation effects on the heat and mass transport are taken into account using the empirical formulation of Beard and Pruppacher (1971), as discussed by Pruppacher and Klett (1978, p. 443). With this adjustment for heat dissipation, the contribution of the mass growth rate due to vapor deposition is calculated from:

$$\left. \frac{dm}{dt} \right|_{\text{dep}} = 4\pi R_p D_v \left[ \rho_{v,\infty} - \rho_{v,\text{ice}}(T_s) \right] f_m$$

where $m$ is the instantaneous mass of the precipitation particle having an equivalent radius of $R_p$, $D_v$ is the diffusion coefficient of water vapor in air at the environmental conditions, and $f_m$ is the ventilation coefficient for mass transfer.

The other major process by which the precipitation particles acquire water mass is hydrodynamic collection. The rate of growth due to accretion of cloud water, with integrated liquid-water content LWC, is calculated using the continuous collection model in the form:

$$\left. \frac{dm}{dt} \right|_{\text{acc}} = \pi R_p^2 E_c v \times \text{LWC}$$

where $v$ is the fall speed of the precipitation particle relative to that of the cloud drops, computed as the mass-weighted average of the speed of an unrimed, vapor-grown crystal (Davis, 1974, as reported by Pruppacher and Klett, 1978, p. 340) and that of a graupel particle (Auer, 1972). The collection efficiency $E_c$ is a function of both the size of the precipitation particle and the sizes of the drops being collected. For simplification of the calculations, we use the values of $E_c$ derived theoretically for oblate spheroids by Pitter (1977). Aggregation, the hydrodynamic collection of ice particles, is not treated here.

When the cloud water is supercooled, the accretional growth process leads to the formation of rime ice on the precipitation particle. As indicated by the downward-pointing arrow in Fig. 3, the freezing of the cloud drops on contact
with the large ice particle may lead, at least partially, to the expulsion of volatile trace species previously in heterogeneous equilibrium with the liquid phase. The fraction of the originally dissolved amount which remains with the rime ice, that is, the entrapped fraction, has been measured experimentally in various laboratories and has been found to vary substantially with the type of gas (Iribarne and Pyshonov, 1988) and the environmental conditions, particularly the temperature (Lamb and Blumenstein, 1987). This model is used in part to explore the sensitivity of the removal efficiency to such microphysical fractionation processes, so a range of values and formulations for the entrapped fraction is used. In general, for a specified value of the entrapped fraction \( f \) at a particular temperature \( T \), the molar amount, \( \Delta N_i \), of solute added to the precipitation particle, because of the addition of water volume \( \Delta V_d \), is calculated from:

\[
\Delta N_i = f \cdot C_i \cdot \Delta V_d
\]  

(12)

where \( C_i \) is the molar concentration of species \( i \) in the supercooled drops just prior to collection. In this paper, particular emphasis is placed on the functional form for \( f \) given by Lamb and Blumenstein (1987) applicable to sulfur dioxide:

\[
f = (5.8 \times 10^{-3}) \cdot (T_0 - T) + 0.012
\]

(13)

where \( T_0 = 273.15 \text{ K} \) is the thermodynamic melting point. This parameterization simply states that the entrapped fraction is proportional to the supercooling at the time of collection. While this parameterization may or may not be applicable to other trace gases, we do assume that all of the volatile compounds behave similarly in this model. In order to compare this parameterization with others, such as those implied by the recent empirical findings of Iribarne and Pyshnov (1988), we have also run the model with \( f \) maintained at various values between 0.1 and 1 independent of temperature. Non-volatile compounds, such as sulfate, are always retained with the rime ice completely.

Other fractionation or scavenging processes are likely to be active in clouds and thus able to influence the relative removal efficiency. Two additional classes of microphysical process are also shown in Fig. 3. The central, vertical arrow suggests that trace gases may be taken up directly by the ice phase. While previous laboratory studies have indicated that hydrocarbons (Orem and Adamson, 1969), CO\(_2\) (Ocampo and Klinger, 1982), and SO\(_2\) (Sommerfeld and Lamb, 1986; Molina et al., 1987) can adsorb onto the surface of the ice, recent evidence suggests that some species (SO\(_2\), at least) may also be taken up in part by the bulk ice (Clapsaddle and Lamb, 1989). Although such sorption behavior is real and treatable in a cloud model such as this, no attempt has been made here to include the direct uptake of trace gases by ice. Similarly, despite some evidence for the reality and importance of aerosol scavenging (Vittori and Prodi, 1967; Prodi, 1976; Carstens and Martin, 1982), the pho-
etically enhanced scavenging of aerosol particles by ice growing by the Berge-
ron process is also not treated in this model at this time.

RESULTS AND DISCUSSION

The computed results from this model of an isolated precipitation particle falling through the given background cloud are presented in Figs. 4–7. The precipitation embryo started its fall through the cloud at the $-30^\circ$C level (pressure, 512 mb) as a vapor-grown oblate spheroid with an axial ratio of 1:10 and a mass-equivalent radius $R_0 = 100 \mu$m. The fallspeed of the ice particle against a background updraft speed assumed here to be negligible, increased gradually in response to its growth by vapor deposition and cloud water accretion, from 10 cm s$^{-1}$ initially to about 6 m s$^{-1}$ by the time it reached the melting level. Thus, most of the residence time in the cloud was spent in the cold, upper parts of the mixed-phase zone where it was growing slowly by vapor deposition in cloud containing small values of excess vapor density and liquid-water content. Once the crystal exceeded a radius of about 200 $\mu$m, the collection efficiency became appreciable, causing the riming growth rate to increase rapidly. Fig. 4 (dot-dashed curve) shows the fraction of the ice growth contributed by riming in each “layer” of the ice throughout its fall. At large particle sizes, toward the end of the fall trajectory the added mass was due almost entirely to riming. The contribution due to vapor deposition must become small near the

![Graph](https://via.placeholder.com/150)

**Fig. 4.** Differential concentrations of CCN and gaseous components in the precipitation particle at various stages in its growth. The fraction of water mass acquired in each differential layer through accretion is also shown (dot-dashed curve).
melting level since the driving force for the condensation, the difference in vapor pressures in equilibrium with liquid and solid, gradually vanishes. Computations were stopped when the precipitation particle reached the 0 °C level.

The differential, or “layer”, concentrations of the various ionic constituents are also shown in Fig. 4, as functions of the equivalent radius of the precipitation particle. No mechanisms for incorporation of solute into purely vapor-grown crystals have been included in this version of the model, so the concentrations of all chemical constituents are initially zero. As the particle grew beyond a radius of 200 μm, riming became a significant part of the growth and transferred significant solute amounts to the precipitation particle. The upper two solid curves in Fig. 4 give the concentrations of the CCN components, while the lower two curves show the concentrations of the dissolved gases SO$_2$ and CO$_2$. Although heterogeneous equilibrium was also maintained with NH$_3$, the relatively high NH$_4^+$ concentrations reflect the dominating effect of the ion balances that must also be maintained within the concentrated solutions arising during drop freezing. The tendency of the concentrations of the CCN constituent to increase toward the end of the growth period is due to the lower liquid-water content, or mean size of the cloud drops near cloud base (see Fig. 2), reflecting a simple dilution effect of the cloud water.

By contrast, the tendency of the concentrations of the gaseous constituents to decrease in the outer layers of the precipitation particle as it grows predominantly by riming is due to the relatively high temperatures in the base of the cloud and consequently low values of the entrapped fraction (c.f. eq. 13). This interpretation is borne out by using other parameterizations for the entrapped fraction $f$, the results of which are shown in Fig. 5 for dissolved SO$_2$. The solid curve is the same as that for S(IV) in Fig. 4 and reflects the variation when the temperature-dependent parameterization of Lamb and Blumenstein (1987) is used. The dashed curves show the effect of using various other temperature-independent value for $f$ between 0.1 and 1. The experimental findings of Iribarne and Pyshnov (1988), yielding a value for $f=0.66$, imply that substantially more S(IV) would be scavenged by the riming process, especially at higher temperatures. The sharp increase in [S(IV)] in the outer layer of large ice particles is due to the relatively high pH of the cloud water and consequently large solubility of SO$_2$ near cloud base, a result of the effective pH-buffering ability of the imposed ambient NH$_3$.

Although analysis of differential or layer concentrations, as presented in Figs. 4 and 5, is conceptually valuable and may even find application in field studies of hailstone growth (Knight et al., 1975; Federer et al., 1982), one normally collects precipitation for composite chemical analysis. The pertinent variables are therefore cumulative concentrations derived from integrations of the differential solute contents and water mass acquired by the precipitation particle from its origin ($R_0=100$ μm in our case). Direct comparison of the cumulative concentration of solute in the precipitation with the mixing ratio
of the parent species in the pre-cloud air yields a measure of the relative removal efficiency, as discussed in conjunction with eq. 9.

The relative removal efficiencies of the various components, computed from eq. 9, are plotted in Fig. 6 as functions of the temperature level at which the precipitation was conceptually “collected”. Recall that the precipitation embryo began its fall at the $-30^\circ$C level in the cloud. For comparison with the primary microphysical process of precipitation formation responsible for solute acquisition, the cumulative rime fraction of the precipitation particle is also shown (dot-dashed curve). Note that half of the mass of the precipitation particle was composed of rime ice by the time it reached the $-16^\circ$C level. Thus, there are strong increases in the cumulative concentrations and removal efficiencies of the various solute components following the onset of the riming process (near the $-20^\circ$C level). It is during this early state of precipitation growth that the trace chemical removal efficiency tends to be most sensitive to the precipitation growth mechanism.

During later stages of development, the precipitation particle tends to gather both water mass and solute content primarily from the riming process, so variations in the relative removal efficiencies reflect changes with temperature and level in the cloud of the concentrations of solute in the cloud water and in the temperature variation of the entrapped fraction. In this regime, the relative efficiencies with which the CCN components $\text{NH}_4^+$ and $\text{S(VI)}$ are removed
increase more toward the base of the cloud, where the liquid-water content is lower, while the relative efficiency of S(IV) removal is reduced in that region primarily because the entrapped fraction of dissolved SO$_2$ becomes small as the temperature approaches the melting point. Nevertheless, it is noteworthy that the actual magnitudes of the S(IV) relative removal efficiency remain much greater than unity, reflecting the relatively large solubilities of SO$_2$ in water in this temperature range when the solution pH is buffered by the presence of even small mixing ratios of NH$_3$.

Using an entirely different approach, Hegg and Hobbs (1988) calculated chemical scavenging efficiencies of sulfate and SO$_2$ which were each only about half the water vapor removal efficiency, implying relative removal efficiencies very much smaller than those obtained by our calculations. The reasons for the differences are certainly varied, but may be partially related to the larger riming fraction the precipitation in our model cloud experienced. It must also be realized that the precipitation scavenging processes in our model are decoupled from the background cloud and so the calculated relative removal efficiencies represent upper limits. As the absolute magnitude of the precipitation efficiency increases to realistic values, we should expect depletion of the chemical components in the cloud and hence reduced chemical removal efficiencies. Future efforts must therefore be directed toward the use of models in which the background cloud chemistry is coupled to the precipitation scavenging mechanisms.
It is also instructive to compare our model calculations with the normalized scavenging ratios obtained by Engelmann (1988) from a variety of field observations. Although field data are naturally scattered, they demonstrate that CCN constituents, sulfate in particular, tend to be removed with five to ten times the efficiency with which water vapor is removed, a range more consistent with our findings. At the same time, however, Engelmann finds that SO$_2$ is removed less efficiently than is water vapor. As pointed out by Engelmann, some unknown fraction of the S(IV) generally oxidizes to sulfate, a chemical process which simultaneously increases the apparent scavenging ratio (and removal efficiency) of the sulfate and decreases that of the SO$_2$. In our model SO$_2$ and sulfate are tracked as though they were chemically inert species. Permitting the S(IV) to oxidize to S(VI) in our model, while confusing the microphysical impacts we were trying to study, would have worked in the direction of better agreement with the field results.

In order to demonstrate the sensitivity of trace gas removal efficiency to the entrapment process, we have again employed alternative functional forms and values to the entrapped fraction $f$. These results are shown in Fig. 7, where it should be noted that the scale on the ordinate has been changed from that used in Fig. 6. The solid curve again shows the expected form of the SO$_2$ removal efficiency, based on cumulative concentrations, when the temperature-dependent parameterization of Lamb and Blumenstein (1987) is used. When $f$ is maintained at specific values between 0.1 and 1, as implied by the results of Iribarne and Pyshnov (1988), the dashed curves in Fig. 7 are obtained. Note

![Fig. 7. Effect of different parameterizations for the rime-ice-entrapped fraction $f$ on the calculated relative removal efficiency of S(IV).](image-url)
that the magnitudes of the SO$_2$ removal efficiencies become very large relative to water vapor removal as $f$ approaches unity. Again, it must be remembered that such relative removal efficiencies are upper limits and that no S(IV) oxidation has been included in this version of the model. Nevertheless, the potential importance of this particular microphysical process of fractionation, gaseous entrapment in rime ice, can be appreciated when it is realized that in models in which this ice-phase process is ignored, $f=0$ and the relative removal efficiency of SO$_2$ would also be zero. Alternative and potentially competitive processes of solute capture, such as direct gaseous sorption by growing ice, must also be considered before the overall impact of the ice phase on the cloud scavenging of trace chemicals can be assessed.

CONCLUSIONS

This conceptually simple model, in which individual ice precipitation particles fall through a cloud containing SO$_2$, CO$_2$, NH$_3$ and sulfate in equilibrium with a mixed-phase cloud, demonstrates some of the mechanistic links that exist between the chemical removal efficiency and the microphysical processes of precipitation formation and scavenging. The riming process is seen to be important in "cold" clouds for the acquisition of both water mass and trace chemical constituents contained in the cloud water. Depending on the ability of the rime ice to retain dissolved gases, the removal efficiency of volatile, but at least modestly soluble gases can be large compared with the efficiency with which water vapor is removed from the atmosphere. Nevertheless, because of gaseous expulsion during the phase change of the accreted cloud water, the relative removal efficiencies in cold clouds may be less than those in the warm clouds. The relative removal efficiency, the ratio of the trace chemical to water vapor removal efficiencies, is a powerful concept since it is insensitive to the complicated macroscopic structure of a storm while providing a direct measure of microphysical fractionation during precipitation formation.

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Note added in proof. An internal error associated with the computation of the relative removal efficiencies in Figs. 6 and 7 caused the original magnitudes to be excessively large. Although these figures have been replaced and are now accurate, the associated text is partially incorrect or misleading. Now, the actual magnitudes of the S(IV) relative removal efficiencies are less than unity, implying that SO$_2$ is removed from the atmosphere less effectively than is water vapor, a reflection of the finite, but limited solubility of SO$_2$ in acidic cloud water. Our calculated efficiency is less than those determined by Hegg and Hobbs (1988) and Engelmann (1988) by factors roughly equivalent to the measured entrapment fraction, a distinction that may stem from warm-cloud processes active in their cloud systems that are not accounted for here. The stated depletion of chemical components in the clouds by precipitation now appears to be a secondary effect. SO$_2$ can well be expected to be removed more effectively via in-cloud oxidation, a process to be included in a later model. Finally, the general conclusion expressed in the last paragraph of the paper should now state that the removal efficiency of a volatile, modestly soluble gas is likely to be less than, but generally comparable to the efficiency with which water vapor is removed from the atmosphere.