

A MECHANISM FOR HYDROCHLORIC ACID PRODUCTION IN CLOUD

GLENN K. YUE* and VOLKER A. MOHNEN

*Department of Atmospheric Science,
State University of New York at Albany, Albany, New York 12222, U.S.A.*

and

C. S. KIANG

*National Center for Atmospheric Research, †
P.O. Box 3000, Boulder, Colorado 80302, U.S.A.*

(Received 26 March, 1976)

Abstract. A theoretical model describing the general interaction between atmospheric trace gases, such as SO_2 , NH_3 , CO_2 and O_2 , chemical reactant gaseous product H_2SO_4 and hydrometeors containing NaCl is proposed to study a possible mechanism for HCl production in non-precipitating cloud and the determination of the pH value of cloud droplets.

Four different cloud droplet distributions have been used to estimate the upper limit of the amount of gaseous HCl released into the atmosphere resulting from the evaporation of cloud droplets. It is shown that the acid production and the amount of HCl released depend on the following factors: (a) the temperature of the cloud; (b) the oxidation rates; (c) the ambient concentration of SO_2 , NH_3 , and H_2SO_4 ; (d) the life cycle of the cloud; and (e) the liquid content of the cloud.

This proposed chemical model also predicts a pH value spectrum depending on the cloud droplet distribution. Field measurements for the dependence of pH value on particle size and spatial distribution of gaseous HCl are recommended.

1. Introduction

Recently there is a growing awareness of the acidity of precipitation produced by clouds in a polluted environment. This is due to the acid rain which has detrimental effects on local fishing industry, agricultural crops and forest ecosystem, and also because it has no country boundary. One country's industrial activity may produce acid rain in another country. Although in the field of air pollution scientists focus almost exclusively on the emission of SO_2 from burning of fossil fuel and the subsequently low pH value of the rain drop in the polluted atmosphere, H_2SO_4 is by no means the unique acid in the rain drop. As a matter of fact, more recently there is an increasing urgency to better understand the role of free HCl in the atmosphere due to the following reasons:

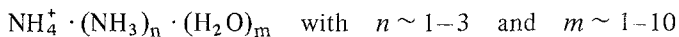
(a) HCl plays an important role in the air chemistry. Previous interest in the HCl problem resulted mainly from the research to explain the changing Na to Cl ratio from the ocean [1, 2]. Indeed, the general tendency of the increase of that ratio with distance from the coast can easily be explained by assuming the release of free HCl from cloud nuclei during their courses toward a continent. Currently attention has been given to the air chemistry of the stratosphere in which HCl will compete if present in the natural

* Present address is National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80302.

† The National Center for Atmospheric Research is sponsored by the National Science Foundation.

stratosphere with NO, OH, etc., in the catalytic destruction chain of O₃ (HCl + OH → H₂O + Cl, Cl + O₃ → ClO + O₂, ClO + O → Cl + O₂) [3].

(b) Positive small ions at tropospheric and lower stratospheric levels consist of clusters of the type:



depending on temperature and ambient (NH₃) and (H₂O) concentration. The presence of these ions in the atmosphere may induce reactions leading to the formation of aerosols, or at least to the existence of free NH₄Cl molecules whenever traces of NH₃ and HCl are in collisional contact with ions. Calculation shows that by assuming an ion density of 10³ cm⁻³ would result in an average lifetime for HCl in the order of 10 days (HCl → NH₄Cl). If NH₄Cl is absorbed by cloud droplets, the possibility of subsequent HCl formation and release cannot be excluded, i.e., some HCl could be continuously recycled. On the other hand, if aerosol NH₄Cl is formed, that may be a significant sink for atmospheric HCl.

(c) It is believed that most of the gaseous HCl molecules in the atmosphere is the end product of interactions between trace gases and hydrometeors. According to Duce [4] the annual production rate of HCl in a global scale through this mechanism is 6 × 10⁸ metric t. Because HCl is highly dissolvable, the subsequent absorption of HCl into the rain drops will further lower the pH value and increase the acidity of acid rain during the rain-out process. Since HCl is vitally linked with other trace gases in the atmosphere and the acidity of rain, a full understanding of HCl will be helpful in understanding the fate of other atmospheric trace gases and the sources of acid rain.

It is the purpose of this paper to suggest a model to estimate the upper limit of the amount of gaseous HCl released into the atmosphere resulting from the interactions between the trace gases and hydrometeors and the evaporation of cloud droplets. The proposed model includes both the liquid phase oxidation mechanism and gas phase oxidation mechanisms. In addition to the interactions between the trace gases such as SO₂, NH₃, CO₂ and O₂ and the hydrometeors containing NaCl, the model also introduces the interaction between chemical reactant gaseous product H₂SO₄ and the hydrometeors containing NaCl. However, it is important to point out here that the accuracy of this model is severely limited by insufficient parameters for most precursor reactions leading to the formation of HCl and governing its fate in the intricate atmospheric system. Though quantitatively our estimations are highly speculative, qualitatively we have identified some of the important parameters that govern the amount of HCl liberated from the evaporation of the cloud droplets, thus providing a framework for further studies in this interesting subject.

This proposed model is also utilized to determine the pH value of cloud droplets. Because of the introduction of the kinetic effect into the model, a pH value spectrum depending on the cloud droplet distribution is found.

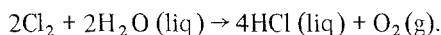
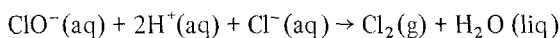
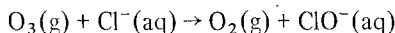
In Section 2, we briefly review various mechanisms proposed to study the production of HCl in the atmosphere. The pH value of the cloud droplets estimated by our model including both the liquid and gas phase oxidation of trace gases is presented in

Section 3. In Section 4 we utilize our proposed model to estimate the amount of HCl released from cloud droplets. Finally, we discuss the important factors for the production of HCl and recommend future field experiments on this subject.

2. Overview

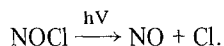
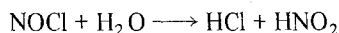
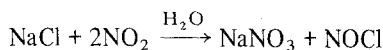
In this section, we briefly review various mechanisms proposed to study the production of HCl in the atmosphere.

Cauer [5] suggested that the oxidation of Cl by O₃ is responsible for the low pH values of precipitation. In his studies of atmospheric condensation nuclei, he assumes that the Na and Cl added to the atmosphere by bursting bubbles or breaking waves go through entirely different cycles. In the presence of small amounts of O₃ in the lowest strata of the atmosphere (0 to 100 μg m⁻³), those Cl ions contained in sea spray droplets may be oxidized to free Cl gas, which in turn, under the influence of sunlight and water vapor, can be hydrolyzed to form HCl. The proposed reaction scheme to form HCl can be summarized as follows:



However, these reactions are unlikely to happen in the atmosphere, because experimentally Kohler and Bath [6] have carried out simulated experiments and found that the reaction is insufficient to account for the observed geographical variation of Na to chloride ratio.

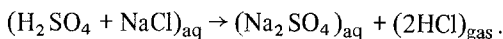
Later on the following route was suggested for converting particulate chloride to hydrogen chloride or Cl into the atmosphere [7]



However, Robbins *et al.* [8] did not observe the formation of nitrosyl chloride, thus the free HCl in the atmosphere cannot come from direct reaction between sea-salt particles and NO₂.

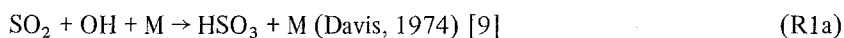
Based on experimental results, Robbins *et al.* suggested the reaction route via hydrolysis of NO₂ to form HNO₃ vapor followed by either adsorption of HNO₃ vapor by dry NaCl particle at low relative humidities, or by solution droplets containing NaCl when relative humidities were high. The final step is the chemical reaction of HNO₃ with NaCl leading to the desorption of hydrogen chloride, either immediately following the reaction or during subsequent evaporation of the droplets. Since the existence of gaseous HNO₃ in urban area is well recognized today, we do believe that this HCl-

formation mechanism in the presence of HNO_3 produced by gas phase oxidation process is one of the important mechanisms to form HCl and lower the pH value of the cloud droplets containing NaCl. However, among all the possibilities, the process most often quoted is summarized by the following chemical reaction sequence:

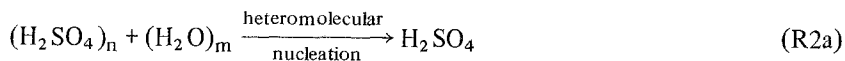


This leads us to the still controversial problem in atmospheric chemistry dealing with the production of SO_4^{2-} in liquid droplet through the oxidation of SO_2 . There are two possible pathways to produce SO_4^{2-} in aqueous solution droplet in the atmosphere. The most recognized pathway is the oxidation of dissolved SO_2 in liquid phase. However, the process involving the oxidation of SO_2 to form gaseous H_2SO_4 and followed by vapor transfer to the liquid droplet should also be considered.

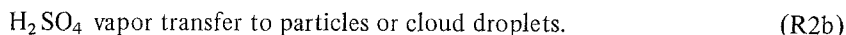
For gas phase oxidation, in the presence of third body, gaseous SO_2 can be oxidized in the atmosphere through the following schemes:



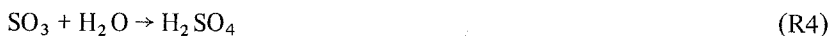
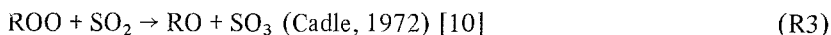
R1b steps have not been established yet, however the (R1a) is assumed to be rate determining for the formation of H_2SO_4 molecules.



droplets.

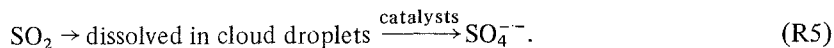


On the other hand, organic radicals can also be used to oxidize SO_2 :



followed by reaction (R3).

Most authors believe that in the lower troposphere, the most likely source of sulfate is through the oxidation of dissolved SO_2 in cloud droplets:



In the lower troposphere, NH_3 is probably one of the best candidates of catalyst for that reaction. In fact, the $\text{SO}_2 - \text{NH}_3 - \text{CO}_2 - \text{water}$ system has been treated by Scott and Hobbs [12] and recently by Easter and Hobbs [12] who also critically reviewed the published rate constants entering the reaction scheme.

In this paper, we estimate the amount of HCl production by considering $(\text{H}_2\text{SO}_4 + \text{NaCl})_{\text{aq}} \rightarrow (\text{Na}_2\text{SO}_4)_{\text{aq}} + (2\text{H}_2\text{O})_{\text{gas}}$ chemical reaction mechanism. Both liquid phase and gas phase oxidation of SO_2 to form SO_4^{2-} in liquid droplet will be considered.

3. Estimation of the pH Value of the Cloud Droplets

3.1. LIQUID PHASE OXIDATION (see Figure 1a)

As noted earlier, the NH_3 catalyzed SO_2 oxidation in the liquid phase is currently considered as the most likely route to produce sulfate compounds. However, if NaCl is present in the droplets, free H and chloride ions will combine and finally be released into the atmosphere in the form of free HCl during the evaporation process of cloud

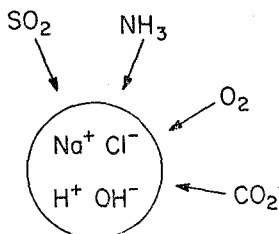


Fig. 1a. A diagram to show the interaction between trace gases (SO_2 , NH_3 , CO_2), O_2 and hydrometeors containing NaCl .

droplets in a non-precipitating cloud. We therefore incorporate this process in our model calculation and determine the pH value of the cloud droplet and the amount of HCl that could be liberated from the cloud droplets.

Scott and Hobbs [11] have summed up the chemical reaction equations involved and the corresponding equilibrium constants (see Table I). As pointed out by McKay [13], those equilibrium constants are highly dependent upon the temperature. McKay has

TABLE I
Liquid-phase reactions in the SO_2 - NH_3 - CO_2 -water system

Eq.	Chemical equilibrium equation	Equilibrium constant
(1)	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	$K_w = [\text{H}^+][\text{OH}^-]$
(2)	$(\text{SO}_2)_g + \text{H}_2\text{O} \rightleftharpoons \text{SO}_2 \cdot \text{H}_2\text{O}$	$K_{hs} = [\text{SO}_2 \cdot \text{H}_2\text{O}] / P_{\text{SO}_2}$
(3)	$\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ \text{HSO}_3^-$	$K_{1s} = [\text{H}^+][\text{HSO}_3^-] / [\text{SO}_2 \cdot \text{H}_2\text{O}]$
(4)	$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$K_{2s} = [\text{H}^+][\text{SO}_3^{2-}] / [\text{HSO}_3^-]$
(5)	$(\text{NH}_3)_g + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 \cdot \text{H}_2\text{O}$	$K_{ha} = [\text{NH}_3 \cdot \text{H}_2\text{O}] / P_{\text{NH}_3}$
(6)	$\text{NH}_3 \cdot \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$K_{1a} = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3 \cdot \text{H}_2\text{O}]$
(7)	$(\text{CO}_2)_g + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 \cdot \text{H}_2\text{O}$	$K_{hc} = [\text{CO}_2 \cdot \text{H}_2\text{O}] / P_{\text{CO}_2}$
(8)	$\text{CO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$K_{1c} = [\text{H}^+][\text{HCO}_3^-] / [\text{CO}_2 \cdot \text{H}_2\text{O}]$

listed these equilibrium constants at 25°C and 15°C . By assuming constant enthalpy for each set of constants, those constants can be extrapolated to values at other temperatures.

In our model we assume that chemical equilibria between SO_2 and NH_3 and their various dissolved forms in liquid are established at all time. It is also assumed that, in the aqueous phase, the diffusion of SO_2 is so fast that the oxidation rate rather than

diffusion is a controlling factor. We also assume that the cloud is at the 600 mb level and its temperature is 0°C.

The concentration of H⁺ ions and SO₄⁻ ions can be estimated by solving the following equations:

$$\frac{d[\text{SO}_4^-]}{dt} = K[\text{SO}_3^-] \quad (1)$$

$$[\text{SO}_3^-] = K_{2s} K_{1s} K_{hs} \frac{P_{\text{SO}_2}}{[\text{H}^+]^2} \quad (2)$$

$$\left\{ 1 + \frac{K_{ha} K_{1a}}{K_w} \right\} P_{\text{NH}_3} [\text{H}^+]^3 - 2[\text{SO}_4^-] [\text{H}^+]^2 - \{ K_w + K_{1c} K_{1c} P_{\text{CO}_2} + K_{hs} K_{1s} P_{\text{SO}_2} \} [\text{H}^+] - 2K_{hs} K_{1s} K_{2s} P_{\text{SO}_2} = 0. \quad (3)$$

The oxidation rate constant k in Equation (1) is still a controversial subject. Up to now three different expressions have been suggested. Their differences are so large that further experimentation to clarify this problem is urgently needed.

The first expression was suggested by Scott and Hobbs [11] in 1967. Based upon the experimental results of Van den Heuvel and Mason [14] they evaluated the value of k at 25°C was 0.0017 s⁻¹.

Using the experimental results of Fuller and Crist [15], McKay [13] in 1971 suggested a rate value depending upon the H ion concentration. This rate value k at 25°C can be expressed as the following:

$$k = 0.013 + 59 [\text{H}^+]^{1/2} \text{ s}^{-1}$$

$$= 0.032 \text{ s}^{-1} \text{ at neutrality.}$$

In 1972, Miller and de Pena [16] used a different value of k , 0.003 s⁻¹, to do their calculations.

All these oxidation rate constants depend on the temperature. As suggested by McKay [13], and Easter and Hobbs [12], an activation energy of 18.3 k cal mole⁻¹ should be used to obtain the rate constant at varying temperatures. Rate constants of k suggested by different authors and calculated at different temperatures are shown in Table II.

TABLE II
Rate constant k (s⁻¹)
Suggested by different authors and at different temperatures

Author	25°C	15°C	10°C	0°C	-3°C
Scott and Hobbs	0.0017	0.00058	0.00033	0.0001	0.000069
McKay	0.013 + 59 [H ⁺] ^{1/2}	0.0048 20 [H ⁺] ^{1/2}	0.0026 + 11.57 [H ⁺] ^{1/2}	0.00078 + 3.43 [H ⁺] ^{1/2}	0.00054 + 2.44 [H ⁺] ^{1/2}
(at neutrality)	0.032	0.011	0.00628	0.00192	0.00133
Miller and dePena	0.003	0.001	0.0059	0.00018	0.000124

3.2. GAS PHASE OXIDATION (see Figure 1b)

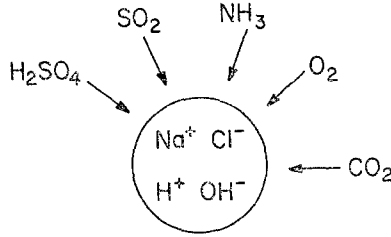


Fig. 1b. A diagram to show the interaction between trace gases (SO_2 , NH_3 , CO_2), O_2 and hydrometeors containing NaCl with the impinging of chemical reactant gaseous production H_2SO_4 molecules.

In order to have a more realistic model, the gas phase oxidation of trace gases to produce acid molecules should not be neglected. As noted earlier, the gas phase oxidation of SO_2 leading to the formation of H_2SO_4 in the atmosphere is through the following scheme:



where M is the third body responsible to take away the excess energy produced in the reaction. On the basis of micro-observations [17] the steps following the reaction to produce H_2SO_4 are so fast, we can assume that the rate-limiting process leading to the formation of H_2SO_4 is (R1a). The rate constant of reaction (R1a) can be approximated to be $3 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ [9]. The OH concentration is taken to be $5 \times 10^6 \text{ cm}^{-3}$. By assuming the cloud is at 2 km, the value of the third body concentration M can be taken as $2.09 \times 10^{19} \text{ cm}^{-3}$ [18]. The conversion rate of SO_2 to H_2SO_4 is then expressed as a function of the environment concentration of SO_2 . If we set $\text{SO}_2 = m$ ppbv, then the production rate of H_2SO_4 is:

$$P_1 = \frac{d[\text{H}_2\text{SO}_4]}{dt} = k [\text{OH}] [M] [\text{SO}_2]$$

$$= 6.6 \times 10^4 m \text{ molecules cm}^{-3} \text{ s}^{-1}.$$

It is obvious that the relative importance of the gas phase oxidation rate is dependent on the ambient concentration.

In order to determine the actual number of acid molecules sticking on the cloud droplets, we assume an accommodation factor of 1 and the impinging rate (i.e., the number of molecules that arrive at the surface of the droplet per unit area per unit time) is estimated by the formula:

$$\beta = \frac{P}{\sqrt{2\pi mkt}} = \left(\frac{kT}{2\pi m}\right)^{1/2} N_B = bN_B, \tag{4}$$

$$b = \left(\frac{kT}{2\pi m}\right)^{1/2}$$

where P is the pressure of H_2SO_4 , k is the Boltzmann constant, m is the mass of one acid molecule, and N_B is the number concentration of the gaseous acid which we can assume equal to the production rate of that species times a certain factor.

The concentration of H_2SO_4 in the cloud droplet due to impinging can be expressed as:

$$\begin{aligned} C &= \frac{bs}{AV} N_B t \times 10^3 \text{ (moles l}^{-1}\text{)} \\ &= \frac{3bt}{Ar} N_B t \times 10^3 \text{ (moles l}^{-1}\text{)} \end{aligned} \quad (5)$$

where

r = radius (cm)

S = area (cm^2)

V = volume (cm^3)

$b = \left(\frac{KT}{2\pi m}\right)^{1/2}$ (cm s^{-1})

A = Avogadro Number

t = time (s)

N_B = concentration (cm^{-3}).

It is obvious from Equation (5) that the smaller the droplet size and the longer the time of reaction, the greater the importance of the gas phase reaction followed by impinging to produce H^+ ions in the droplet.

Indeed, the gas phase reaction must be incorporated with the liquid phase reaction since those two processes are acting simultaneously. Consequently, Equation (3) should be modified to include the gas phase reaction term as the following:

$$\begin{aligned} &\left\{1 + \frac{K_{ha} K_{1a}}{K_w} P_{\text{NH}_3}\right\} [\text{H}^+]_t^3 - \left\{2[\text{SO}_4^-]_t + \sum_{ji} a_j n_i \frac{3b_j t}{Ar_i} N_j \times 10^3\right\} [\text{H}^+]_t^2 \\ &- \{K_w + K_{hc} K_{1c} P_{\text{CO}_2} + K_{hs} K_{1s} P_{\text{SO}_2}\} [\text{H}^+]_t - K_{hs} K_{1s} K_{2s} P_{\text{SO}_2} = 0 \end{aligned} \quad (6)$$

where

i refers to size index

j refers to species index

n_i is the number of droplets with radius r_i

a_j is the covalence of species j .

Equations (1), (2), and (6) form a closed set from which concentrations of different species in the droplet can be evaluated as a function of time for a given set of initial concentrations of ambient SO_2 and NH_3 . The initial concentration of H^+ is a solution to Equation (6) with an initial condition where $[\text{SO}_4^-]$ equals zero. The substitution of the value of $[\text{H}^+]$ to Equation (2) will yield the value of $[\text{SO}_3^-]$. The $[\text{SO}_4^-]$ at a later time will then be determined from Equation (1). The whole calculation scheme may then be repeated and the pH value of the droplet at any instant can then be evaluated.

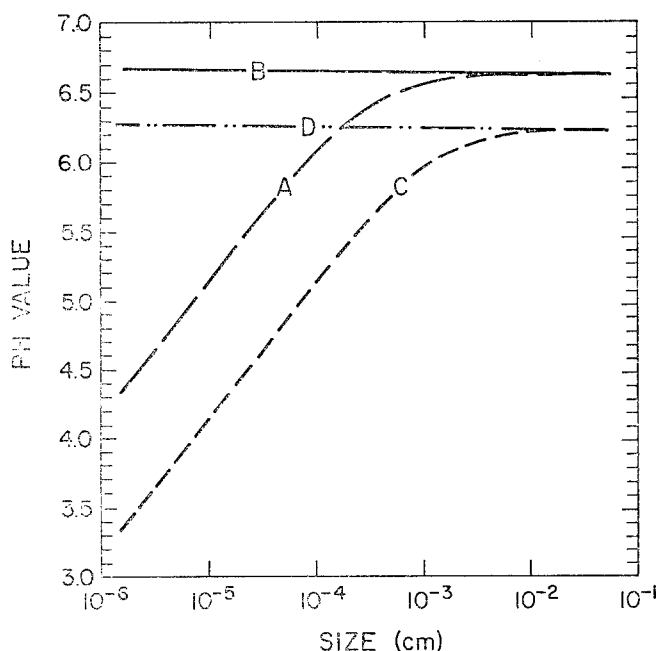


Fig. 2. The pH value of the cloud droplet as a function of its size. Curves A and B correspond to an environmental SO_2 and NH_3 concentrations 1 ppbv and 3 ppbv, respectively. Curves C and D correspond to an environmental SO_2 and NH_3 concentration 10 ppbv and 3 ppbv, respectively. Curves A and C are obtained by considering both the gases phase and liquid phase oxidation, but curves B and D are obtained by considering the liquid phase oxidation alone. All values are obtained by using the oxidation rate suggested by McKay, and by assuming the cloud is at a level of 600 mb and the temperature is 0°C . The time of reaction is 10 min.

Figure (2) is a graph indicating the variation of pH value with the droplet size distribution. Curves A and B correspond to an ordinary cloud at 0°C with ambient SO_2 and NH_3 gas concentrations 1 ppbv and 3 ppbv, respectively. Curves C and D correspond to a polluted cloud with ambient SO_2 and NH_3 gas concentrations 10 ppbv and 3 ppbv, respectively. Curves A and C have included the production of H_2SO_4 through gas phase oxidation. In an unpolluted environment, concentrations of gaseous H_2SO_4 molecules have been estimated as 1×10^7 .

Here, we estimate the concentration of H_2SO_4 molecules by:

$$N_B = \frac{C_B}{Sb}, \quad b = \sqrt{\frac{kT}{2\pi m}} \quad (7)$$

where C_B is the rate of production of H_2SO_4 and can be obtained by $C_B = k[\text{OH}][\text{SO}_2][\text{M}] = 6.6 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ for 1 ppb SO_2 , and S is the total surface area of aerosol per cubic centimeter ($\approx 10^2 \mu\text{m}^2 \text{ cm}^{-3}$ in a rural area and $\approx 10^3 \mu\text{m}^2 \text{ cm}^{-3}$ in an urban area [19]). Equation (7) gives a steady state concentration of H_2SO_4 . $N_B Sb$ is the total rate of the loss of H_2SO_4 to aerosol surface and in a steady state the total rate of the loss is assumed to be equal to the total rate of production (C_B). Thus, in the rural area the steady state concentration of H_2SO_4 is in the order of

10^7 molecules cm^{-3} . In a polluted environment, their concentrations are accordingly increased by 10-fold. Curves B and D correspond to the result obtained without considering the gas phase oxidation. Results shown in Figure (2) are obtained by assuming a cloud of liquid water content 0.2 gm m^{-3} of air and exposed to the trace gases for 10 min. Here we used McKay's oxidation rate constant.

A comparison of curves A, C with B, D indicates that the additional consideration of gas phase oxidation will produce a pH value spectrum depending on the droplet size distribution, while the ignoring of gas phase oxidation will produce a pH value which is independent of the droplet size distribution. It is obvious that the consideration of gas phase oxidation in addition to the liquid phase oxidation will produce a lower pH value of cloud droplets.

Curve C indicates that a droplet with radius $0.01 \mu\text{m}$ will have a pH value as low as 3.0. This is true as long as the droplet remains small, because in this case the H ions in the droplet are mainly due to the impinging of gaseous acid molecules. The concentration of H ions in the droplet due to impinging is inversely proportional to its radius. In the real atmosphere the droplet will grow. The lower the pH value of the droplet, the smaller its partial water vapor pressure, and the greater the number of water vapor molecules impinging on its surface. Consequently, the pH value will increase due to the growth of droplet.

In order to see the effect of temperature on the pH value of the cloud droplets, Figure 3 has been plotted by assuming a temperature of 10°C . A comparison of these two figures indicates that the lower the temperature, the higher the pH value. Figure 4 is

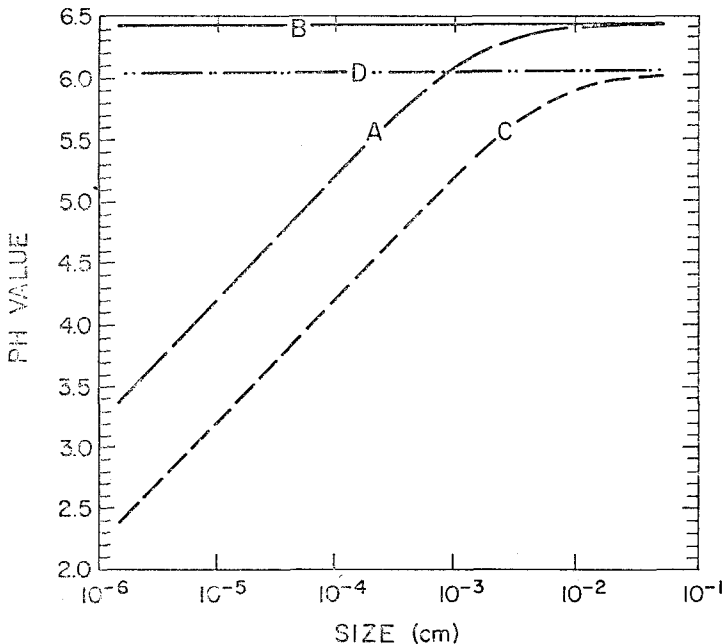


Fig. 3. The same as Fig. 1, except the temperature of the cloud is 10°C .

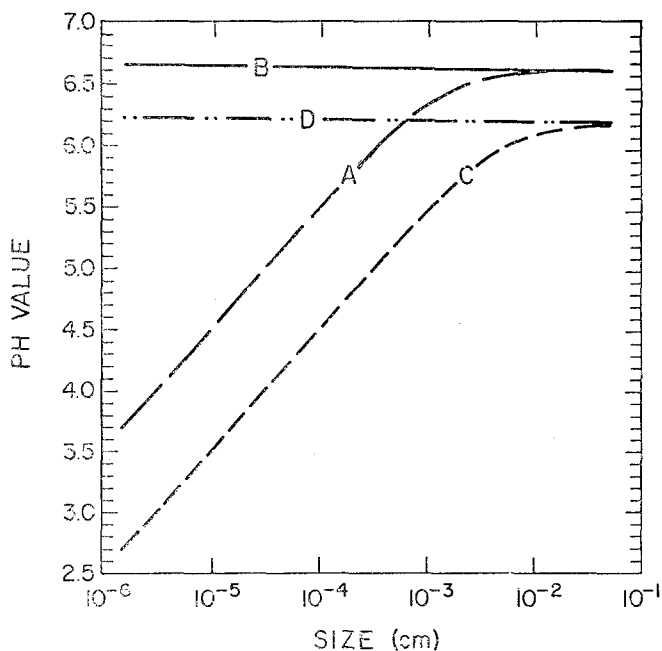


Fig. 4. The same as Fig. 2, except the oxidation rate is the one suggested by Scott and Hobbs and the H_2SO_4 concentration has been decreased by a factor of 2.

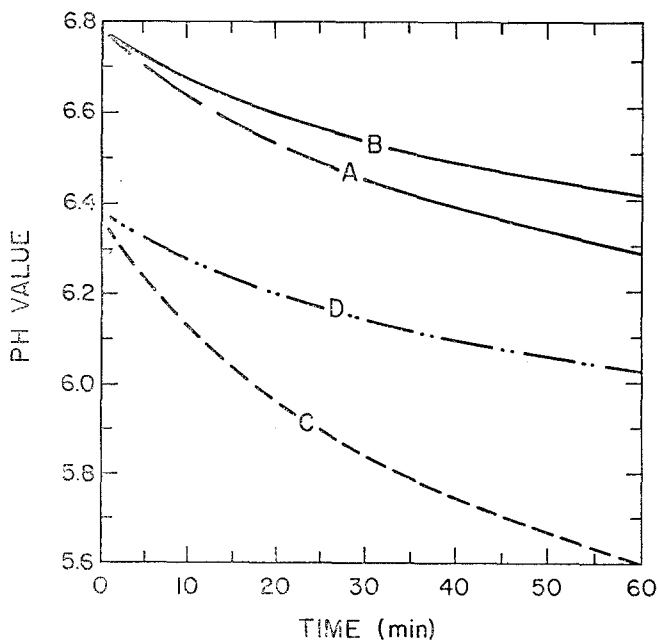


Fig. 5. The average pH value of the cloud as a function of time. Curves A and B correspond to an environmental SO_2 and NH_3 concentrations 1 ppbv and 3 ppbv, respectively. Curves C and D correspond to an environmental SO_2 and NH_3 concentrations 10 ppbv and 3 ppbv, respectively. Curves A and C are obtained by considering both the gas phase oxidation and the liquid phase oxidation, but curves B and D are obtained by considering the liquid phase oxidation alone. All values are obtained by using the oxidation rate suggested by McKay and by assuming the cloud is at a level of 600 mb and the temperature is 0°C .

obtained with the same environmental conditions as that of Figure 2 except here we use Scott and Hobbs' oxidation rate constant.

Finally, in order to see the effect of time duration on the average pH value of the cloud, a plot of average pH value versus time at 0°C with McKay's rate constant is shown in Figure 5. At the beginning, the difference between the two models, considering both the gas and liquid phase oxidations, and only the liquid phase oxidation is small. However, as the reactions continue, their differences increase. This is because the gas phase oxidation is proportional to time, the longer the time of reaction, the more important the gas phase oxidation. On the other hand, the liquid phase oxidation is slowed down due to the increasing amount of free H ions in the droplet as the reaction proceeds.

4. Estimation of the Amount of HCl Released from the Cloud Droplets (see Figure 6)

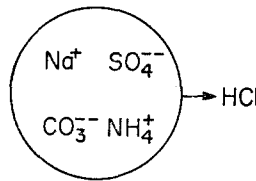


Fig. 6. A diagram to show the release of HCl into the atmosphere from the hydrometeors during the evaporation process.

In order to estimate the amount of HCl released into the atmosphere we must know the distribution of cloud droplets containing NaCl. Though different forms of sea-salt nuclei distributions have been suggested, four types are widely used (Arnason and Greenfield) [20].

Based on nuclei distributions in the trade wind region [21] Eriksson [22] suggested the following analytical form:

$$\frac{dn}{dr} = n(r) = a_1 \exp(-br^{1/2})$$

where n is the number of sea-salt particles per cubic centimeter of radii smaller than r , and a_1 and b are constants having the values 6.31×10^2 and 6.9 respectively, when r is measured in μm . Another distribution, given by Mordy [23] in his numerical simulation of condensation, represents maritime conditions also based on observations by Woodcock. The third distribution, also maritime, is used by Warner [24] in a computation of droplet growth by condensation.

In contrast to the above three maritime distributions, the fourth one is more or less typical of continental conditions [25]:

$$\frac{dn}{dr} = n(r) = \frac{c}{2.30} r^{-4} \quad (9)$$

where c is a constant in the order of 10^{-7} to 10^{-8} if r is given in μm .

The equilibrium radii in response to a change in supersaturation S can be computed by means of the following equilibrium Equation (26):

$$S - \frac{a}{r} + \frac{b}{r^3} = 0 \quad (10)$$

where $a \approx 3.3 \times 10/T$ (T is absolute temperature), and $b \approx 4.3 \text{ im}/M$.

The amount of hydrogen chloride released into the atmosphere from a cloud at a supersaturation S after it moves to an unsaturated environment can be estimated by the following formula:

$$M_j = 36.5 \times 10^{-3} \sum_{K=1}^n \frac{4}{3} \Pi \left(\frac{r_s^k + r_s^{k+1}}{2} \right)^3 \cdot \Delta N_j^k \cdot [\text{H}^+]_k \quad (11)$$

where

M_j is the amount of HCl released into the atmosphere in units of $\mu\text{g m}^{-3}$ of air

r_s^k is the equilibrium radius at supersaturation S with group index k

ΔN_j^k is a particular distribution (f) of nuclei per cubic centimeter for a range r with group index k to $k + 1$

$[\text{H}^+]$ is the concentration of H^+ ions for a particular cloud at the end of its life cycle and its unit is in moles l^{-1} .

The amount of HCl released into the atmosphere as a function of life cycles of the cloud at 0°C for different types of nuclei distribution at an environment of zero per cent supersaturation is shown in Figures 7 and 8. Curves A, B, C and D in Figures 7 and 8 correspond to the results obtained by using the above-mentioned four types of nuclei distributions respectively. Here we use McKay's oxidation rate and assume the ambient concentration of SO_2 and NH_3 are 1 ppbv and 3 ppbv, respectively. Graphs in Figure 7 are results obtained by considering both the gas and liquid phase oxidation of SO_2 . Graphs in Figure 8 are results obtained by considering only the liquid phase oxidation of SO_2 . A non-precipitating cloud may go through more than one cycle and more HCl will be released from an 'older' cloud (recycled cloud condensation nuclei). Here the life cycle is assumed to be 1 h.

Figures 9 and 10 are obtained by assuming the cloud is at a polluted environment; i.e., the ambient concentration of SO_2 and NH_3 are 10 ppbv and 3 ppbv, respectively. Results in Figure 9 are obtained by considering both the gas and liquid phase oxidation of SO_2 . Results in Figure 10 are obtained by considering only the liquid phase oxidation of SO_2 .

As the supersaturation of the environment changes the liquid water content of the cloud will change accordingly. Consequently, the amount of HCl released from such cloud will change. In order to see the effect of liquid water content of the cloud on the amount of HCl released into the atmosphere, plots of the amounts of HCl released as a function of the liquid water content of the cloud for different environmental conditions

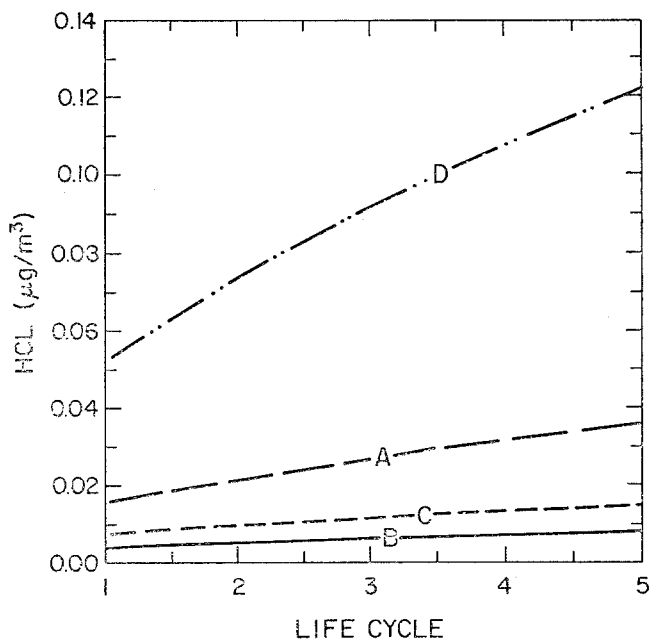


Fig. 7. Amount of HCl released into the atmosphere from the cloud as a function of its life cycle. The cloud is at 600 mb and its temperature is 0°C. The environmental SO₂ and NH₃ concentrations are 1 ppbv and 3 ppbv, respectively. The life cycle is assumed to be 1 h. The results are obtained by using McKay's oxidation rate and considering both the liquid and gas phase oxidation of SO₂. Curves A, B, C and D correspond to nuclei distributions suggested by Erikson, Mordy, Warner and Junge, respectively.

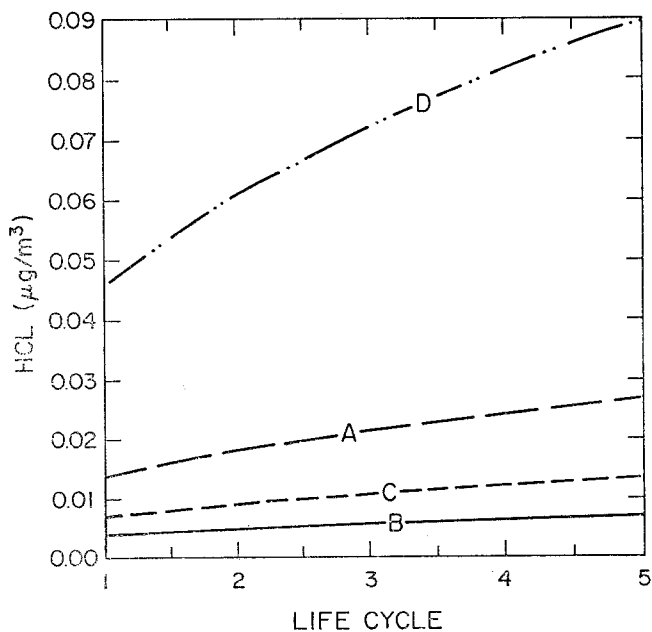


Fig. 8. The same as Fig. 7, except only the liquid phase oxidation of SO₂ has been considered.

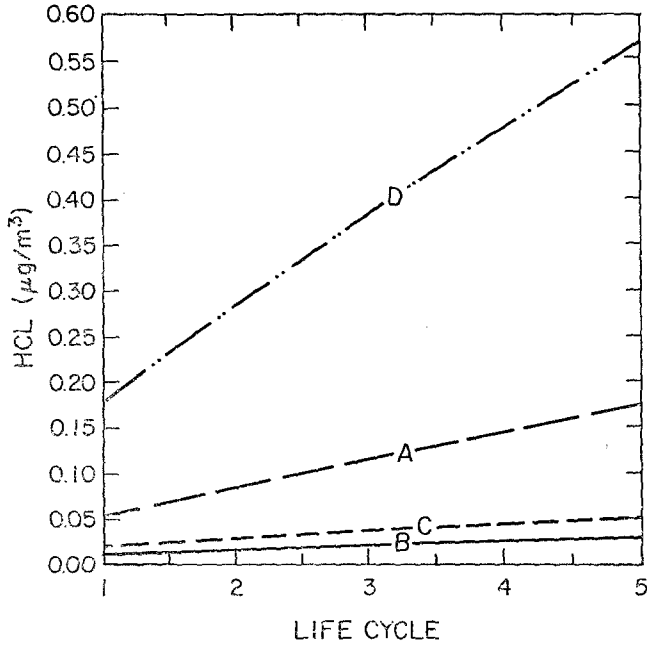


Fig. 9. The same as Fig. 7, except the cloud is at a polluted environment in which the concentrations of SO_2 and NH_3 are 10 ppbv and 3 ppbv, respectively.

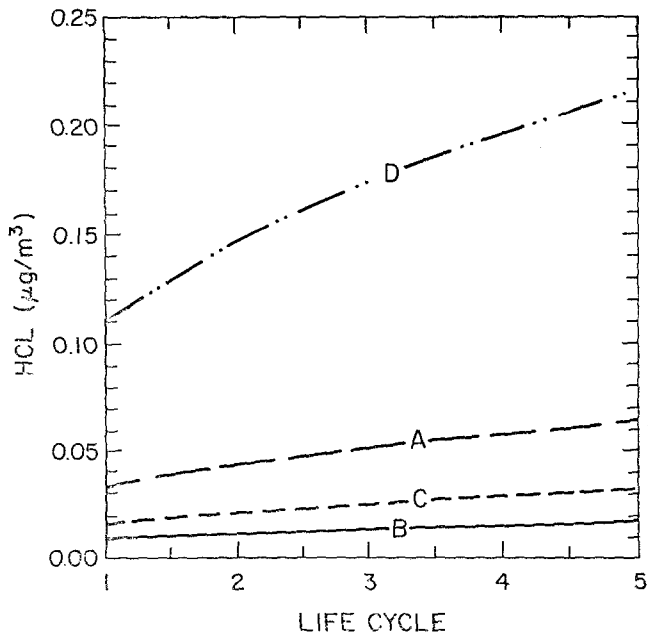


Fig. 10. The same as Fig. 9, except only the liquid phase oxidation of SO_2 has been considered.

at the end of the first life cycle of the cloud are shown in Figure 11. Results are obtained by considering both the liquid and gas phase oxidation of SO_2 . Here we assume that the concentration of ambient SO_2 is 1 ppbv, and curves A, B, and C correspond to concentration of NH_3 , 1 ppbv, 2 ppbv and 3 ppbv, respectively. The increases of environmental NH_3 concentration will decrease the production of HCl from a non-precipitating cloud.

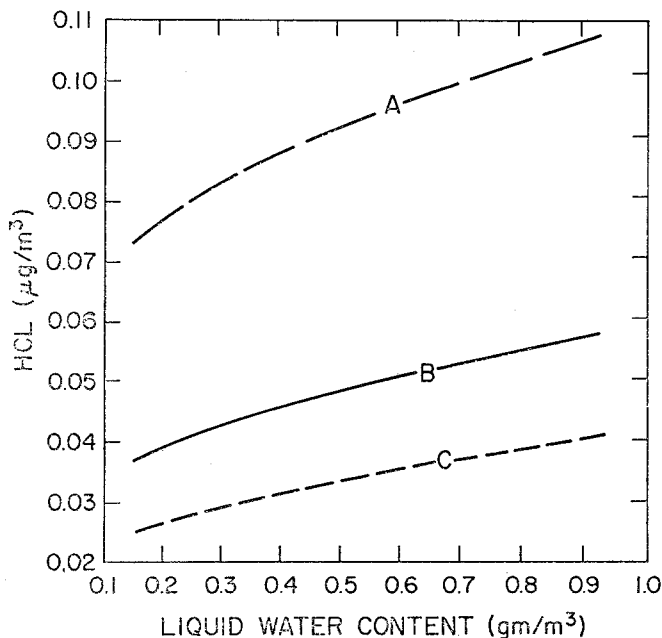


Fig. 11. Amount of HCl released into the atmosphere from the cloud as a function of its liquid water content. The environmental SO_2 concentration is 1 ppbv and curves A, B and C correspond to environmental concentration of NH_3 , 1 ppbv, 2 ppbv and 3 ppbv, respectively. Here results are obtained by considering both the liquid and gas phase oxidation of SO_2 .

In order to evaluate the significance of the production of HCl through the mechanism discussed in this paper, here we present a rough estimation of the global production of HCl through the interaction between trace gases and hydrometeors. We assume an average cloud thickness of 2000 m and the mean global cloud cover as 0.54 [27]. We further assume that the life cycle of a cloud is 1 h and a cloud can go through five cycles which takes 10 h. If the SO_2 and NH_3 concentrations are both 1 ppbv and we only consider liquid phase oxidation, the global production of HCl is $1.73 \times 10^8 \text{ t yr}^{-1}$. However if additionally we consider the gas phase oxidation, the global production of HCl changes to $2.2 \times 10^8 \text{ t yr}^{-1}$. If we assume the SO_2 concentration is 10 ppbv and the NH_3 concentration is 1 ppbv and consider both the gas and liquid phase oxidation, the global production of HCl is $9.32 \times 10^8 \text{ t yr}^{-1}$. Our estimation is of the same order of magnitude as the annual production rate of $6 \times 10^8 \text{ t}$ calculated by Duce [4].

It is important to point out here that the above calculations for the amount of HCl

production due to the interactions between the trace gases and hydrometeors are based on the assumptions that the HCl gaseous molecules are released from the cloud droplets only when the cloud droplet is undergoing evaporation process. For a non-evaporating cloud droplet the amount of HCl released from the cloud droplet is dependent on the concentration of HCl in the air around the cloud droplet and the partial pressure of HCl in the cloud droplet. If the partial pressure of HCl in the air is much less than the partial pressure of HCl in the cloud droplet, our calculation would be essentially correct. Therefore, the calculations presented in this paper represent an upper limit for HCl production. A more accurate calculation for the production of HCl by the proposed mechanism should consider the difference of the partial pressures of HCl in the cloud droplet and its surrounding air.

5. Conclusions and Discussions

We have discussed the differences between the chemical model considering only the liquid phase oxidation of trace gases and the more realistic model considering both the gas and liquid phase oxidations. The additional consideration of gas phase oxidation of trace gases will further lower the pH value of the cloud droplets and will produce a pH value spectrum depending on the drop size distribution. Generally speaking, the relative importance of these two mechanisms depends on the size distribution of droplets, the time duration of the reaction, the relative abundance of trace gases, and the assumed oxidation rate.

We have demonstrated that non-precipitating clouds containing NaCl can produce a source of free HCl in the atmosphere. The amount of HCl liberated from cloud droplets depends on the following factors: (a) the temperature of the cloud; a higher temperature of the cloud will produce more HCl; (b) the assumed oxidation rate; by using McKay's oxidation rate constant will produce more HCl; (c) the ambient concentration of SO₂ and NH₃; more SO₂ in the environment will produce more HCl, however more NH₃ in the environment will produce less HCl; (d) the concentration of gaseous acid molecules; more gaseous acid molecules in the environment will produce more HCl; (e) the life cycle of the cloud; more HCl will be released from an 'older' cloud; (f) the liquid water content of the cloud; a cloud with higher liquid water content will produce more HCl.

The amount of HCl released into the atmosphere is a combined result of the intricate physical and chemical processes occurring inside the cloud. Due to the complexity of the problem, here we consider only the case in which the droplet is static and does not grow. The macro- and micro-physical processes of a cloud will certainly influence the pH value of the cloud droplets and the effectiveness of HCl production mechanism. Field measurements are urgently needed to reveal the droplet size distribution of the pH value and the spatial distribution of HCl.

Acknowledgment

This work was supported by the National Science Foundation, Atmospheric Science Section through Grant No. A022760003.

References

- [1] Junge, C. E.: 1963, *Air Chemistry and Radioactivity*, Academic Press, New York and London.
- [2] Rossby, C. G. and Egner, H.: 1955, *Tellus* **VII**, 118.
- [3] Stolarski, R. S. and Cicerone, R. J.: 1974, *Canadian J. Chem.* **52**, 1610.
- [4] Duce, R. A.: 1969, *J. Geophys. Res.* **74**, 4597.
- [5] Cauet, H.: 1938, *Der Balneologes* **5**, 409.
- [6] Kohler, H. and Bath, M.: 1953, *Nova acta Regiol Societatis Scient, Upsaliensis* **15**, 7, 24.
- [7] Yost, D. M. and Russell, H., Jr.: 1944, *Systematic Inorganic Chemistry*, Prentice Hall, Inc., New York, 42.
- [8] Robbins, R. C., Cadle, R. D., and Eckhardt, D. L.: 1959, *J. of Meteorology* **16**, 53.
- [9] Davis, D. D.: 1974, *Can. J. Chem.* **52**, 1405.
- [10] Cadle, R. D.: 1972, *J. Colloid Interface Sci.* **39**, 25.
- [11] Scott, W. D. and Hobbs, P. V.: 1967, *J. Atmos. Sci.* **24**, 54.
- [12] Eastman, R. C. and Hobbs, P. V.: 1974, *J. Atmos. Sci.* **31**, 1586.
- [13] McKay, H. A. G.: 1971, *Atmospheric Environment* **5**, 7.
- [14] Van der Heuval, A. P. and Mason, B. J.: 1963, *Quart. J. R. Meteor. Soc.* **89**, 271.
- [15] Fuller, E. C. and Crist, R. H.: 1941, *J. Am. Chem. Soc.* **63**, 1644.
- [16] Miller, J. M. and de Pena, R. G.: 1972, *J. Geophys. Res.* **77**, 5905.
- [17] Castleman, A. W., Jr., Davis, R. E., Munkelwitz, H. R., Tang, I. N., and Wood, W. P.: 1976, *J. of Chem. Kinetics*, to be published.
- [18] *Handbook of Geophysics*: 1961, Macmillan, New York.
- [19] Whitley, K. T., Clark, W. E., Marple, V. A., Sverdrup, G. M., Sem, G. J., Willeke, K., Liu, B. Y. H., and Pui, D. Y. H.: 1972, *Aerosols and Atmospheric Chemistry*, Academic Press, New York.
- [20] Arnason, G. and Greenfield, R. S.: 1972, *J. Atmos. Sci.* **29**, 342.
- [21] Woodcock, A. H.: 1957, *Tellus* **9**, 521.
- [22] Eriksson, E.: 1959, *Tellus* **II**, 375.
- [23] Mordy, W.: 1959, *Tellus* **II**, 16.
- [24] Warner, J.: 1959, *J. Atmos. Sci.* **26**, 1272.
- [25] Junge, C. E.: 1951, *Ber. Deut. Wetterdienstes* **35**, 261.
- [26] Fletch, N. H.: 1952, *The Physics of Rain Clouds*, Cambridge University Press, 59.
- [27] Paltridge, G. W.: 1974, *J. Atmos. Sci.* **31**, 1571.