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Hydrogen Chloride Vapor Pressure over Metal Chloride Aerosols from Rocket Exhausts

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The importance of chloride coatings in determining the atmospheric properties of solid fuel exhaust particles is examined using a rigorous thermodynamic treatment of HCl-$AlCl_3$-H_2O and HCl-$BeCl_2$-H_2O mixtures. Although chloride salts represent only about 5% of the mass of the particles, their hygroscopic nature means that they dominate the control of the liquid water content of exhaust clouds with low water vapor content. In the presence of chloride particles, liquid water and dissolved HCl persist over a wider range of conditions than in a pure HCl-H_2O cloud. An equilibrium model of HCl partitioning in the Space Shuttle exhaust cloud satisfactorily represents the measured distributions and suggests that cloud lifetime is a function of ambient relative humidity. Beryllium chloride particles show similar properties to those of aluminum.

Nomenclature

a = dispersion constant
aW = thermodynamic activity of water
aY = thermodynamic activity of component Y (mol kg^{-1})
C^{ϕ} = pure electrolyte Pitzer model parameter
c = mixing ratio, ppm, of total HCl at time t, min
c_o = mixing ratio at t equal to 1 min
$F(I)$ = Debye-Huckel constant
G^{ex}/n_w = excess Gibbs energy per kg of water
K_H = thermodynamic Henry's law constant, mol^2-kg^{-2}atm^{-1}
I = ionic strength, mol-kg^{-1}
$I_{\max}$ = maximum ionic strength to fit
mY or m_Y = the concentration of component Y, mol-kg^{-1}
RH = relative humidity, %
V_t = volume of a mol of gas at temperature t, m^3
W = mass of condensed water in the modeled air mass, kg
X = the mol fraction of a solution component
$\beta^{(i)}$ = pure electrolyte Pitzer parameters, $i = 0, 1, 2$
γ_{HCl} = the mean activity coefficient of HCl in the aqueous phase
$\theta_{i,j}$ = mixed electrolyte Pitzer parameter for ions i and j
ϕ = osmotic coefficient of the aqueous droplets
$\psi_{i,j,k}$ = mixed electrolyte Pitzer parameter for ions i, j, and k

Subscript
T = total quantities

Introduction

ALUMINUM is an important constituent of solid fuel rocket propellants, and beryllium has also been used in specialized applications.[1,2] The Space Shuttle boosters discharge some 3×10^5 kg Al_2O_3 during a launch, and there is considerable interest in the environmental impact of these emissions[3] and the way in which they may act as condensation nuclei.[4,5] The high toxicity of Be (Ref. 6) makes a thorough understanding of its behavior in exhaust particles necessary if the potential dangers involved in its use in propellants are to be assessed.

The Space Shuttle ground cloud, which has been well studied is largely composed of HCL, Al_2O_3, and water. Cofer et al. estimate concentrations as 70-ppm HCl (by volume) and 80-mg-m^{-4} Al_2O_3 for a cloud 2 min after launch. The total concentration of HCl decreases rapidly due to dispersion effects and rainout.[7,8] The surfaces of aluminum oxide particles become coated with hygroscopic chlorides through exposure to high concentrations of HCl.[9] Cofer et al.[10] show that the surfaces of these chloride-coated particles behave as $AlCl_3$, even though their true stoichiometry is more complex. Analogous processes involving BeO, the exhaust product from beryllium solid propellants,[1] have not been studied. Although toxicological considerations limit the use of beryllium as a fuel in the troposphere, it still seems necessary to consider the likely nature of the hygroscopic $BeCl_2$ that could be produced.

Where liquid water is present, the metal salt will exist in solution and may significantly influence the properties of the exhaust cloud. However, the thermodynamic properties of aerosol solutions are difficult to predict because they may be very concentrated in atmospheres of low relative humidity and exhibit highly nonideal behavior.

In natural cloud and aerosol systems, the partitioning of gases such as HCl can usually be treated as being close to equilibrium.[11] A similar assumption regarding the Space Shuttle ground cloud would simplify prediction of the evolution and environmental impact. This assumption has yet to be validated for the high concentrations of HCl in the Shuttle plume, although attainment of equilibrium is likely to be controlled by first-order processes that are unaffected by concentration.

In this paper, a simple equilibrium model is applied to the ground cloud and the results compared with field data. A rigorous treatment of solution thermodynamics enables the importance of chlorides in controlling cloud properties to be investigated.

Thermodynamics

In earlier papers[12,13] it has been argued that the heterogeneous equilibrium between aerosol and gas-phase HCl is most appropriately described in terms of the equilibrium

$$HCl_{(g)} = H^+_{(aq)} + Cl^-_{(aq)} \tag{1}$$

yielding the following expression for the thermodynamic Henry's law constant K_H (mol^{2}kg^{-2}atm^{-1}):

$$K_H = \gamma^2_{HCl} mH^+ mCl^- / pHCl = aH^+ aCl^- / pHCl \tag{2}$$

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Table 1 Thermodynamic Henry's law constant (K_H) of HCl[24]

Temperature, °C	k_H, mol^2 kg^{-2} atm^{-1}
40	4.66×10^5
35	7.54×10^5
30	1.23×10^6
25	2.04×10^6
20	3.37×10^6
15	5.68×10^6
10	9.71×10^6
5	1.68×10^7
0	2.95×10^7

Table 2 Pitzer model parameters at 25°C

	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
$BeCl_2$	0.4495	1.899	0	−0.00210
$AlCl_3$	0.6993	5.845	0	0.00273
HCl	0.1775	0.2945	0	0.00080
c c'	$\theta_{c,c'}$	$\psi_{c,c',Cl}$	I_{Cl}	
Be H	0.190	−0.0224	8	
Al H	0.185	0.0130	5	

The Henry's law constant of HCl is well known and is given as a function of temperature in Table 1. The mean activity coefficient γ_{HCl} is more difficult to establish in the concentrated solutions encountered in aerosols. The values calculated using the formalism of Pitzer[14] and Pitzer and Mayorga[15] have been successfully applied to atmospheric aerosol systems.[16,17] In Pitzer's approach, the Gibbs excess free energy of a mixed electrolyte solution and derived properties (osmotic and mean activity coefficients) are represented by a virial expansion of terms in concentration, similar to the series used to describe the properties of the nonideal gases. The excess Gibbs energy, from which thermodynamic activity may be calculated is described by [Eq. (24), Ref. 14]:

$$G^{ex}/n_w RT = F(I) + \Sigma\Sigma\lambda_{ij}(I) m_i m_j + \Sigma\Sigma\Sigma\mu_{ijk} m_i m_j m_k \tag{3}$$

The Debye-Huckel term $F(I)$ represents long-range electrostatic forces that dominate in very dilute solutions. Short-range interactions are accounted for by virial coefficients λ_{ij} for binary and μ_{ijk} for ternary interactions. Coefficients λ_{ij}, which are also used for interactions between ions of like sign, are dependent upon ionic strength. Ternary interaction coefficients are considered to be independent of ionic strength and are omitted for triplets of ions of like sign. The full equations for osmotic and mean activity coefficients are given by Pitzer [Eqs. (17-33)].[18] In these expressions, the virial coefficients are grouped into observable combinations, and the resulting interaction parameters may be evaluated empirically from available data.

Calculation of the osmotic and activity coefficients in a multicomponent solution requires up to six model parameters. Four parameters are used to describe the properties of pure electrolytes (see Table 2). One of these, $\beta^{(2)}$, is set to zero for all except 2:2 and higher valency metal sulphates. In mixed solutions, the further parameters θ_{ij} and ψ_{ijk} account for interactions between pairs of ions of like sign and triplets of ions (two of like sign and one of the opposite sign), respectively.

Pure solution parameters are available for HCl over a range of temperatures and for $AlCl_3$ at 25°C, as are the mixture parameters for the system. Activity and osmotic coefficients of $BeCl_2$ are not available for either pure solutions or mixtures. This deficiency is the most serious obstacle in predicting the properties of solutions that contain beryllium and chloride ions, so the significant parameters involving $BeCl_2$ were estimated in an earlier part of the project.[19] Parameters used in this work are drawn from the compilation of Pitzer[14] and the evaluations of the present authors (Table 2).

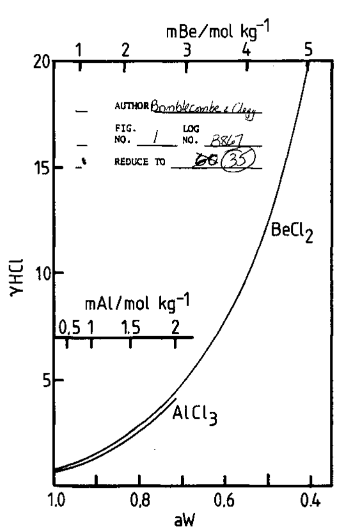

Fig. 1 Mean activity of HCl (γ_{HCl}) in $AlCl_3$ and $BeCl_2$ solutions.

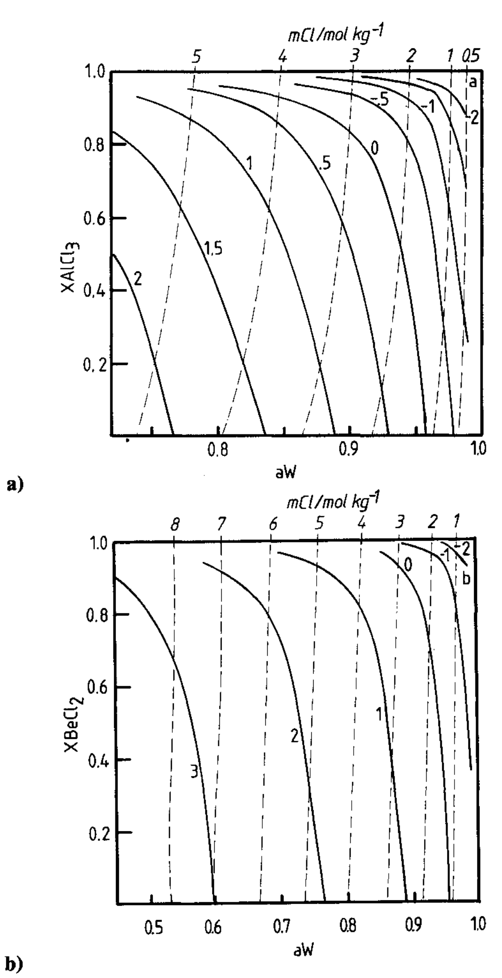

Fig. 2 HCl activity product (———) and Cl^- concentrations (– – – –) in $AlCl_3$ and $BeCl_2$ solutions.

Solution Behavior

The behavior of trace amounts of HCl in solutions of $BeCl_2$ and $AlCl_3$ are shown in Fig. 1. Because the solutions have different stoichiometry, they are best compared on a water activity rather than concentration basis. This has the added advantage that water activity is equivalent to the equilibrium relative humidity above such solutions. In concentrated solutions of $BeCl_2$, the mean activity coefficient rises to large values (about

20 at 5 mol kg^{-1}). This "salting out" means that HCl is up to 400 times less soluble in these solutions than would be predicted on the basis of a simple hydrogen-chloride ion product that ignored the activity coefficient [see Eq. (2)].

The partial pressure of HCl above a given solution at different temperatures is a function of γ and K_H. The mean activity coefficient γ_{HCl} varies only slightly with temperature, but the thermodynamic Henry's Law constant decreases significantly with increasing temperature (Table 1). Therefore, the "activity product" $\gamma^2_{HCl} \cdot mH^+ \cdot mCl^-$ has been plotted as this can be divided by K_H at the appropriate temperature to obtain the equilibrium HCl partial pressure.

Figure 2 shows the hydrogen chloride activity product in HCl-$AlCl_3$ and HCl-$BeCl_2$ aqueous solution mixtures. The logarithms of the molal activity products are shown as solid lines on each of these diagrams as a function of water activity and mole fraction of the metal chloride defined by

$$XMeCl_n = mMeCl_n/mMeCl_n + mHCl \tag{4}$$

As water activity is not linearly related to the chloride concentration, *m*Cl is shown as fine dashed lines labeled at the top of each figure.

The change in the activity product may be ascribed to three factors. First, the change of composition from pure aqueous HCl ($XAlCl_3$ equal to zero) to a pure $AlCl_3$ solution ($XAlCl_3$ equal to unity) necessarily causes the activity product to decrease due to the diminishing H^+ concentration. Second, as water activity decreases from unity (an infinitely dilute solution), solute concentrations are increased and nonideal effects expressed in the activity coefficients become significant. Third, differences in the stoichiometry of the end-member salts are reflected in the sloping contours for Cl^- concentration.

It is clear from Fig. 2a that under most conditions, HCl partial pressures over HCl-$AlCl_3$ aerosols are high compared to natural systems. For example, the 0 contour represents HCl concentrations of 0.5 ppm at ambient temperatures, which can be compared with the much lower value of 0.01 ppm typical of the marine troposphere.[20]

Figure 2b shows a similar contour plot for HCl-$BeCl_2$ mixtures. Because of the high solubility of $BeCl_2$, very-high-activity products are maintained in solutions of low water activity where $AlCl_3$ would precipitate out. The most important point of comparison between Figs. 2a and 2b is that the activity product of HCl takes similar values in both solutions at the same water activity. This extends the similarity of behavior found for trace-activity coefficients of HCl in the salt solution (Fig. 1).

Equilibrium Model Calculations

In studies of Shuttle ground clouds, Sebacher et al.[21] found that total concentrations of HCl decreased with time according to the equation

$$c = c_o t^a \tag{5}$$

In the case of HCl in the Shuttle cloud, *a* has an average value of about -1.3. Equilibrium calculations by Rhein[22] indicate that most of the HCl in the Shuttle exhaust cloud should be in the aqueous phase early in the cloud history. Field observations confirm this result and show that the ratio of aqueous to gaseous HCl decreases rapidly with time as HCl is displaced.[7] Studies of Titan III exhaust clouds further suggest that observed cloud properties and HCl partitioning are consistent with phase equilibrium.[8]

The effect of dissolved $AlCl_3$ on cloud behavior and persistence was investigated over a wide range of conditions using a simple equilibrium box model in which the exhaust cloud composition and the partition ratio of HCl were calculated as functions of time. Sebacher et al.'s empirical relationship[21] [Eq. (5)] was used to fix the total HCl concentration in the box. A value of c_o equal to 160 ppm was used, to correspond to the data shown in Fig. 1 of Cofer et al.[7] When Al was present (as soluble $AlCl_3$), its initial concentration was taken as 5 mg m^{-3} at $t = 2$ min, consistent with expected Al_2O_3 concentrations in the plume and assuming about 6% conversion to $AlCl_3$.[7] The temperature was set at 15°C, corresponding to typical ambient values 1.5 km above the launch site.[5]

The partitioning of HCl is controlled by the total amounts of HCl and water in the cloud. The evolution of cloud liquid water content is unknown. Accordingly, HCl partitioning was calculated for specified quantities of total HCl and metal chloride over a range of relative humidities corresponding to various liquid water contents. Equilibrium conditions in the modeled air volume were expressed in terms of the following equations:

$$RH/100 = \exp\{-0.018(\Sigma m_i)\phi\} \tag{6}$$

$$H^+_T = mH^+ \cdot W + mH^+ \cdot mCl^- \cdot \gamma^2_{HCl}/K_H \cdot V_t \tag{7}$$

Values of γ_{HCl} and ϕ were calculated using the Pitzer equations with parameters listed in Table 2. Equations (6) and (7) were expressed in terms of *W* and the total number of moles of H^+ present in solution and solved simultaneously using a commercially available FORTRAN subroutine.[23]

Two systems, consisting of HCl-H_2O and HCl-$AlCl_3$-H_2O, were modeled and the results compared to the field measurements of Cofer et al.[7] As has been stated, cloud liquid water content is not known independently, but calculations suggest that most water is supplied from the surrounding air in all but the earliest stages of exhaust plume evolution, where there is significant vaporization and entrainment of deluge water. For example, taking the molar ratio HCl/H_2O in the exhaust as 0.266 (Ref. 3) and a total in-cloud HCl concentration of 160 ppm,[7] then exhaust-derived water amounts to only 4% of the total water content of the cloud (at an ambient temperature of 15°C and relative humidity of 90%). Thus, it is reasonable to assume that the total water content of the model system approximates that of the ambient air as characterized by the relative humidity and is fixed over the lifetime of the modeled

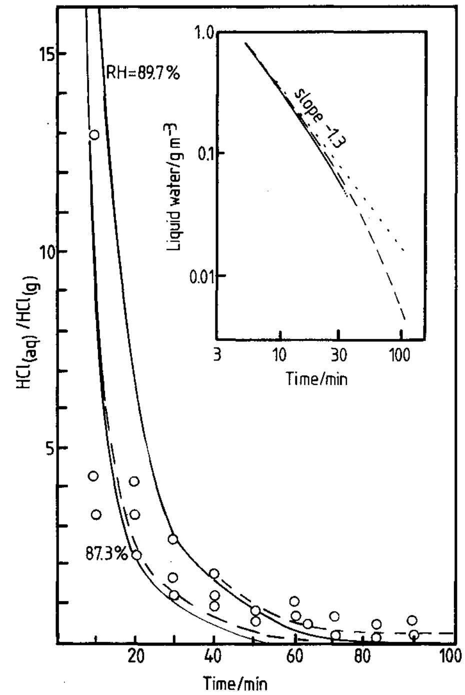

Fig. 3 Predicted (———) and (– – – –) and observed (○) HCl distributions and liquid water content of Shuttle exhaust cloud.

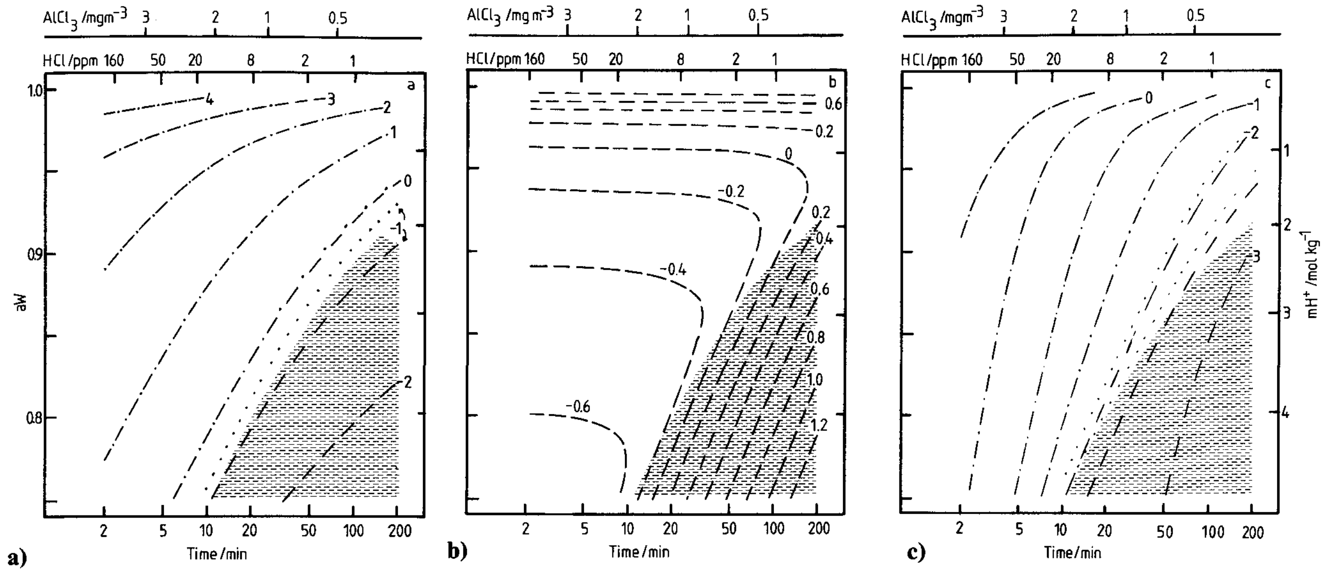

Fig. 4 Shuttle exhaust cloud: a) predicted HCl partition ratio; b) log (mH$^+$); and c) liquid water content.

cloud. Such an approach has been shown to be consistent with field measurements.[8]

Figure 3 compares observations of HCl_{aq}/HCl_g made by Cofer et al.[7] during Shuttle launches STS-1, STS-2, and STS-5. The distributions are calculated assuming constant relative humidities (87.3 and 89.7%) in the presence and absence of chlorided aluminum particles. In the main figure, the solid lines give the results for pure aqueous HCl and dashed lines those for systems including $AlCl_3$.

The calculated partitioning ratios for *RH* between 87.3 and 89.7% agree well with the field data shown in Fig. 3, supporting the assumption that the cloud is close to equilibrium. The results also suggest that the cloud persists longest in the presence of $AlCl_3$, which is able to sustain low water activities where, for the pure $HCl\text{-}H_2O$ system, both components can exist only in the gas phase. These and other calculations show that cloud lifetimes are shortest under relatively dry conditions, although the persistence of the cloud in the presence of $AlCl_3$ means that a reasonable fraction of the HCl remains associated with the liquid phase for relatively longer periods of time.

The insert in Fig. 3 shows the decrease in calculated cloud liquid water content in the 89.7%-*RH* case for both the $HCl\text{-}H_2O$ aerosol (solid line) and the $HCl\text{-}AlCl_3\text{-}H_2O$ aerosol (dashed line). A slope of -1.3 is given for comparison. As previously mentioned, the liquid water accounts for only a small fraction of the total water content of the air, but it can be described by a similar dispersion law to that for HCl. The slope is slightly greater than that of HCl (i.e., -1.4) and becomes steeper as the exhaust cloud evolves. The rapid decrease is consistent with the simultaneous dispersion and evaporation of liquid water. This decrease is a consequence of the decrease in total HCl concentration, which leads to progressively smaller quantities of water being required to support the constant aqueous HCl concentrations in the cold drops. Beyond 30 min aqueous water persists only in the system with $AlCl_3$ present.

The rate of aluminum loss from the system is known to be rather less than that of HCl.[1] For the calculations used to construct Fig. 3, the best agreement with the field data was obtained with aluminum removal constant *a* set to about -0.65. While it is unclear if this value is realistic, this calculation at least demonstrates that the presence of salts is likely to increase the cloud survival time and contribute to a longer-lived visible aerosol. It is important to remember that for the pure aqueous HCl system, a fixed *RH* in the cloud implies both constant gaseous HCl concentrations and constant HCl concentrations in the droplets. Thus, simultaneous measurements of in-cloud *RH* and gaseous HCl can show the extent to which the cloud remains at equilibrium.

A more general representation of equilibrium within the exhaust cloud system is shown in Fig. 4. Here, HCl was assumed to disperse as described by Sebacher et al.[22] and the aluminum aerosol more slowly, as previously noted. The shading in these figures denotes the region where no aqueous phase exists for the pure $HCl\text{-}H_2O$ system. The H^+ ion concentration scale given on the right-hand side of Fig. 4c refers only to the pure $HCl\text{-}H_2O$ case, where water activity uniquely specifies solute concentrations. The partition ratio of HCl is given in Fig. 4a, where the contours represent the logarithm of HCl_{aq}/HCl_g for clouds consisting of $HCl\text{-}H_2O$ (dotted line) and $HCl\text{-}AlCl_3\text{-}H_2O$ (dashed line). Note that partition ratios shown in Fig. 3 can also be obtained from Fig. 4 by moving parallel to the abscissa at the specified relative humidity or water activity. It is clear that at ambient relative humidities of less than 80% there is insufficient HCl to sustain the cloud for more than about 10 min, but that this figure rises quite rapidly with *RH*. The calculations also indicate that the ratio HCl_{aq}/HCl_g decreases sharply under dry conditions. This is consistent with measurements of the ratio in the ground cloud of Space Shuttle I by Sebacher et al.,[22] where ambient relative humidities of 75-90% and 25% were observed at different altitudes, with HCl_{aq}/HCl_g ratios equal to approximately 4:1 and 0.5:1, respectively.

With the present model it is not possible to estimate quantitatively the observed persistence of clouds at very low relative humidities such as those described. This limitation is due to the limitations in the description of the solution thermodynamics at very high aqueous phase concentrations. The model is also limited by the exclusion of dynamic factors.

Figure 4b shows the change in aqueous H^+ concentration with time as $-\log(mH^+)$ for the $HCl\text{-}AlCl_3\text{-}H_2O$ aerosol. For the pure aqueous HCl system mH^+ is constant at a given *RH*, but the mixed $HCl\text{-}AlCl_3\text{-}H_2O$ system shows more complex behavior. Early in cloud evolution mH^+ in the mixed cloud system approximates the pure HCl case, since $mHCl >> mAlCl_3$. However, mH^+ decreases with time (at constant RH) as HCl is lost through dispersion. Then, in the region where the cloud vanishes in the pure HCl case, a transition occurs. Figure 4a shows this to be the area where aqueous H^+

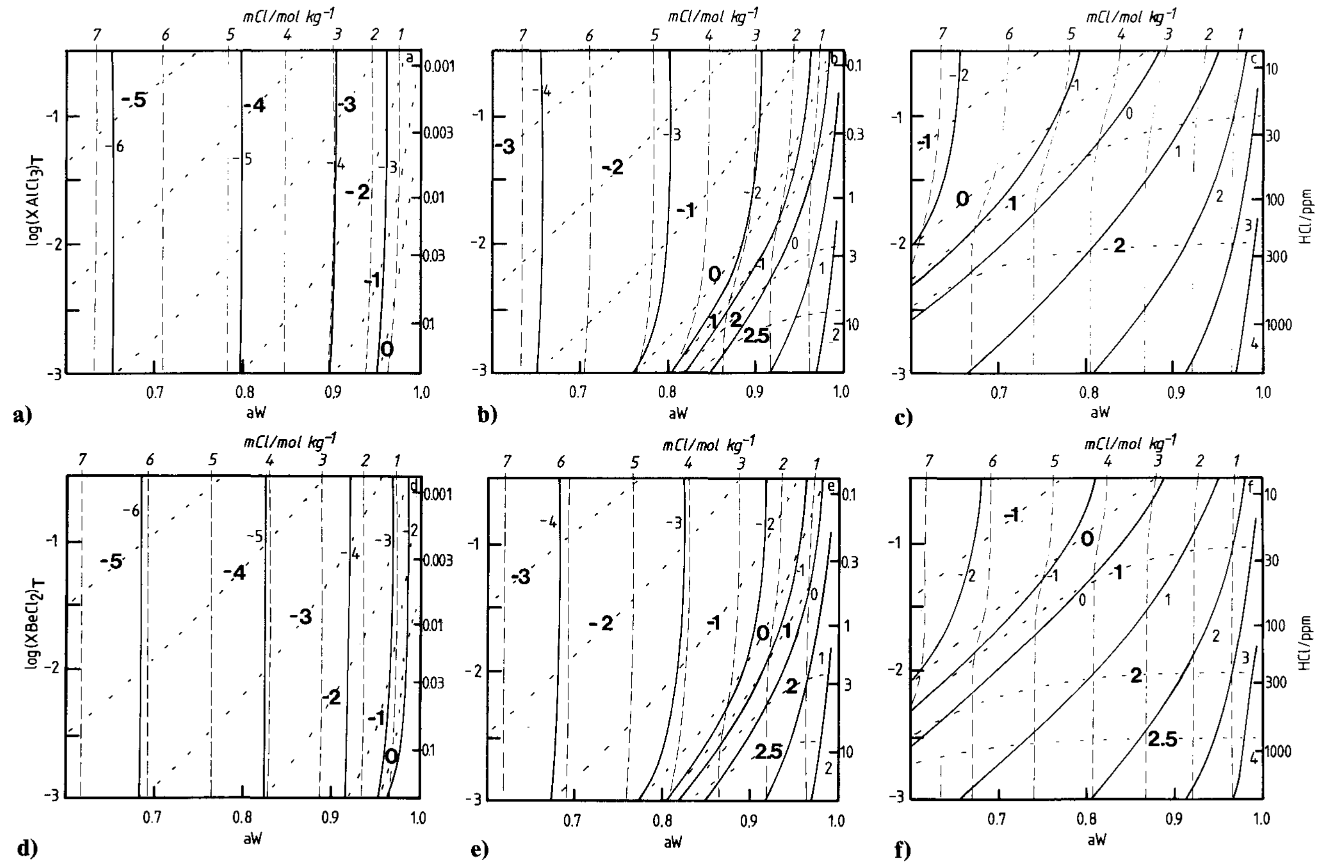

Fig. 5 Model results for some acidified aerosol systems: (———) log (HCl_{aq}/HCl_g), (- - - -) log (mH^+/mMe^{n+}), (— — —) mCl$^-$.

makes up about 10% of the total HCl in the cloud. Beyond this point the solution is dominated by aqueous $AlCl_3$, and mH^+ decreases very rapidly.

Figure 4c shows that although $AlCl_3$ is able to maintain the presence of liquid water in the later stages of cloud evolution, the amounts are quite small. In this plot, cloud water content is given as the logarithm of the mass liquid in g m^{-3} (intermediate contours are at $3x$ the value of the contour to the right). Results for pure HCl-H_2O clouds are represented by dotted lines and HCl-$AlCl_3$-H_2O clouds by dashed lines. Initially the lines coincide, indicating the dominance of HCl in controlling both systems.

Similar calculations were made for beryllium chloride aerosols. As might be expected from Fig. 1, the results resemble those described for aluminum-containing exhausts.

Modeled Behavior of Acidified $AlCl_3$ and $BeCl_2$ Aerosols

Further equilibrium calculations of the distribution of HCl between the gaseous $AlCl_3$ or $BeCl_2$ aerosol phases were made for the wide range of cloud concentrations found during exhaust cloud evolution. Typically the 80 mg m^{-3} aluminum oxide found in the Shuttle plume represents an $AlCl_3$ concentration of 30 μmol m^{-3}, assuming that about 5% of the oxide is present as the chloride.[5] In calculations here, which do not require assumptions about the way in which the exhaust cloud disperses, metal chloride concentrations were fixed at 0.01, 1.0, or 100 μmol m^{-3} to bracket this observed value.

The results of these calculations are presented as contour plots in Fig. 5 for systems containing either $AlCl_3$ or $BeCl_2$. Each plot was produced from calculations for approximately 400 equispaced grid points. The bold contours show the ratio HCl_g/HCl_{aq} as a function of water activity and log ($XMeCl_n$). The quantity log (mH^+/mMe^{n+}) is shown as a dotted line on each diagram. Total metal chloride concentrations were 0.01, 1.0, and 100 μmol m^{-3} in graphs a–c and d–f respectively. The quantity mCl appears as fine dashed lines labeled at the top of each diagram. These complicated figures can be used as "nomograms" to obtain the composition of exhaust clouds without detailed calculation. It should be noted that the constant temperature of 25°C leads to an overestimation of the HCl partitioning ratio at lower cloud temperatures. It is important to notice that while the axes are similar to those in Fig. 2, the mole fraction of the metal salt is plotted as a logarithm (here, the mole fraction refers to the total amount in the model system). The right-hand ordinate has been graduated in terms of the total amount of HCl present, which is the most frequently measured quantity.

The calculations undertaken in this study highlight the types of measurements that ought to be considered in future monitoring programs. The liquid water content of clouds is a key parameter for verifying the equilibrium status of the cloud and understanding its evolution. Other data that need to be reported more frequently, in addition to hydrogen chloride concentrations, are the amounts of aerosol aluminum chloride in the cloud as it disperses.

Conclusions

While assumptions have been made concerning quantities such as the total liquid water content of the model ground cloud and the dispersion rate of $AlCl_3$, the calculations made here show that the partitioning of HCl within ground cloud systems is quite well described by a purely equilibrium model. Furthermore, the presence of metal chlorides on exhaust particles only becomes important in changing the phase distribution of exhaust substances in long-lived clouds (10–100 min) where the aqueous HCl concentration becomes comparable to that of the metal chloride. In such situations the dissolved nonvolatile salt is more important than HCl in maintaining the presence of liquid water. Chlorided beryllium particles are likely to behave in a similar way to aluminum ones.

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