

Growth of Aqueous Solution Droplets of HNO₃ and HCl in the Atmosphere

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ABSTRACT

Computed values of equilibrium sizes and composition of uncharged and charged aqueous solution droplets of HNO₃ and HCl at 25°C, relative humidities from 5 to 101%, and solute vapor activities from 10⁻⁴ to 10⁷ are presented. Threshold concentrations for heteromolecular nucleation of HNO₃ and HCl at 40, 30, 20, 10, 0, and -10°C are also given as a function of the relative humidity. It is shown that atmospheric concentrations of HNO₃ and HCl can participate in nucleation at temperatures below 20°C and relative humidities above 98%. The nature of the nucleation of HNO₃ and HCl in the atmosphere including ion-induced nucleation for which there is no threshold and some of the available experimental results are discussed.

1. Introduction

Growth of condensation nuclei, composed of water soluble substances in the moist air and the related problem of nucleation in binary systems have been studied by several investigators, including Mason (1959), Doyle (1961), Low (1969), Vohra and Nair (1971), Winkler and Junge (1972), Kiang and Stauffer (1973), Mirabel and Katz (1974), Nair and Vohra (1975), Takahashi *et al.* (1975), Boulaud *et al.* (1977) and Yue (1979a,b). While sulphuric acid has been recognized as an important trace constituent of the atmosphere and is known to give rise to heteromolecular nucleation of droplets in the presence of water vapor (Stauffer *et al.*, 1973; Cox, 1973), the role of other trace constituents like HNO₃ and HCl has not been thoroughly investigated.

In gas-to-particle conversion processes occurring in the atmosphere, nitric acid, which is believed to be an important link in the tropospheric NO_x cycle, is next in importance to sulphuric acid. Rainout and washout are likely to be the major removal mechanisms for HNO₃ in the atmosphere and studies on the interaction of the acid at different concentrations with water vapor is relevant in the estimation of the residence time of HNO₃.

Hydrochloric acid is another important nucleogenic trace gas in the atmosphere. Sea salt is a natural source of HCl. There is considerable evidence that a large fraction of the chlorides in the atmosphere exists as hydrogen chloride (Cadle, 1972). Furthermore, there is an increased interest in the fate of anthropogenic tropospheric hydrogen chloride as it is increasingly being introduced into the atmosphere by the burning of fossil fuels, especially coal, incineration of plastic materials and by space flights. When NASA

takes up routine operation of the Space Shuttle, the estimated mass of HCl generated will be ~35 200 kg per launch. (Sebacher *et al.*, 1980). Measured concentrations of HCl range from 0.30 to 118 ppb in the working areas (Williams and Jacobi, 1978) to as high as 3030 ppm in the incinerator flue gases (Sebacher *et al.*, 1980).

Atmospheric concentrations of NO_x, HNO₃ and HCl vary from a fraction of 1 ppb in remote areas to a few thousand ppm in flue gases. While the natural and anthropogenic sources of these gases have been identified, their sinks and removal mechanisms are not well understood. In order to estimate the rates of different removal processes, it is necessary to assess the contributions from homogeneous and heterogeneous gas-to-particle conversion mechanisms which depend on the equilibrium concentration of the species in the gas and liquid phases and the concentration of particles of critical size and composition.

In gas-to-particle conversion, the phase transition process involved may be heteromolecular homogeneous or heterogeneous nucleation. In a radiation environment, due to the reduced free energy barrier for the phase transition of ions, heterogeneous nucleation can take place on the ions, which act as centers of nucleation. Investigations on nucleation of both charged and uncharged solution droplets are useful in atmospheric studies.

Studies on the formation of clouds in planetary atmospheres and aerosol layers in the stratosphere, have been carried out for HCl-H₂O solution droplets for the Venus atmosphere (Lewis, 1968) and HNO₃-H₂O droplets for the earth's stratosphere (Toon and Pollack, 1973). Similar work using the heteromolecular nucleation approach on HNO₃-H₂O by Kiang and Stauffer (1973) and HCl-H₂O in the cloud base

TABLE 1a. Density ρ , $d\rho/dx$, surface tension σ , $d\sigma/dx$, water activity, acid activity, m_w/m_0 and n_w/n_0 for HNO₃ solution at different concentrations at 25°C.

HNO ₃ mass percent X	ρ (kg m ⁻³ × 10 ³)	$d\rho/dx$	σ (N m ⁻¹ × 10 ⁻³)	$d\sigma/dx$ (×10 ⁻⁵)	a_w	a_0	m_w/m_0	n_w/n_0
0.5	1.000	5.0	72.0	8.4	0.995	3.98 × 10 ⁻³	199.0	695.8
1.0	1.002	5.1	71.9	8.5	0.990	1.26 × 10 ⁻²	99.0	346.2
5.0	1.022	5.5	71.5	9.0	0.975	3.16 × 10 ⁻¹	19.0	66.4
10.0	1.052	5.9	71.1	9.5	0.947	1.66 × 10 ⁰	9.0	31.5
20.0	1.112	6.3	70.0	11.0	0.866	2.51 × 10 ¹	4.0	14.0
30.0	1.175	6.3	68.8	13.5	0.749	3.55 × 10 ²	2.3	8.2
40.0	1.235	6.4	67.3	18.0	0.614	5.02 × 10 ³	1.5	5.3
50.0	1.300	6.4	65.2	25.0	0.450	1.63 × 10 ⁴	1.0	3.5
60.0	1.355	5.5	61.8	57.0	0.324	5.06 × 10 ⁴	0.7	2.3
70.0	1.405	4.2	57.3	115.0	0.231	1.72 × 10 ⁵	0.4	1.5

levels of the Venus by Stauffer and Kiang (1974) have been reported. However, the formation of aerosols from binary and multicomponent systems in a polluted environment at ambient temperatures and pressures in the lower atmosphere, needs further study. The present investigation on HNO₃ and HCl will be helpful in understanding the fate of the gases at low ambient concentrations as well as at high concentrations from stack emissions.

2. Equilibrium sizes and composition

The characteristics of aqueous solution droplets of HNO₃ and HCl in the atmosphere at 25°C and relative humidities ranging from 5 to 101% and solute vapor activities ranging from 10⁻⁴ to 10⁷ have been estimated using the generalized Kelvin equations for two-component systems, developed by Nair and Vohra (1975) and modified by Yue (1979a,b). The equations given below have been successfully applied by the investigators to heteromolecular nucleation of H₂SO₄-H₂O solution droplets. They can also be applied to other aqueous solution droplets of electrolytes such as HNO₃ and HCl for which data on activity, surface tension and density are available.

Formation and growth of spherical solution droplets through binary heteromolecular nucleation are controlled by the free energy change, represented by

$$\Delta G = n_A(\mu_{A1} - \mu_{Ag}) + n_B(\mu_{B1} - \mu_{Bg}) + 4\pi r^2 \sigma,$$

where A refers to water or the solvent, B to the solute or the acid, n is the number of moles, μ the chemical potential taken for the bulk phase of the same composition, r the radius of the solution droplet and σ the macroscopic surface tension.

At equilibrium, it is known that

$$(\partial\Delta G/\partial n_A)_{n_B} = 0,$$

$$(\partial\Delta G/\partial n_B)_{n_A} = 0.$$

Moreover, $4\pi r^3 \rho/3 = n_A M_A + n_B M_B$ where ρ is the bulk density and M_A , M_B are the molecular weights of water and acid, respectively. The percent mass of the acid is given by $X = 100n_B M_B / (n_B M_B + n_A M_A)$.

Let $S_A = P_A/P_{A0}$ be the relative humidity, and $S_B = P_B/P_{B0}$ be the relative acidity (where P_A and P_B represent ambient vapor pressures and P_{A0} , P_{B0} the equilibrium vapor pressures of A and B over a flat surface of pure substance and standard state, respectively). We also define $(a_A) = P_{A\text{sol}}/P_{A0}$ as the water activity, $(a_B) = P_{B\text{sol}}/P_{B0}$ as the acid activity (where $P_{i\text{sol}}$ is the equilibrium partial vapor pressure of i over a flat surface of the solution).

On partial differentiation of ΔG and simplification, it can be shown that

TABLE 1b. Density ρ , $d\rho/dx$, surface tension σ , $d\sigma/dx$, water activity, acid activity, m_w/m_0 and n_w/n_0 for HCl solution at different concentrations, at 25°C.

HCl mass percent X	ρ (kg m ⁻³ × 10 ³)	$d\rho/dx$	σ (N m ⁻¹ × 10 ⁻³)	$d\sigma/dx$ (×10 ⁻⁵)	a_w	a_0	m_w/m_0	n_w/n_0
0.5	1.000	4.9	71.9	-9.5	0.994	1.41 × 10 ⁻²	199.0	402.6
1.0	1.002	4.9	71.8	-9.3	0.986	3.98 × 10 ⁻²	99.0	200.3
5.0	1.021	4.9	71.6	-8.0	0.933	1.66 × 10 ⁰	19.0	38.4
10.0	1.046	4.9	71.3	-7.7	0.838	1.78 × 10 ¹	9.0	18.2
20.0	1.095	4.9	70.5	-12.2	0.588	7.94 × 10 ²	4.0	8.1
30.0	1.144	4.9	68.4	-27.0	0.313	3.55 × 10 ⁴	2.3	4.7
40.0	1.193	4.9	64.8	-51.0	0.117	1.58 × 10 ⁶	1.5	3.0
42.5	1.206	4.9	63.5	-60.5	0.091	3.16 × 10 ⁶	1.4	2.7

$$\ln(S_A/a_A) = (2/RT)(M_A/\rho)(\sigma/r) \times [1 + (X/\rho)(d\rho/dX) - (3/2)(X/\sigma)(d\sigma/dX)], \quad (1)$$

$$\ln(S_B/a_B) = (2/RT)(M_B/\rho)(\sigma/r) \{1 - [(100 - X)/\rho] \times (d\rho/dX) + (3/2)[(100 - X)/\sigma](d\sigma/dX)\}. \quad (2)$$

Eqs. (1) and (2) can be rearranged as follows (Yue, 1979a):

$$\log S_B = [\log a_B - (M_B/M_A)\alpha \log a_A] - (M_B\alpha/M_A) \log S_A, \quad (3)$$

where

$$\alpha = \frac{1 - (100 - X)(\rho)(d\rho/dX) + (3/2)[(100 - X)/\sigma](d\sigma/dX)}{[1 + (X/\rho)(d\rho/dX)] - (3/2)(X/\sigma)(d\sigma/dX)},$$

$$r^{-1} = [(-\log a_A + \log S_A)/(2/RT)(M_A/\rho)] \times [1 + (d \ln \rho / d \ln X) - (3/2) \times (d \ln \sigma / d \ln X)](\sigma \log e). \quad (4)$$

For charged droplets carrying charge Q , the term $(Q^2/2)(1 - 1/\epsilon)(r^{-1} - r_0^{-1})$ is added to ΔG so that

$$\ln(S_A/a_A) = (2/RT)(M_A\sigma/\rho)(1/r)(1 - Q^2/16\pi\sigma r^3) \times [1 + (X/\rho)(d\rho/dX) - (3/2)(X/\sigma)(d\sigma/dX)], \quad (5)$$

$$\ln(S_B/a_B) = (2/RT)(M_B\sigma/\rho)(1/r)(1 - Q^2/16\pi\sigma r^3) \times \{1 - [(100 - X)/\rho](d\rho/dX) + (3/2)[(100 - X)/\sigma](d\sigma/dX)\}, \quad (6)$$

where ϵ is the dielectric constant of the solution and r_0 the radius of the ion core.

Equilibrium sizes are computed for a range of acid

concentrations X (percentage by mass of the acid) from 10 to 70% for HNO_3 and from 5 to 40% for HCl for which density, surface tension and water activity are available (International Critical Tables, 1928; Robinson and Stokes, 1959; Timmermans, 1960; Handbook of Chemistry and Physics, 1965). The acid activities a_B are computed from activity coefficients (Robinson and Stokes, 1959) relative to the hypothetical standard states. The partial pressures of HNO_3 and HCl were obtained in pascals (Pa) on the basis of the partial pressure of 40% HNO_3 and 18% HCl which are 0.12 mm of mercury (0.1599×10^2 Pa) and 0.148 mm (0.1973×10^2 Pa), respectively (International Critical Tables, Vol. I, 1928). Detailed tables are given elsewhere (Nair, 1975) and have been summarized in Tables 1a and 1b.

For different environmental vapor pressures of water and acid as represented by relative humidity and relative acidity, defined with respect to the vapor pressure over a flat surface of pure water and of standard solution, respectively, at 25°C, the equilibrium composition of unchanged aqueous solution droplets of HNO_3 and HCl are presented in Fig. 1. The inverse of the corresponding equilibrium sizes for known composition and varying relative humidities are given in Fig. 2. The environmental concentration of acid is also expressed as the partial pressure of acid (Pa) in Figs. 1 and 3. The partial pressure of 1 torr of Hg (1.3332×10^2 Pa) is indicated on one of the scales for convenience of conversion. Once the composition is determined from Fig. 1, the equilibrium size for that composition and any relative humidity can be determined from Fig. 2.

In the case of charged droplets, Eqs. (5) and (6) represent the relationship between environmental saturation ratios, compositions and equilibrium sizes.

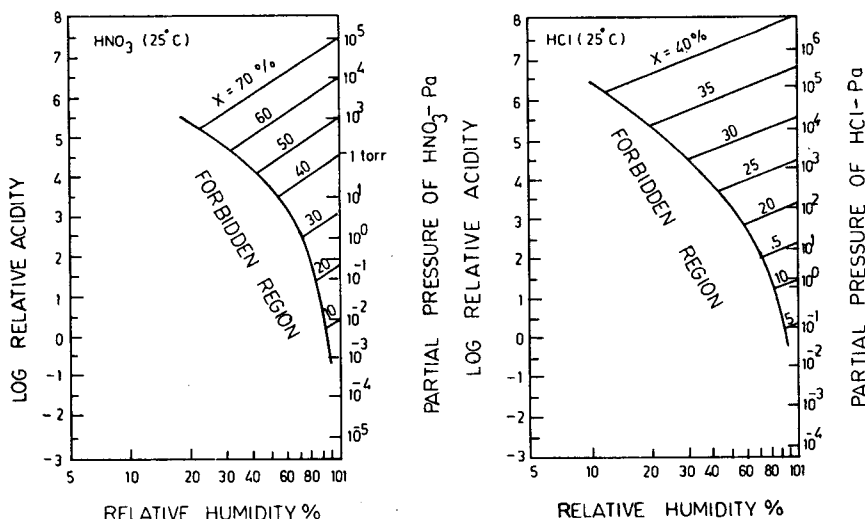


FIG. 1. Critical composition of HNO_3 and HCl aerosols at various relative acidities and relative humidities.

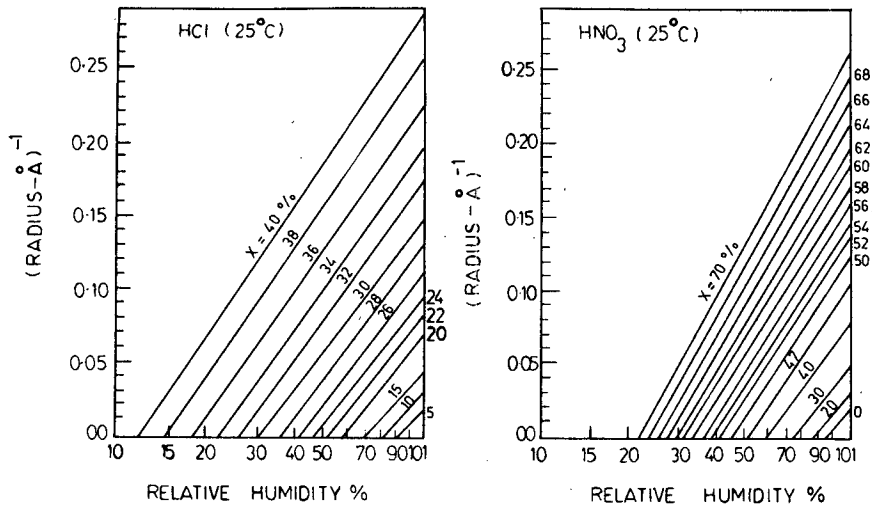


FIG. 2. Equilibrium sizes of HCl and HNO₃ solution droplets as a function of relative humidity for various compositions.

Critical composition of charged HNO₃ and HCl aerosols at various relative humidities and relative acidities are plotted in Fig. 3, whereas the inverse of equilibrium sizes of the droplets are given in Fig. 4.

The curves in Figs. 1 and 2 are plots of Eqs. (3) and (4) and are useful for determining the sizes and compositions of small droplets relevant for nucleation. For large droplets, plots of Eqs. (1) and (2) are more useful and are given in Figs. 5 and 6 for HNO₃ and HCl, respectively.

3. Threshold concentrations for nucleation

At any given temperature and relative humidity, there is a minimum concentration of the solute vapor required for nucleation to proceed as is implied in the concept of "zero supersaturation curve" (Kiang

and Stauffer, 1973) and the "forbidden region" (Yue, 1979a). Rhein (1973) has given the threshold concentrations of HCl in the gas phase required for nucleation at different relative humidities in the atmosphere for some temperatures and HCl concentrations in the range 1 to 1000 ppm.

The present study extends the estimation of threshold concentration for nucleation to HNO₃ as well as HCl over a concentration range of 10⁻³ (1 ppb) to 10⁴ ppm covering a range from background levels to flue gas concentrations, as shown in Fig. 7. Most of the values of the partial pressures of HNO₃ and H₂O at different temperatures were estimated from the basic data (Perry and Chilton, 1973; Robinson and Stokes, 1959). As data for the entire range were not available, extrapolations indicated by broken lines based on an integrated form of Clausius-Clapeyron

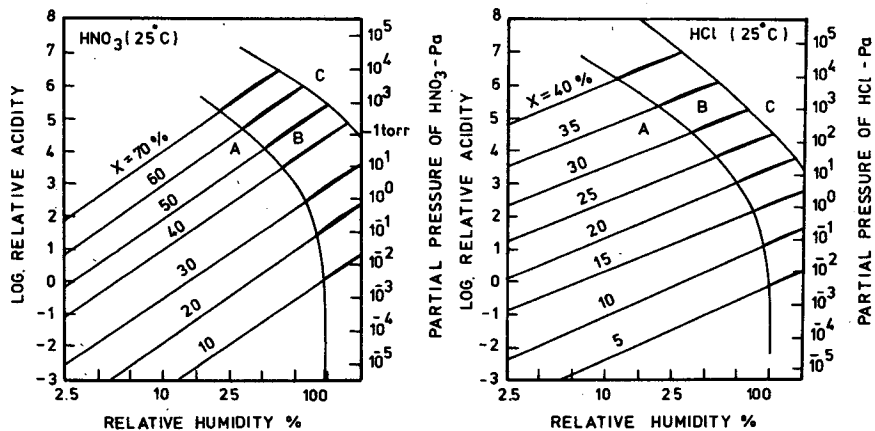


FIG. 3. Critical composition of charged HNO₃ and HCl aerosols at various relative humidities and relative acidities. A, stable region; B, transitory region; C, unstable region.

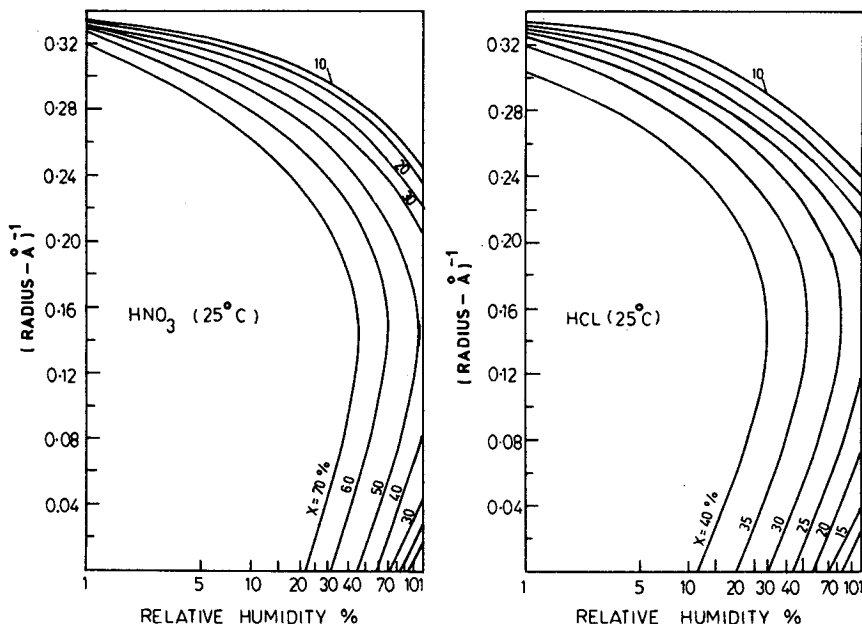


FIG. 4. Equilibrium sizes of charged HNO₃ and HCl solution droplets as a function of relative humidity for various compositions.

equation were necessary, for comparison with the HCl values. The equation used is (Perry and Chilton, 1973)

$$\ln P = AT^{-1} + B, \quad (7)$$

where P is the partial pressure (mm of Hg), T the

temperature (K), and A and B are constants in the temperature range of interest for a particular concentration of the solution. The constants will be different for the partial pressures of solute and solvent at different concentrations. In the case of HCl solution, the constants are available in a tabulated form for con-

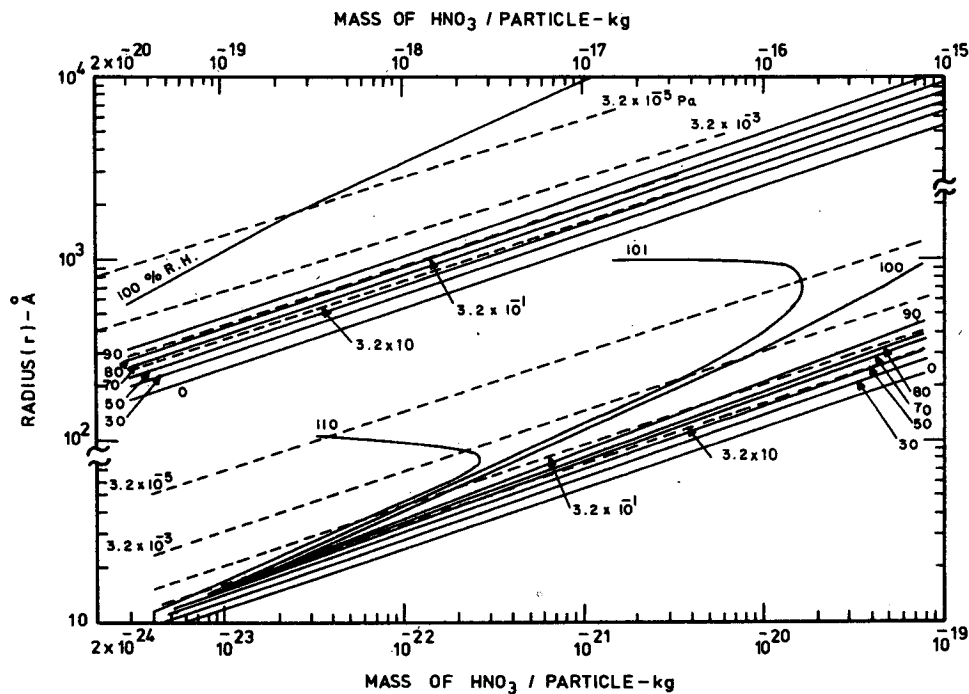


FIG. 5. Equilibrium sizes of aqueous solution droplets of HNO₃ for different relative humidities, solute masses and partial pressures of HNO₃.

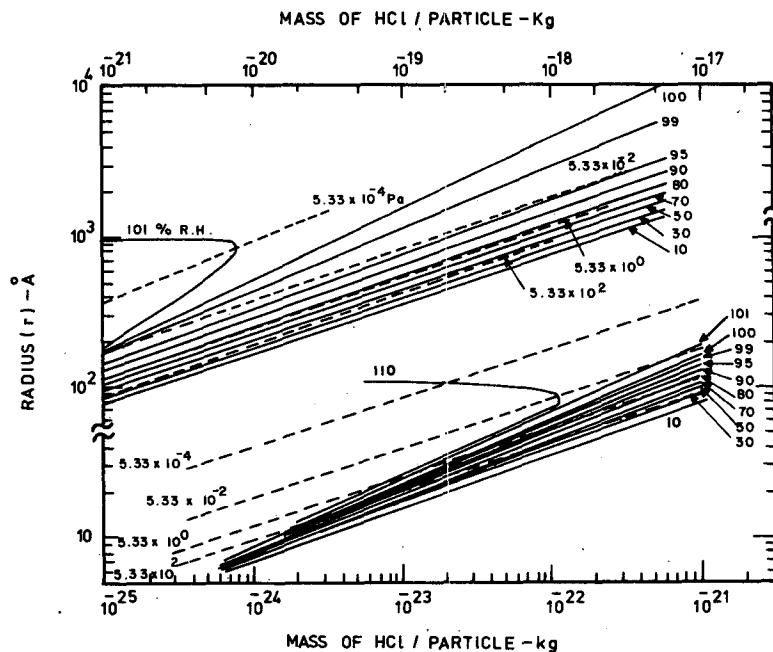


FIG. 6. Equilibrium sizes of aqueous solution droplets of HCl for different relative humidities, solute masses and partial pressures of HCl.

centrations from $X = 2$ to 44%, for partial pressures of HCl and from $X = 6$ to 42%, for partial pressures of H_2O (Perry and Chilton, 1973). Extrapolations were necessary only for 0.25, 0.5 and 3% concentrations and consisted of determining values of A and B from plots of A versus concentrations and B versus concentration. Dilute solutions tend toward ideal behavior and no drastic variations are expected in their partial pressures. A and B ranged from 8.99156 and 2282 at 6% to 9.44953 and 2709 at 42%. For partial pressures of water vapor, extrapolation gave 9.0724 and 2295 at 0.25% concentration and 9.0547 and 2307 at 3.0% concentration. For partial pressures of HCl, A and B ranged from 11.8037 and 4736 at 2% to 8.9925 and 1800 at 42%. Extrapolation gave 11.85 and 5358 at 0.25% and 11.74 and 4600 at 3% concentration for values of A and B , respectively. The values obtained on extrapolation are expected to have an error of less than 2–10% as assessed from the interpolations as well as by comparison with values derived from activity coefficients at 25°C (Robinson and Stokes, 1959).

For HNO_3 solutions, Perry and Chilton (1973) have given tabulated data on the vapor pressures of HNO_3 and H_2O for concentrations ranging from $X = 20$ –100% for temperatures from 0°C to more than 100°C. Though application of (7) is not indicated in the reference cited for HNO_3 , it is found that the data can be fitted quite accurately to the equation wherein A and B are constants, for any fixed concentration

over the range of temperatures from 0 to 40°C. The vapor pressures estimated are correct within an accuracy of 2 to 15%. Extrapolations have been done to obtain data at $-10^\circ C$ and also for HNO_3 vapor pressures below about 10 ppm using values of A and B at 2, 5 and 10%, obtained from plots of the constants estimated from tabulated vapor pressures at higher concentrations. The extrapolations are indicated by broken lines. The percentage concentrations of the solute in the binary solution at equilibrium are indicated by vertical curves connecting equal X values as shown in Fig. 7.

4. Experimental studies

Data on direct measurement of nucleation and growth of aqueous solution droplets of HNO_3 and HCl are few. Measurements of HNO_3 vapor and particulate NO_3^- in equilibrium in the atmosphere are available (Huebert and Lazrus, 1978) but without any information on the relative humidity and the nature of nitrates. Sebacher *et al.* (1980) have estimated partitioning of hydrogen chloride between hydrochloric acid aerosols and gaseous HCl in the plume of a Titan III rocket and have obtained results in agreement with theory.

Nair (1975) has measured the concentration and sizes of solution droplets which are formed in equilibrium with the acid solution of known concentration in bulk. The study was on the particles generated

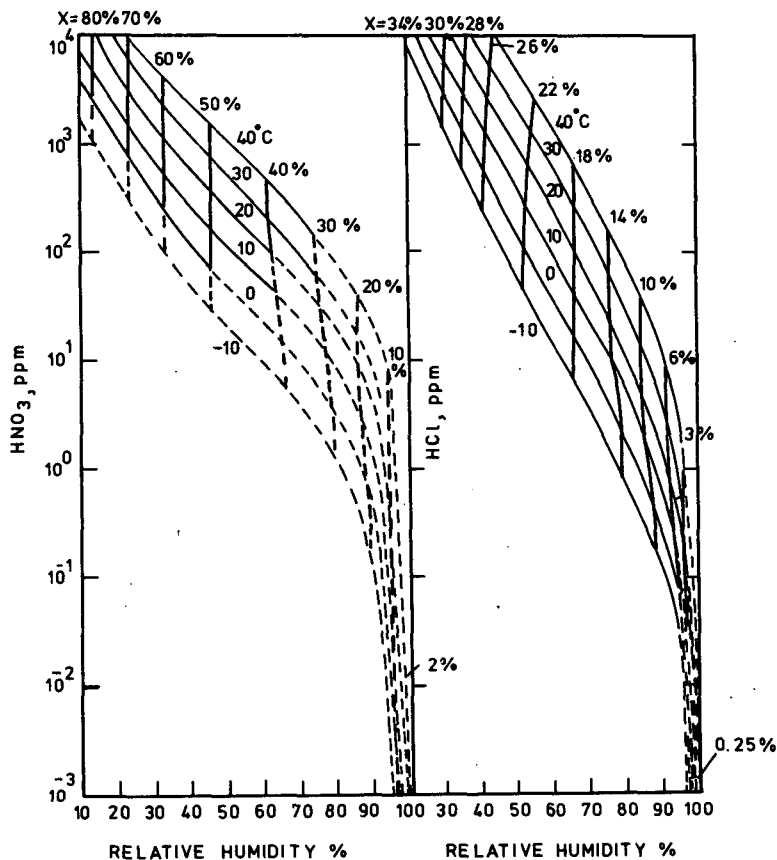


FIG. 7. Nucleation threshold concentrations of HNO₃ and HCl at different relative humidities as a function of temperature. Critical compositions are also indicated.

and grown in a closed system containing vapors of known composition in pure nitrogen. The system consisted of a 12 L spherical flask containing about 50 mL of an aqueous solution of HNO₃ or HCl. The flask was connected to filtered, pure tank nitrogen on one side and a nucleus counter on the other. The nucleus counter is used for concentration measurements and also for size estimates based on calibration by the static diffusion technique. The concentration of the solution in the flask was increased by adding the solute gradually until the nucleus counter showed a particle concentration of 10¹⁰ m⁻³. Thus it may be noted that as the concentration of the solution increased, the nuclei concentration increased gradually from about 10⁷ to 10⁸ m⁻³ and thereafter, it abruptly rose to 10¹⁰ m⁻³. The values of relative humidity and acid activity in equilibrium with the solution of critical composition were taken from standard references. The vapor concentrations required for heteromolecular nucleation at a fixed relative humidity was computed for the two acids in the presence of H₂O vapor. The results obtained are compared with the theoretical values.

5. Discussions

Growth parameters of uncharged as well as charged aqueous solution droplets of HNO₃ and HCl are presented in Figs. 1–6. The range of partial pressures covered are from 3.19 × 10⁻³ to 3.19 × 10⁴ Pa for HNO₃, 5.27 × 10⁻³ to 5.27 × 10⁵ Pa for HCl at 25°C and partial pressures of water vapor from 3.20 × 10¹ (RH = 1.0%) to 3.23 × 10³ Pa (RH = 101%). In addition, Fig. 7 gives threshold values of vapor concentration for nucleation of HNO₃ and HCl as a function of relative humidity for different compositions and temperatures. The following points may be specially noted:

1) Figs. 1–6 show that the concentrations of HNO₃ or HCl needed for binary heteromolecular homogeneous nucleation with water vapor in the atmosphere, are high (10–100 ppm) at moderate humidities (RH = 50–80%). Homogeneous nucleation leading to the formation of aerosols of pure aqueous solution droplets of HNO₃ or HCl cannot occur except when the atmosphere is highly polluted with these acids. How-

ever, at high relative humidities, heterogeneous nucleation can take place at concentration levels normally found in the atmosphere (Figs. 3, 4 and 7). This is true for nucleation on charged droplets, as explained later, and is also true for wettable uncharged particles $>1000 \text{ \AA}$ in radius. At 20°C , 1.6 ppb of HCl or 1 ppb of nitric acid can give rise to nucleation at 99% RH and 11 ppb of nitric acid or 17 ppb of HCl can nucleate at 98% RH on wettable particles larger than $1000\text{--}5000 \text{ \AA}$ radius. Relative humidities of 98–99%, though not common, are observed in the atmosphere (Meteorological Office, 1978). At these relative humidities, particles five times larger can nucleate HNO_3 or HCl at one-tenth of the above concentrations. This is important in the wet removal of the trace gases and formation of haze or fog in the atmosphere. This can also lead to enhancement in the haze or fog initiated by other nucleogenic species like H_2SO_4 but depends on the composition and acidity of the droplets. It may be noted that at relative humidities $>95\%$ a substantial fraction of the atmospheric aerosols undergo deliquescence and form solution droplets. The interaction of such droplets with the acid vapor molecules is in the nature of absorption, or to be more precise, multi-component heteromolecular heterogeneous nucleation and condensation. These phenomena are more complicated than the binary heteromolecular processes considered so far and need to be studied in detail. The interaction is controlled by changes in Gibb's free energy which depends on the activities of the solutes and the solvent, and the details can be worked out if the actual composition and related properties are known. It is likely that in some cases a deliquescent droplet will lower the threshold for nucleation. It should be emphasized that heterogeneous and not homogeneous heteromolecular nucleation is important for HNO_3 and HCl in the atmosphere.

2) The curves of nucleation threshold values for HNO_3 and HCl as a function of the relative humidity, for the different compositions and temperatures shown in Fig. 7, are equivalent to those of the "zero supersaturation" values given by Kiang and Stauffer (1973) but are smaller by 2–3 orders of magnitude than the levels needed for a nucleation rate of $1 \text{ cm}^{-3} \text{ s}^{-1}$ given in Kiang *et al.* (1973) and Mirabel and Katz (1974). This is because in the latter cases, the nucleation considered is either homogeneous or on embryos of small radii, whereas the smaller values reported here are for nucleation on flat surfaces or large particles of negligible radii of curvature ($>1000 \text{ \AA}$). Further, the rate of nucleation in this case depends on the concentration and properties of the particles present, and can be estimated in a detailed study.

It may be seen that the threshold concentration decreases rapidly with increase in the relative humidity and decrease in the temperature. Thus, at 10% RH and 0°C temperature, the required gas phase concentration of HNO_3 for aerosol formation is about

$2.6 \times 10^3 \text{ ppm}$, and at 20°C it is $\sim 10^4 \text{ ppm}$, but it is 4–5 orders of magnitude less at 95% RH. For HCl at 95% RH and 40°C temperature, the threshold concentration is 2 ppm and at 10°C about 40 ppb whereas at 20% RH, it is above 10^4 ppm at both the temperatures. When the concentration of the species exceeds the threshold value, the excess gets converted to solution droplets mainly by heterogeneous nucleation and the equilibrium concentrations of the solute in the droplets are indicated by the vertical curves (Figure 7).

3) Yue (1979a,b) has worked out the characteristics of uncharged as well as charged aqueous solution droplets of H_2SO_4 . Our curves for uncharged solution droplets of HNO_3 and HCl are similar to those of Yue for H_2SO_4 . However, the range of relative acidity for which no stable uncharged particle can exist, as indicated by the forbidden region in Fig. 1, at 25°C , extends up to 10 torr ($>10^3 \text{ Pa}$) at 10% RH and about 1 ppm at 90% RH for HNO_3 . It approaches 10^3 torr ($>10^5 \text{ Pa}$) at 10% RH and is more than 1 ppm at 90% RH for HCl compared to a fraction of 1 ppb at 10% RH and $\sim 10^6 \text{ ppb}$ at 90% RH for H_2SO_4 . The forbidden region, which represents compositions for which no particles of finite size can exist, is separated in Fig. 1 by the threshold concentration curve, from the finite-size range. It shows clearly that unlike $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$, homogeneous heteromolecular nucleation is improbable for $\text{HNO}_3\text{--H}_2\text{O}$ and $\text{HCl--H}_2\text{O}$ in the atmosphere and heterogeneous nucleation is likely only at high relative humidities.

4) Nucleation on charged droplets of aqueous solutions of HNO_3 and HCl is more complicated and differs considerably from that of uncharged droplets. While there is no forbidden region, an unstable region where partial pressures are too high for droplets of finite size to be stable, exists. Charged droplets formed or those which are growing may be said to attain stable, transitory or unstable equilibrium with vapors, depending on environmental conditions as indicated in Figs. 3 and 4. It depends on the variation of Gibb's free energy of formation for different concentrations and when plotted against radius it may have (i) a local minimum giving stable droplets, (ii) a local minimum followed by a local maximum giving transitory stability for the solution droplets within a size range, or (iii) monotonic decrease so that droplets will continue to grow without attaining equilibrium (Yue, 1979b). Different degrees of stability may also be understood in terms of the direction of change in equilibrium vapor pressure for any change in size. If the equilibrium partial pressure of the solute or solvent tends to increase for a small increase in the size, the particles tend to be stable. They are unstable if the equilibrium vapor pressure reduces on an increase in the size as it helps in further growth by condensation from the environment. It may be noted that the stable particles are small ($r < 10 \text{ \AA}$) and the unstable particles are large. Particles of an intermediate size range tend to

be stable for small changes but are unstable against large fluctuations in the size. This is seen in the transitory region B in Fig. 3. In this region, for every value of relative acidity or relative humidity there are two values of r , one corresponding to the free energy minimum and the other to the free energy maximum.

When two uncharged droplets collide and coalesce, the equilibrium vapor pressure decreases as is clear from Eqs. (1) and (2). The decrease in the vapor pressure can lead to the growth and hence the equilibrium sizes attained for uncharged droplets are unstable. This is not generally true for charged droplets as seen from Figs. 3 and 4. In the case of charged aqueous solution droplets, it can be shown that on coalescence, droplets may be stable, transitory or unstable, depending on the initial size range and the state of charging of the droplets.

5) Experiments in the laboratory performed with known concentrations of HNO_3 or HCl at controlled relative humidity values have been used to test the theoretical predictions on threshold concentrations for nucleation. Measurements showed that 200 ppm of HNO_3 at 60% RH and 1.5×10^4 ppm of HCl at 33% RH gave rise to binary nucleation at 25°C as indicated by a steady concentration of 10^{10} m^{-3} nuclei in the measuring flask which is estimated to correspond to a nucleation rate of 10^6 – $5 \times 10^6 \text{ m}^{-3} \text{ s}^{-1}$, on the basis of expected wall losses of the small nuclei formed. Fig. 7, gives 190 ppm of HNO_3 as the threshold concentration for nucleation at 60% RH and 1.7×10^4 ppm of HCl at 33% RH, which is in close agreement with the experimental values. The agreement is surprising because Fig. 7 gives the threshold concentration for all nucleation but effectively for heterogeneous nucleation, whereas the measurements were carried out with filtered gases and the nucleation involved is more likely to be either homogeneous or on ions produced by natural background radiation. The simple experimental setup used cannot distinguish between homogeneous nucleation and ion-induced nucleation and the results provide only qualitative agreement with theory. Further experiments are necessary to determine the threshold concentrations accurately.

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