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# IN-CLOUD AND BELOW-CLOUD SCAVENGING OF NITRIC ACID VAPOR

S. Z. LEVINE and S. E. SCHWARTZ
Environmental Chemistry Division, Department of Energy and Environment, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.

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**Abstract**—Scavenging coefficients, Λ, for the removal of $HNO_3$ vapor from the atmosphere by both cloud and rain drops have been calculated for assumed models of drop-size distribution. For cumulus clouds a value of $0.2\,s^{-1}$ is estimated for Λ. Evaluation of rainfall washout coefficients gives values of Λ ranging from $1.3 \times 10^{-5}$ to $1.5 \times 10^{-3}\,s^{-1}$, depending upon the rainfall rate, upon the drop-size distribution function employed, and, strongly upon the lower limit of the raindrop size employed in the calculations. The concentration of soluble gas dissolved within a falling drop per unit fall distance is found to be a function of drop size, with the smaller drops accumulating the greater concentration. The long-term average rate of heterogeneous removal of $HNO_3$ is estimated in the range $1–8 \times 10^{-6}\,s^{-1}$, representing comparable contributions from dry deposition and rainfall scavenging.

## 1. INTRODUCTION

Nitrogen oxides—NO and to a lesser extent $NO_2$—are introduced into the atmosphere as by-products of fossil fuel combustion by electric power generation and other stationary facilities, by vehicles and by aircraft. A major fraction of these oxides of nitrogen is further oxidized by gas-phase reactions to $NO_2$ and in turn to nitric acid vapor, $HNO_3$. The elementary reactions that comprise these processes are now rather well understood (Baulch *et al.*, 1980; Levine and Schwartz, 1982). The formation rate of $HNO_3$ vapor has been estimated in model calculations to be as great as $0.2\,ppb\,min^{-1}$ for conditions associated with urban photochemical smog (Calvert and McQuigg, 1975) and $NO_x$ transformation rates (to $HNO_3$ and, to a lesser extent, PAN) have been reported as great as $0.14–0.24\,h^{-1}$ in an urban plume (Spicer, 1980). Concentrations of $HNO_3$ as great as 5–10 ppb have been reported in regions influenced by the transport of air pollutants (Spicer, 1977; Okita and Ohta, 1979). However, measured $HNO_3$ concentrations in clean air are reported as substantially lower. Huebert and Lazrus (1979) report $HNO_3$ concentrations of 0.15–0.8 ppb in mid-latitudes, but substantially lower ($< 0.03$ to 0.11 ppb) in the remote continental boundary layer. Similarly low values ($< 0.03$ to 0.11 ppb) are reported for clean air by Kelly *et al.* (1980), who find nitric acid concentrations invariably less than $NO_x$ ($\equiv NO + NO_2$) concentrations.

Similar considerations pertain to $HNO_3$ in the stratosphere, where again this species is expected to be the principal chemical sink for nitrogen oxides. Mixing ratios of up to 10 ppb are reported for $HNO_3$ in the mid-stratosphere (25 km) (Lazrus and Gandrud, 1975; Harries *et al.*, 1976), diminishing to substantially lower values at the tropopause.

These considerations have led to heightened interest in $HNO_3$ removal processes, since in the absence of a rather fast removal rate of $HNO_3$ this species would be expected to accumulate to concentrations substantially greater than are observed (Huebert and Lazrus, 1979). Rates of gas-phase free radical reactions (e.g. with HO to form $NO_3$) appear to be slight and lead ultimately back to $HNO_3$. Hence it appears that heterogeneous processes will dominate $HNO_3$ removal. Among these, reaction with aerosol particles appears to be a potentially important sink. However, as noted by Tang (1980) only basic particles would be effective in this regard, because of the high vapor pressure of $HNO_3$ above acidic salts. Hence this process is self-limiting in the absence of base such as $NH_3$. These considerations, as well as the high solubility of $HNO_3$ in water (as the ions $H^+$ and $NO_3^-$) suggest that $HNO_3$ is removed from the atmosphere principally as $HNO_3$, either by dry deposition (to the ocean or to the ubiquitous layer of water that coats virtually all surfaces) or by precipitation scavenging (Chameides, 1975; Stedman *et al.*, 1975). The importance of heterogeneous removal processes upon calculated concentration profiles of tropospheric $HNO_3$ has been emphasized by Fishman and Crutzen (1977) who have shown, by model calculations, an order of magnitude decrease in $HNO_3$ concentrations as a consequence of an assumed heterogeneous removal rate of $2 \times 10^{-6}\,s^{-1}$ (mean residence time $\approx 6$ days) arbitrarily ascribed to $HNO_3$ in the lowest 6 km. Such tropospheric removal processes would appear to serve also as the ultimate removal mechanism for stratospheric $HNO_3$, subsequent to transport of $HNO_3$-containing stratospheric air across the tropopause (Fishman and Crutzen, 1977). The description of aqueous-phase $HNO_3$ removal rates is thus of interest in consideration of $HNO_3$ budgets and residence times (Rodhe and Grandell, 1972; Slinn *et al.*, 1978), as well as in the quantitative description of acid deposition in precipitation.

In this paper we address scavenging of $HNO_3$ vapor by atmospheric liquid water, i.e. cloud and rain droplets. Characteristic times are identified for these processes and estimates are presented for the fractional rate of $HNO_3$ removal for several models of drop-size distributions. Consideration is given also to the potentially observable dependence of the dissolved $HNO_3$ concentration upon fall distance and size of a raindrop. In these calculations $HNO_3$ is treated as an irreversibly soluble gas, an assumption that is subsequently justified. Thus, in addition to treating the in-cloud (rainout) problem, the present paper extends to irreversibly soluble gases a treatment presented previously for the calculation of rates for the reversible washout of moderately soluble gases such as $SO_2$, $NH_3$ and $CO_2$ (Dana *et al.*, 1975; Hill and Adamowicz, 1977; Adamowicz, 1979; Overton *et al.*, 1979).

## 2. MATHEMATICAL MODEL

The rate of uptake of a gas by a cloud or rain drop may be evaluated according to the equation of mass transfer,

$$F = k_g(C_g - C_g^*), \tag{1}$$

where $F$ = the flux of gas to the drop, moles $\mathrm{cm^{-2}\,s^{-1}}$; $k_g$ = the gas-phase mass transfer coefficient, $\mathrm{cm\,s^{-1}}$; $C_g$ = the bulk gas-phase concentration of the gas, moles $\mathrm{cm^{-3}}$ and $C_g^*$ = the concentration of the gas in equilibrium with the aqueous concentration of the dissolved gas at the surface of the drop, moles $\mathrm{cm^{-3}}$.

The convective–diffusive mass-transfer coefficient can be estimated by the semi-empirical Frössling (1938) equation,

$$k_g = \frac{\mathscr{D}_g}{D_0}\left[2 + 0.6\left(\frac{D_0 u}{\nu}\right)^{1/2}\left(\frac{\nu}{\mathscr{D}_g}\right)^{1/3}\right]. \tag{2}$$

The nomenclature used in the above equation is as follows:

$\mathscr{D}_g$ = diffusivity of the gas in air, $\mathrm{cm^2\,s^{-1}}$; $\nu$ = kinematic viscosity of air, $\mathrm{cm^2\,s^{-1}}$; $u$ = terminal velocity of the drop, $\mathrm{cm\,s^{-1}}$ and $D_0$ = equivalent drop diameter, cm.

Equivalent diameter is defined as the diameter of a sphere of the same volume as a deformed falling raindrop (Pruppacher and Beard, 1970). The two terms on the right hand side of (2) correspond to mass transfer by diffusion and convection, respectively; for larger drop sizes ($D_0 \geqslant 0.02$ cm) the second term dominates the expression, whereas for smaller drop sizes the first term becomes increasingly important. Equation (2) has been compared to experimental studies (Pruppacher and Klett, 1978, p. 442) and is shown to provide a close approximation to the observed gas mass-transfer coefficient.

Before applying (1) and (2), consideration must be given also to mass transport within the aqueous phase, which will determine the surface concentration of the dissolved gas and in turn $C_g^*$. For water drops in the atmosphere such mass transport will occur by both molecular diffusion and by convection as induced by momentum transfer to the falling drop (Hales, 1972; Slinn, 1982). The problem of mixing by diffusion only, which has been treated by Crank (1975, p. 96), serves to set an upper bound to the departure of the surface concentration from the average value. From that treatment it is readily established that the aqueous phase surface concentration of dissolved solute, $C_s$, within a drop exposed to a constant flux $F$ for time $t$ is bounded by

$$C_s \leqslant \frac{6Ft}{D_0}\left(1 + \frac{D_0^2}{60\mathscr{D}_a t}\right), \tag{3}$$

where $\mathscr{D}_a$ is the aqueous phase diffusion coefficient. The first term of this equation represents the average concentration in the drop and the second term represents the departure at the surface. From (3) it is readily seen that the surface concentration is adequately represented by the average concentration for all cases of practical interest, so that the drop may be considered well mixed.

For an irreversibly soluble gas equation (1) may be simplified by setting $C_g^* = 0$ as was apparently done by Engelmann (1968) and Fenton *et al.* (1980) in their consideration of the scavenging of highly soluble gases by water drops. Such a simplification is justified provided that $C_g \gg C_g^*$. In the case of $HNO_3$, which is virtually entirely ionized in aqueous solution, the primary equilibria governing solubility are the Henry's law partition for the un-ionized acid and the aqueous phase equilibrium for the formation of the $H^+$ and $NO_3^-$ ions. These equilibria may be combined to give the overall reaction

$$HNO_3(g) = H^+ + NO_3^- \tag{4}$$

with an equilibrium constant of

$$K_{eq} = [H^+][NO_3^-]/p_{HNO_3}. \tag{5}$$

The equilibrium constant can be represented over the temperature range of interest as $K_{eq} = 1.59 \times 10^{19}\, e^{-8710/T}\,\mathrm{M^2\,atm^{-1}}$ and has a value of $3.26 \times 10^6\,\mathrm{M^2\,atm^{-1}}$ at 25 °C (Schwartz and White, 1981). (Units are employed with $K_{eq}$ to facilitate application; cf. Daniels and Alberty, 1975.) Equation (5) permits evaluation of the equilibrium vapor pressure (in atmospheres) from the molar concentration of the dissolved nitric acid according to the equilibrium equation

$$p^* = \frac{\{HNO_3\}^2}{K_{eq}}; \tag{6}$$

where $\{HNO_3\}$ represents the formal (formula-weight per liter) concentration of aqueous $HNO_3$, and where it is assumed there are no other significant sources for or sinks of $H^+$. For a typical atmospheric water content $L = 10^{-6}\,\mathrm{g\,cm^{-3}}$, $HNO_3$ at a partial pressure of $p = 10^{-8}$ atm would, if totally dissolved, result in an aqueous phase concentration of the dissolved gas of $\{HNO_3\} = 4 \times 10^{-4}$ M. From (6) we see that such an aqueous phase concentration will result in an equilibrium vapor pressure $p^*$ of only $5 \times 10^{-14}$ atm. Thus, the simplification to (1) achieved by setting $C_g^* = 0$ is justified for the uptake of $HNO_3$ by atmospheric water droplets and is employed here. It is instructive to consider also the equilibrium ratio of $HNO_3$ concentration in the aqueous phase to that in the gas phase,

$$C_{\mathrm{HNO_3(a)}}/C_{\mathrm{HNO_3(g)}} = K_{\mathrm{eq}}^{1/2}\, LRT/p_{\mathrm{HNO_3}}^{1/2}, \qquad (7)$$

where $R$ is the gas constant. For $p_{\mathrm{HNO_3}} = 10^{-8}$ and $10^{-10}$ atm the equilibrium ratio of the concentrations of dissolved to gaseous $HNO_3$ is 500 and 5000, respectively, for $L = 10^{-6}\,\mathrm{g\,cm^{-3}}$. This calculation illustrates the ability of a liquid water cloud to act as a reservoir for atmospheric $HNO_3$ capable of storing high concentrations of this substance, of transporting it both horizontally and vertically, and of subsequently releasing it either back into the atmosphere upon evaporation or to the surface in rainfall.

In addressing the scavenging of a gas such as $HNO_3$ there are two possible approaches that are useful. First, one may address the rate of increase with time or with fall distance of the concentration of dissolved gas for droplets of various sizes. Alternatively one may address the rate of decrease of the gas phase concentration of the soluble gas under conditions of interest, i.e. clouds or rain. The former calculation requires specification of the vertical profile of the concentration of the gas being scavenged, i.e. $HNO_3$. The latter calculation requires specification of and integration over the drop-size spectrum characterizing the cloud or rain system of interest. Consequently, both approaches necessarily require rather arbitrary assumptions in any general treatment such as is undertaken here. Nevertheless, by proceeding with such calculations, valuable insights may be developed that enhance our quantitative understanding of these processes.

The rate of increase, within a drop, of the concentration of a dissolved gas may be evaluated as

$$\mathrm{d}C_a/\mathrm{d}t = FS/V \qquad (8a)$$

$$= \pi D_0^2 k_g C_g/(\pi D_0^3/6) \qquad (8b)$$

$$= 6 k_g C_g/D_0 \qquad (8c)$$

where we have now introduced:

$S$ = drop surface area $= \pi D_0^2, \mathrm{cm^2}$ and $V$ = drop volume $= \pi D_0^3/6, \mathrm{cm^3}$.

For the situation of a raindrop falling at its terminal velocity through uniformly mixed static air, the change in concentration with altitude may be evaluated according to

$$\frac{\mathrm{d}C_a}{\mathrm{d}Z} = \frac{1}{u}\frac{\mathrm{d}C_a}{\mathrm{d}t}, \qquad (9)$$

where $Z$, cm, is the fall distance. By substituting (8) into (9) and integrating one readily obtains an expression for the concentration of material within the falling raindrop as a function of distance,

$$C_a = \frac{6k_g}{D_0 u} C_g Z = \frac{6k_g}{D_0 u RT} pZ = \gamma pZ. \qquad (10)$$

The quantity $\gamma$ represents the concentration of dissolved $HNO_3$ per unit fall distance and per unit partial pressure of the gas.

Calculations of the rate of change in the concentration of the gas-phase species undergoing dissolution are facilitated by the introduction of the washout coefficient, $\Lambda$, the fractional rate of removal of the gas by the indicated process:

$$\Lambda = R/C_g, \qquad (11)$$

where $R$ is the rate of the process, moles $\mathrm{cm^{-3}}$ (gas)$\mathrm{s^{-1}}$. The quantity $\Lambda$, which has dimension of $\mathrm{time^{-1}}$, may be considered to be an effective instantaneous first-order rate constant for the process. If we take $\mathrm{d}N/\mathrm{d}D_0$ to represent the drop-size distribution of a cloud or rain event, expressed here as the number of drops, $\mathrm{cm^{-3}\,cm^{-1}}$, then the rate of removal of an irreversibly soluble gas such as $HNO_3$ is obtained by evaluation of the integral of this rate over the drop-size distribution:

$$R = \int k_g(\pi D_0^2) C_g \left(\frac{\mathrm{d}N}{\mathrm{d}D_0}\right) \mathrm{d}D_0. \qquad (12)$$

Hence

$$\Lambda = \pi \int D_0^2 k_g \left(\frac{\mathrm{d}N}{\mathrm{d}D_0}\right) \mathrm{d}D_0. \qquad (13)$$

The dependence of $k_g$ upon $D_0$ (implicit via the dependence of $k_g$ upon $u$ and of $u$ upon $D_0$) has been previously noted. Equation (13) along with (10) forms the basis of the calculations reported in this paper.

## 3. IN-CLOUD SCAVENGING

The scavenging of gases by liquid clouds is a complicated process comprising material flows through the cloud (the apparent motion of the cloud being less than that of the wind field), and condensation and evaporation of water, as well as dissolution and possible re-evaporation of the gaseous solute. The question examined here is that of the characteristic time of dissolution of a soluble gas, calculated under the assumption of a static (i.e. non-flowing) system. If this characteristic time is short compared to the residence time of an air parcel within the cloud or to cloud lifetimes, then the solute may be treated as entirely present in the aqueous phase. The ultimate fate of such a "scrubbed" gaseous solute would depend upon the fate of the water drop in which it is dissolved: deposition to the ground in rainfall or re-release into the vapor phase upon drop evaporation (Slinn, 1974). Calculations of the effective first-order rate constant $\Lambda$ by (13) may be readily made for an assumed drop-size distribution for cloud liquid water Mean distributions for fair-weather cumulus and for cumulus congestus have been presented by Battan and Reitan (1957) and will be used as the basis of the present calculations. These distributions are closely approximated over the range of measurements, which extended upwards from 5 $\mu$m, by the form

$$dN/dD_0 = A e^{-BD_0}; \tag{14}$$

measured drop distributions continued to increase with decreasing $D_0$ at the low end of the measurement range, although it is expected that this distribution will reach a maximum at some low value of $D_0$ and then decrease sharply below that value (Pruppacher and Klett, 1978, p. 10). Consequently, a value of $\Lambda$ computed for the partial distribution for drops greater than 5 $\mu$m will represent a lower bound to this quantity, although, as it turns out, the contribution to $\Lambda$ from smaller droplets appears to be small because of the low surface area of such small drops.

Parameters employed in the calculation of $\Lambda$ and the resulting values are given in Table 1; the parameters were obtained from a fit of the data of Battan and Reitan (1957). The value of $\Lambda$ obtained, approximately 0.2 $s^{-1}$, corresponds to a characteristic time of 5 s for dissolution of a highly soluble gas such as $HNO_3$ once it is entrained into a liquid cloud. This calculation sets the time scale for such in-cloud scrubbing and confirms the intuitive supposition that this process is "rapid." Consequently, evaluation of the removal of such a gas from the atmosphere by in-cloud scrubbing will be dominated by considerations of mass transport to the cloud and of the subsequent fate of cloud liquid water, i.e. precipitation to the surface or re-evaporation.

The coupled problem of in-cloud scavenging followed by the removal of the dissolved material by precipitation has been considered by Slinn (1974), who has modeled this problem as two successive first-order processes. The "rate constant" for precipitation removal of cloud liquid water was estimated by Slinn as

$$\Psi = I'/(LZ), \tag{15}$$

where $\Psi$ is the probability per unit time for precipitation removal of liquid water, $s^{-1}$; $I'$ is the precipitation rate, cm $s^{-1}$; $L$ is the cloud liquid water content, g $cm^{-3}$ and $Z$ is the thickness of the raining layer, cm. For a rainfall rate of 1 mm $h^{-1}$, a liquid water content of 1 g $m^{-3}$, and a cloud thickness of 1 km, $\Psi = 2.8 \times 10^{-4}$ $s^{-1}$ or 1 $h^{-1}$. Such estimates of $\Psi$ ranging in the order of $10^{-4}$ to $10^{-3}$ $s^{-1}$ are much less than the rate of scavenging of the soluble gas by the cloud evaluated above and thus represent the rate-determining step of the overall in-cloud removal process.

## 4. BELOW-CLOUD SCAVENGING

For an assumed model of a raindrop falling at its terminal velocity through a well-mixed static atmosphere and accumulating an irreversibly soluble gas uniformly throughout the drop, we may proceed with (10) to calculate the concentration of the dissolved gas as a function of fall distance. In order to make this calculation, as well as determine $k_g$ in (2), it is necessary to know the terminal velocity $u$ as a function of drop size. Terminal velocity and precipitation drop size have been analyzed by Beard (1976), who gives semi-empirical relationships to calculate Reynolds numbers for drops in the three diameter ranges of 0.5–19 $\mu$m, 19 $\mu$m–0.107 cm and 0.107–0.7 cm. These relationships have been used here to determine Reynolds numbers and in turn $u$, using the equivalent spherical diameter. Terminal velocities thus calculated are shown in Fig. 1, along with $k_g$ values, as functions of equivalent diameter. For these calculations the diffusivity of $HNO_3$ gas in air at 25 °C was taken to be 0.112 $cm^2$ $s^{-1}$.

Values of $\gamma$ (per km fall distance) for use with (10) are given in Fig. 1 as a function of $D_0$. As seen in this figure, a decrease in $D_0$ from 0.1 to 0.01 cm results in some two and one-half orders-of-magnitude increase in $\gamma$ as a consequence of the slower fall velocities, greater gas-phase mass transport coefficients, and increased surface to volume ratios of the smaller drops. This tendency of smaller drops to accumulate greater concentrations of dissolved gas is illustrated also in Fig. 2, which gives the calculated $HNO_3$ concentration and equilibrium vapor pressure over drops of different equivalent diameters as a function of fall distance, for a bulk gas phase partial pressure of $HNO_3$ of $10^{-8}$ atm. These results indicate a strong dependence of the

Table 1. Computational parameters and results for calculation of in-cloud dissolution rate of $HNO_3$*

| Cloud type | Fair weather cumulus | | Cumulus congestus | |
|---|---|---|---|---|
| Droplet size range, cm | [5–40] | (−4)† | [5–60] | (−4) |
| $A$, $cm^{-4}$ | 2.87 | (6) | 4.55 | (5) |
| $B$, $cm^{-1}$ | 2.65 | (3) | 1.20 | (3) |
| $N$, $cm^{-3}$ | 288 | | 208 | |
| $L$, g $cm^{-3}$ | 0.17 | (−6) | 0.64 | (−6) |
| $\Lambda$, $s^{-1}$ | 0.19 | | 0.21 | |

* $A$ and $B$ represent parameters of differential drop-size expression $dN/dD_0 = Ae^{-BD_0}$; $N$ is number of drops $cm^{-3}$ within indicated size range; $L$ is liquid water content, g $cm^{-3}$, within indicated size range.

† The notation [5–40] (−4) represents $5 \times 10^{-4}$ to $40 \times 10^{-4}$.

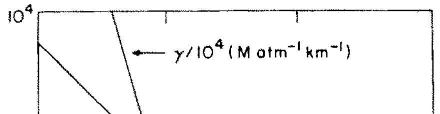

Fig. 1. Dependence upon raindrop diameter $D_0$ of the terminal velocity $u$, the drop surface to volume ratio $S/V$, the gas-phase mass transfer coefficient for the uptake of $HNO_3$ $k_g$, and the concentration of dissolved $HNO_3$ per unit fall distance and atmospheric partial pressure $\gamma$.

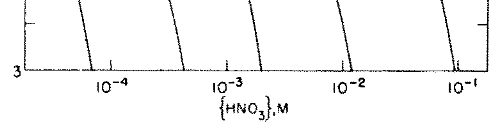

Fig. 2. Calculated formal concentrations of dissolved $HNO_3$ and corresponding equilibrium vapor pressures over drops of different diameters, evaluated as a function of drop fall distance for an atmospheric partial pressure of $HNO_3$ of $10^{-8}$ atm.

concentration of dissolved $HNO_3$ upon the drop size that is potentially observable by field measurements. For example, a ratio of 170, corresponding to 2.2 pH units, is shown for $HNO_3$ in raindrops of 0.02 vs 0.2 cm. It should be emphasized, however, that such a dependence must be taken only as a qualitative indication of expected trends, since the formulation of (10) does not take into account such potentially important processes as evaporation and drop breakup and neglects as well any nonuniformity in $p_{HNO_3}$ and the nonstatic nature of the air through which the raindrops fall.

Figure 2 also permits further examination of the earlier assumption that the uptake of $HNO_3$ by rain may be treated irreversibly, i.e. that $C_g \gg C_g^*$. This assumption is seen to be justified except for very small drops (e.g. $D_0 = 0.01$ cm), which would approach saturation for fall distances of the order of 1 km. However, since drops of such diameters would themselves evaporate within far shorter fall distances (Rogers, 1979, p. 76), the assumption of irreversible uptake by $HNO_3$ by liquid water is seen not to be seriously compromised.

The fractional rate of removal of a soluble gas by rain, $\Lambda$, may be evaluated by the integration indicated in equation (13) over the range of drop diameters constituting the rain. As in the case of clouds, such a calculation requires an assumed drop distribution spectrum for which recourse is again made to empirically developed spectra. Various equations have been given in the literature to fit measured size spectra of raindrops. Perhaps the most frequently used distribution functions are those of Marshall and Palmer (1948)

$$dN/dD_0 = 0.08 \exp[-41 D_0 I^{-0.21}] \qquad (16)$$

and of Best (1950)

$$dN/dD_0 = 2.8 \times 10^{-5} I^{0.324} D_0^{-1.75} \times \exp[-98.5 D_0^{2.25} I^{-0.522}]. \qquad (17)$$

This form of the Best distribution represents a differential expression, analogous to that of Marshall and Palmer, derived from the original integral form. In addition we have also employed the distribution function of Sekhon and Srivastava (1971)

$$dN/dD_0 = 0.07\, I^{0.37} \exp[-38 D_0 I^{-0.14}]. \qquad (18)$$

In all three cases, $dN/dD_0$ and $D_0$ have the units previously defined while the rain intensity, $I$, has units mm h$^{-1}$.

In Figs 3 to 5 we present the differential washout coefficient

$$d\Lambda/dD_0 = \pi D_0^2 k_g dN/dD_0, \qquad (19)$$

evaluated for each of the three drop-size distribution functions. As seen in these figures the small drops ($D_0$ < 0.1 cm) make the greatest contribution to $\Lambda$. This occurs because of both the greater mass transfer rate and greater number of these drops. Consequently, the choice of the lower limit to be employed in the integration will strongly affect the computed value of $\Lambda$. Because small drops may be produced by the evaporation of larger drops as well as themselves undergo evaporation or collection by larger drops, it has proved difficult to formulate a generally applicable expression to describe the small diameter range of rain size spectra. This has been recognized by the pro-

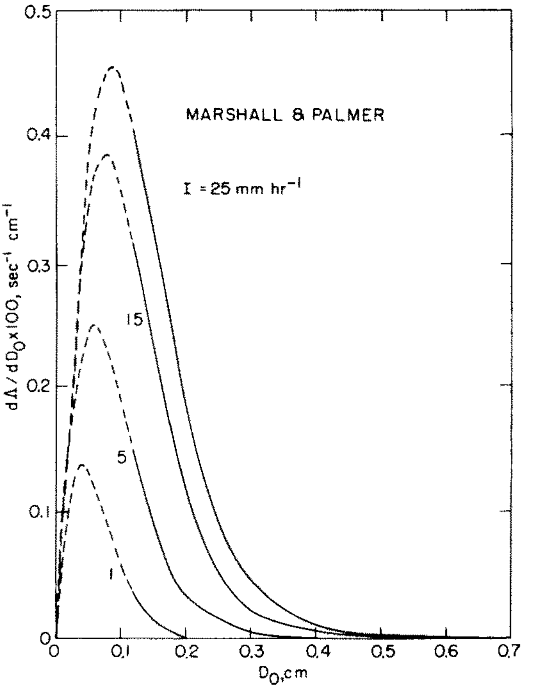

Fig. 3. Differential washout coefficients vs drop diameter, as evaluated with the drop-size distribution function of Marshall and Palmer (1948). The dashed region of each curve represents an extrapolation of the distribution function to diameters less than the cut-off-limit recommended in the original paper.

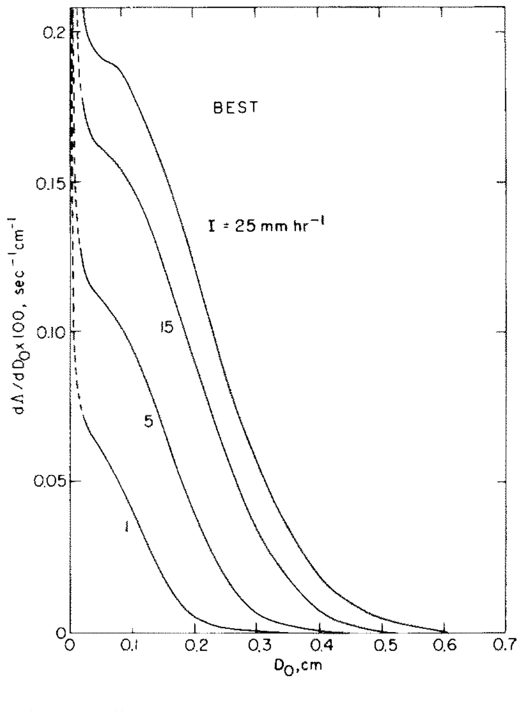

Fig. 4. Differential washout coefficients vs drop diameter, as evaluated with the drop-size distribution function of Best (1950). The dashed region of each curve represents an extrapolation of the distribution function to diameters less than the cut-off-limit recommended in the original paper.

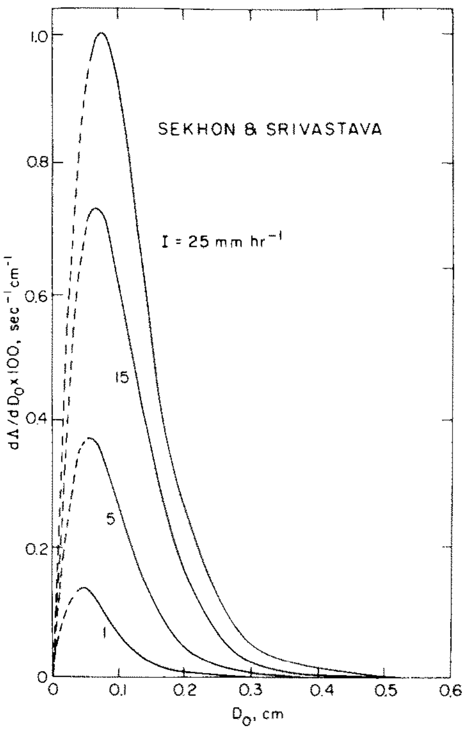

Fig. 5. Differential washout coefficients vs drop diameter as evaluated with the drop-size distribution function of Sekhon and Srivastava (1971). The dashed region of each curve represents an extrapolation of the distribution function to diameters less than the cut-off-limit recommended in the original paper.

ponents of the several distributions, who have suggested lower bounds of about 0.12, 0.025 and 0.06 cm for use with the Marshall–Palmer (MP), Best and Sekhon–Srivastava (SS) equations, respectively. The dashed regions of the several curves given in Figs 3 to 5 represent extrapolations of the several empirical fitting functions to diameters less than their recommended values and should not be taken as representative of actual distributions. In fact, the sharp rise at the lower end of the diameter range in the curves based upon the Best distribution would appear to be entirely an artifact of the mathematical form of Equation (17), which predicts number densities approaching infinity as drop size decreases to zero. In view of these considerations the choice of a lower limit to $D_0$ in the evaluation of $\Lambda$ is somewhat arbitrary. Therefore, we present in Table 2 values of these integrations for the several distribution functions employing several different lower limits to $D_0$ (i.e. $D_{\min}$). The values selected for $D_{\min}$ include the zero cut-off-limit generally employed in such calculations as well as those lower bounds recommended in the original papers for each of the distribution functions. In addition, integrations are carried out with a $D_{\min}$ of 0.02 cm which has been suggested as a reasonable dividing line between cloud and raindrops. Rogers (1979, p. 76) has pointed out that drops with diameters smaller than 0.02 cm are expected to evaporate shortly after leaving a cloud and thus do not stand much of a chance of actually becoming raindrops.

Table 2. Below cloud scavenging coefficients*

| $I$, mm h$^{-1}$ | | $\Lambda$, s$^{-1}$ | |
|---|---|---|---|
| | MP | Best | SS |
| (A) Lower limit to integration: $D_{min} = 0$ | | | |
| 1 | 1.2 (−4)† | 8.8 (−5) | 1.4 (−4) |
| 5 | 2.9 (−4) | 2.3 (−4) | 4.5 (−4) |
| 15 | 5.9 (−4) | 3.8 (−4) | 1.0 (−3) |
| 25 | 7.6 (−4) | 5.1 (−4) | 1.5 (−3) |
| (B) Lower limit to integration: $D_{min} = 0.02$ cm | | | |
| 1 | 1.2 (−4) | 6.8 (−5) | 1.2 (−4) |
| 5 | 2.9 (−4) | 1.9 (−4) | 4.3 (−4) |
| 15 | 5.8 (−4) | 3.2 (−4) | 9.6 (−4) |
| 25 | 7.5 (−4) | 4.3 (−4) | 1.4 (−3) |
| (C) Lower limit to integration: | | | |
| | $D_{min} = 0.12$ cm | $D_{min} = 0.025$ cm | $D_{min} = 0.06$ cm |
| 1 | 1.3 (−5) | 6.3 (−5) | 7.0 (−5) |
| 5 | 7.7 (−5) | 1.6 (−4) | 2.8 (−4) |
| 15 | 2.5 (−4) | 3.3 (−4) | 7.4 (−4) |
| 25 | 3.7 (−4) | 4.2 (−4) | 1.1 (−3) |

* Calculations based upon the rain size distribution functions of Marshall and Palmer (1948), Best (1950) and Sekhon and Srivastava (1971).

† The notation 1.2 (−4) represents $1.2 \times 10^{-4}$.

It is clear from the results given in Table 2 that values of $\Lambda$ determined for a given rainfall rate vary by a factor of 2 to as much as 9 depending upon the distribution function and the value of $D_{min}$ employed. (It should perhaps be pointed out in contrast that the rainfall intensity varies negligibly with variation of $D_{min}$ in this range, because of the low volume and fall velocities of such small drops.) The largest variations in $\Lambda$ represent more than 50% decreases in the values computed with the MP distribution function when $D_{min}$ is increased from zero to the relatively high 0.12 cm cut-off-limit recommended for use with this function; at the lowest rainfall rate (1 mm h$^{-1}$), which is comprised of the greatest proportion of small drops, a decrease of nearly 90% in the calculated value of $\Lambda$ occurs for this increase in $D_{min}$. In general, this high sensitivity of $\Lambda$ to the choice of $D_{min}$ reflects the important contribution of small drops to the precipitation scavenging rates of highly soluble gases such as $HNO_3$ and emphasizes the need for better characterization of rain spectra for small drops. Although a dependence of predicted washout coefficients upon the choice of distribution function has been noted previously (Engelmann, 1968), the much greater sensitivity of such calculations to the choice of $D_{min}$ does not appear to have been fully appreciated. Indeed, a lower integration limit of zero or some value less than that recommended for use with a distribution function continues to be employed without much word of warning (e.g. Engelmann, 1968; Adamowicz, 1979; Overton *et al.*, 1979; Fenton *et al.*, 1980).

Because of the dependence of calculated $\Lambda$ values upon the selection of both the distribution function and the lower limit over which the integrations are performed, the present and similar calculations must be considered artificial in terms of any ability to accurately predict scavenging rates. At best, such calculations must be considered to be representative of washout rates that might be expected in the ambient atmosphere. Nevertheless, within these limitations it is desirable for atmospheric modelers to have some recommendation of those $\Lambda$ values expected to be reasonably characteristic of the washout rates of $HNO_3$ and other such soluble species. For this purpose, calculations involving the MP distribution function appear to be the most appropriate, since exponential functions of this type have been found to give reasonably good approximations of observed rain size spectra (Pruppacher and Klett, 1978, pp. 23–26). Although the pre-exponential and exponential terms employed with such functions may have to be varied from one rainfall to another (Slinn, 1982), it appears (Joss and Waldvogel, 1969) that Equation (16) is fairly representative of widespread rain, which accounts for a major fraction of the volume of global rainfall. As noted above, the high cut-off-limit (0.12 cm) recommended for use with (16) excludes from consideration a large number of small drops responsible for as much as 50–90% of the scavenging rates; thus, one is tempted to employ the MP distribution with a smaller $D_{min}$ value such as 0.02 cm. On the other hand, Marshall and Palmer (1948) have themselves indicated that in comparison to rain size spectra observed by Laws and Parsons (1943) (16) overestimates by as much as 50% the number of drops in the 0.02–0.12 cm diameter range. Therefore, the recommended values for $\Lambda$ based upon the MP distribution function should fall somewhere between those values given in Tables 2(c) and 2(b). To obtain these recommendations we have taken the washout coefficients determined with a $D_{min}$ of 0.02 cm and have applied a 50% downward correction to that fraction of each of these $\Lambda$ values that corresponds to contributions from drops in the 0.02–0.12 cm size range. The $\Lambda$ values determined in this manner are 0.65, 1.8, 4.2 and $5.6 \times 10^{-4}\,s^{-1}$ for rainfall rates of 1, 5, 15 and $25\,mm\,h^{-1}$, respectively.

The rainfall scavenging rates indicated by the present calculations suggest that below-cloud $HNO_3$ vapor will be significantly depleted by rainfall within the duration of typical rain events. The recommended values of $\Lambda$ given in the previous paragraph correspond to scavenging rates of 0.4–3.3 % $min^{-1}$. Such rapid washout rates suggest a potentially observable dependence of dissolved nitrate concentration upon the time following the onset of a rain event, i.e. a decrease with time in the concentration of nitrate to be found in collected rain samples, provided that below-cloud scavenging is an important contribution to rainfall nitrate. In addition, the rapid scavenging of $HNO_3$ by atmospheric liquid water suggests a possibly important mechanism for the vertical transport of this and other highly soluble gases, whereby the dissolved gas is transported to lower altitudes by falling rain and released by drop evaporation. Such a mechanism has been suggested previously by the observations of Huebert (1980), who found increases in vapor nitric acid concentration at the surface when measurements were taken in the vicinity of rain showers.

## 5. AVERAGE DEPOSITION RATE

Based upon the foregoing estimates of the scavenging coefficient $\Lambda$ characteristic of a given rainfall rate, it is desired to evaluate an average deposition rate of nitric acid appropriate for numerical modeling of tropospheric photochemistry. Here we consider both the processes of washout, as treated above, and dry deposition, but exclude in-cloud incorporation of $HNO_3$, since most of the $HNO_3$ so incorporated is subsequently released back into the gas phase upon cloud evaporation.

Perhaps the simplest approach to estimating the average rate of $HNO_3$ wet deposition might be

$$k_{dep} \equiv \overline{\Lambda} = \frac{\int \Lambda(I)\,dI}{\int dI}, \tag{20}$$

where the average is taken over a period of time sufficiently long to be representative of a given location. (For a global average, suitable for use in tropospheric models $k_{dep}$ would then have to be appropriately spatially averaged). Since, as noted below, (20) inherently provides a poor estimate to $k_{dep}$, we make no attempt to evaluate $k_{dep}$ by this expression. However we note that this expression may be readily bounded, since as may be seen by examination of Table 2, the ratio $\Lambda/I$, the fraction of $HNO_3$ removed per mm of rain, is rather narrowly bracketed between 0.05 and $0.5\,mm^{-1}$. Thus for an annual average rainfall of, say, $1000\,mm\,y^{-1}$, $k_{dep}$ evaluated by (20) is seen to lie between the bounds $(50\text{–}500)\,y^{-1}$ or $(1.6\text{–}16) \times 10^{-6}\,s^{-1}$.

A major objection to the evaluation of $k_{dep}$ by (20) is that such an expression fails to properly account for the intermittent nature of rain episodes (Rodhe and Grandell, 1972). Essentially (20) neglects both the long periods between rain events, when $\Lambda = 0$, and the diminishing effect of a given value of $\Lambda$ over the course of a rain event during which the material becomes significantly depleted. Treating this problem according to a stochastic model for the frequency and duration of precipitation events, Rodhe and Grandell give for the expected value of the deposition rate

$$k_{dep} = \frac{\tau_p\Lambda_p + \tau_d\Lambda_d + \tau_p\tau_d\Lambda_p\Lambda_d}{\tau_p + \tau_d + \tau_p\tau_d(\tau_p\Lambda_d + \tau_d\Lambda_p)/(\tau_p + \tau_d)}, \tag{21}$$

where $\Lambda_p$ and $\Lambda_d$ represent the deposition rates during periods of precipitation and dryness, respectively, and $\tau_p$ and $\tau_d$ represent the mean duration of these periods. That treatment also gives $k_{dep}$ for precipitation removal only by setting $\Lambda_d = 0$,

$$k_{dep} = \frac{\tau_p\Lambda_p}{\tau_p + \tau_d + \tau_p\tau_d\Lambda_p/(\tau_p + \tau_d)}. \tag{22}$$

We proceed here to evaluate $k_{dep}$ by (21) and (22), motivated not so much by a desire for the absolute accuracy of the values obtained, but rather by the insights that may be afforded. In this evaluation we therefore assume a single precipitation rate $I = 1\,mm\,h^{-1}$ and an annual average rainfall of $1000\,mm\,y^{-1}$. Following Rodhe and Grandell (1972), who examined rainfall statistics at a station near Stockholm, Sweden, we take $\tau_p = 7$ h and, consistent with the above, $\tau_d = 54.4$ h. These assumptions permit evaluation of $k_{dep}$ by (22), as shown in Table 3 for representative values of $\Lambda_p$ as obtained in Section 4.

To include dry deposition we estimate $\Lambda_d$ as

$$\Lambda_d = k_g/H, \tag{23}$$

where $H$ is the depth of the pertinent atmospheric layer and $k_g$ is the gas-phase mass transfer coefficient (Slinn *et al.*, 1978). For a highly water-soluble gas such as $HNO_3$, gas-phase mass transfer, rather than surface resistance, is expected to be rate limiting. In order to obtain a global-average estimate of $\Lambda_d$ we employ the estimated values for $k_g$ of $0.4\,cm\,s^{-1}$ (Liss and Slater, 1974) and $1.0\,cm\,s^{-1}$ (Slinn *et al.*, 1978) for gas-phase limited deposition of a highly soluble gas to the air–sea interface. For $H$ we employ 2 km, characteristic of the mixed layer, and, in order to compare with previous estimates (Levy, 1974), 5 km. The resulting values obtained for $k_{dep}$ are given in Table 3, again for representative values of $\Lambda_p$.

The values of $k_{dep}$ estimated by these models illustrate several important points. First, comparing the constant-rain model with the intermittent-rain model, it is seen that the former substantially overestimates $k_{dep}$ for the same input parameters, as indicated above. Secondly, we would note the high degree of nonlinearity in the dependence of $k_{dep}$ upon $\Lambda_p$ in the two intermittent-rain models. This occurs because at the higher values of $\Lambda_p$, $k_{dep}$ is increasingly dominated by the duration of the dry periods.

Table 3. Average deposition rate*

| Model | Equation | $H$ km | $k_g$ cm s$^{-1}$ | $\Lambda_p$ s$^{-1}$ | $k_{dep}$ $10^{-6}$ s$^{-1}$ |
|---|---|---|---|---|---|
| "Constant rain" | (20) | — | — | 1.3 (−5)$I$† | 1.6 |
| | | | | 1.3 (−4)$I$ | 16 |
| "Intermittent rain"‡ | (22) | — | — | 1.3 (−5) | 1.2 |
| | | | | 6.5 (−5) | 3.2 |
| | | | | 1.3 (−4) | 4.2 |
| | | | | ∞ | 5.8 |
| "Intermittent rain‡ and dry deposition" § | | 2 | 0.4 | 0 | 1.8 |
| | | | | 1.3 (−5) | 3.1 |
| | | | | 6.5 (−5) | 5.3 |
| | | | | 1.3 (−4) | 6.3 |
| | | | | ∞ | 8.0 |
| | | 2 | 1.0 | 0 | 4.4 |
| | | | | 1.3 (−5) | 5.8 |
| | | | | 6.5 (−5) | 8.3 |
| | | | | 1.3 (−4) | 9.4 |
| | | | | ∞ | 11.4 |
| | (21) | 5 | 0.4 | 0 | 0.7 |
| | | | | 1.3 (−5) | 1.9 |
| | | | | 6.5 (−5) | 4.1 |
| | | | | 1.3 (−4) | 5.0 |
| | | | | ∞ | 6.7 |
| | | 5 | 1.0 | 0 | 1.8 |
| | | | | 1.3 (−5) | 3.1 |
| | | | | 6.5 (−5) | 5.3 |
| | | | | 1.3 (−4) | 6.3 |
| | | | | ∞ | 8.0 |

* Average rainfall assumed to be 1000 mm y$^{-1}$.

† The notation 1.3 (−5) represents $1.3 \times 10^{-5}$; $I$ is the rainfall intensity, mm h$^{-1}$.

‡ Average duration of rain and dry events taken as 7 and 54.4 h, respectively.

§ Dry deposition rate evaluated as $k_g/H$.

While it must again be stressed that, because of the arbitrary assumptions employed, the calculations leading to Table 3 are not to be taken as other than very gross estimates of the actual values of these quantities, it is nonetheless tempting to compare these values (for $H = 5$ km) to the value $2 \times 10^{-6}$ s$^{-1}$ that has been employed previously (Levy, 1974; Fishman and Crutzen, 1977). In both those studies $k_{dep}$ was introduced arbitrarily to avoid unrealistically high accumulation of nitric acid vapor resulting from gas-phase free-radical oxidation of nitrogen oxides. The present calculations confirm the reasonableness of the magnitude of the assumed value and further suggest that rain scavenging and dry deposition are of comparable importance as sink processes for nitric acid vapor.

## 6. SUMMARY

With various assumed models for drop-size distribution of atmospheric liquid water, calculations have been carried out to determine the scavenging coefficients for the removal of $HNO_3$ vapor by both cloud and rain droplets. These calculations indicate that $HNO_3$ and other highly soluble gases are rapidly scavenged by both the in-cloud (rainout) and below-cloud (washout) processes. For cumulus clouds consisting of drops typically in the 5–60 $\mu$m diameter range a value of 0.2 s$^{-1}$ is estimated for the scavenging coefficient. For rainfall rates ranging from 1 to 25 mm h$^{-1}$ the washout scavenging coefficients are calculated to be in the range $1.3 \times 10^{-5}$ to $1.5 \times 10^{-3}$ s$^{-1}$, with the larger values occurring at the higher rainfall intensities. However, these precipitation scavenging rates are found to depend upon the specific raindrop distribution function employed in the calculations and upon the lower limit used in describing the drop-size spectrum. Drops with diameters less than 0.1 cm make the greatest contribution to the washout scavenging coefficient, and consequently the choice of the lower diameter limit employed in these calculations strongly affects the computed results. In addition, calculations show that the concentration of dissolved nitric acid within a falling raindrop is a function of drop size as well as fall distance, with the smaller drops accumulating a greater concentration per fall distance because of their slower velocities, increased gas mass-transfer coefficients, and increased surface to volume ratios. The long-term rate of heterogeneous removal of $HNO_3$ is estimated to be in the range of 1–8 $\times 10^{-6}$ s$^{-1}$, with comparable contributions from both dry deposition and rainfall scavenging.

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