Approximation Formulas for the Equilibrium Size of an Aerosol Particle as a Function of Its Dry Size and Composition and the Ambient Relative Humidity

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ABSTRACT

Approximations to the exact equations describing the variation with relative humidity of the equilibrium size of aqueous solution droplets are developed. For relative humidities between 81 and 99.5%, and for droplets formed by particles composed of greater than 60% by mass of any one of nine common electrolytes and having a dry radius in the range of 0.05 to 3.0 μm, the approximation formulas presented are accurate to within 5%. Using these formulas, an expression is obtained for the size distribution of a chemically homogeneous aerosol as a function of relative humidity.

1. Introduction

A solid particle which is composed wholly, or in part, of a pure water-soluble substance will undergo a rather sudden transition to a saturated (or, in the case of very small particles, supersaturated) solution droplet when some critical value of relative humidity, less than 100%, is reached. The relative humidity at which this transition occurs depends on the size and chemical composition of the particle. The smaller the particle, the lower will be the critical humidity for the transition. Below the transition point, solid particles acquire small amounts of water by the process of adsorption. As indicated by both theory (see, for example, Brunauer, 1945) and experiment, the increase in the size of aerosol particles as a result of physical adsorption is less than 5%. At relative humidities above the phase transition point, a particle (or, more properly, an aqueous solution droplet) grows by the absorption of water vapor. The size of a solution droplet is quite sensitive to ambient relative humidity.

The relationship between relative humidity and the equilibrium size of an aqueous solution droplet is generally formulated by a rather complicated equation expressing the equilibrium saturation ratio \( S \) over the surface of the droplet as a function of droplet size and composition. In order to compute the equilibrium size of a solution droplet at a specified humidity, it is necessary either to invert this equation mathematically or, alternatively, to compute \( S \) as a function of droplet size and then interpolate between values. Computation of droplet size by either of these methods is very time consuming when a large number of such computations are involved, as, for example, in certain studies concerned with the effect of relative humidity on visibility or in numerical studies of the microphysics of fog formation.

The purpose of this paper is to present approximation formulas which facilitate the computation of the equilibrium radius of an aqueous solution droplet as a function of relative humidity. For relative humidities between 81 and 99.3%, the equilibrium radius of a droplet, formed by a particle composed of greater than 60% by mass, of any one of nine common electrolytes and having a dry radius in the range 0.05 to 3.0 μm, may be computed from these formulas to an accuracy of 5% or better.

2. Theory

The relationship between relative humidity and the equilibrium radius of an aqueous solution droplet formed by a pure salt particle may be expressed as (Fletcher, 1962)

\[
\frac{r_p'}{r_p} = \exp \left[ -\frac{2a'}{r_p R T} \left( 1 + \frac{i M_w \sigma_a d^3}{M_s (r_p' - r_s' \rho_d)} \right) \right]^{-1},
\]

where \( r \) is the radius of the droplet; \( r_p' \) and \( r_p \) are the equilibrium vapor pressures over the droplet and over a plane surface of pure water, respectively; \( \sigma' \) and \( \rho' \) are the surface tension and density of the solution; \( R \) is the specific gas constant of water vapor; \( i \) is the van't Hoff factor; \( r_s' \) and \( \rho_d \) are the dry radius and density of the original particle; and \( M_w \) and \( M_s \) are the molecular weights of water and of the salt of which the particle is composed. The quantities \( i, \sigma' \), and \( \rho' \) are functions of the molality of the droplet solution. The
first factor on the right-hand side of (1) accounts for the elevation in the equilibrium vapor pressure over the curved surface of the droplet compared to its value over a plane water surface. The second factor is the mole fraction of water in the droplet and expresses the lowering of the water vapor pressure due to the dissolved salt. Mason (1971) has derived an expression for \( S \) which is identical to (1) except that the exponent on the second factor on the right is given as \( \frac{(\rho_0/\rho')}{\rho_0} \), where \( \rho_0 \) is the density of pure water. The equilibrium saturation ratio has also been formulated in terms of the molal osmotic coefficient (Byers, 1965) or the ionic activity coefficient (Low, 1969b).

A number of investigators (e.g., Junge, 1952; Orr et al., 1958) have found good agreement between the measured and theoretically predicted growth curves for pure salt solution droplets.

Let us now consider a partly soluble particle consisting of a spherical core of insoluble material surrounded by a shell of a pure water-soluble substance. Such a concept of a mixed nucleus was introduced by Junge (1952) to help explain the observed response of atmospheric aerosol particles to increasing humidity. If we denote the mass fraction of soluble material in the particle by \( \epsilon \), then the volume \( v_i \) of insoluble material in the particle is

\[
v_i = \frac{3}{2} \pi (1 - \epsilon) \rho_d \frac{r_d^3}{\rho_i}.
\]  

(2)

where \( \rho_i \) is the density of the insoluble component. It follows that the volume \( v' \) and mass \( m' \) of aqueous solution in a droplet formed by such a particle can be written

\[
v' = \frac{3}{2} \pi r^3 - \frac{3}{2} \pi (1 - \epsilon) \rho_i r^3,
\]  

(3)

\[
m' = \frac{3}{2} \pi \rho \left[ r^3 - r_d^3 (1 - \epsilon) \frac{\rho_d}{\rho_i} \right].
\]  

(4)

The mass of water in the droplet is equal to \( m' \) less the mass of solute, the latter being equal to \( (4/3) \pi \epsilon \rho_d r_d^3 \). If it is assumed that \( \rho_i = \rho_d \), then the number of moles \( n_w \) of water in the droplet is given by

\[
n_w = \left( \frac{3}{2} \pi \rho' \left[ r^3 - r_d^3 (1 - \epsilon) \right] - \frac{3}{2} \pi \epsilon \rho_d r_d^3 \right) / M_w.
\]  

(5)

Also, the effective number of moles of solute in the droplet is

\[
n_s = \frac{3}{2} \pi \epsilon \rho_d r_d^3 / M_s.
\]  

(6)

Calculating the mole fraction of water in the droplet from (5) and (6), and combining this with Kelvin's equation for the effect of surface curvature on vapor pressure, one obtains the following equation for the equilibrium saturation ratio over a solution droplet formed by a mixed aerosol particle conforming to the above model:

\[
\frac{p_r'}{p_0} = \exp \left[ \frac{2\alpha'}{\rho_0 R T} \right] \times \left[ 1 + \frac{i \epsilon \rho M_a r_d^3}{M_s \left( r^3 - r_d^3 (1 - \epsilon) \right)} \right]^{-1}.
\]  

(7)

An equivalent expression for \( S \), in terms of the volume fraction of soluble material, has been derived by Junge and McLaren (1971). Eq. (7) reduces to Eq. (1) when \( \epsilon = 1.0 \).

Junge (1952) found close agreement between the measured growth curves (i.e., equilibrium radius as a function of relative humidity) of artificially produced particles composed of a mixture of CaCl\(_2\) and CaSO\(_4\) and the theoretical curves for such particles. Recent measurements by Winkler (1973) have shown, however, that continental atmospheric aerosol particles exhibit more limited growth with increasing humidity than predicted by Eq. (7) for the amount of insoluble material (40\% on the average) they contain. This deviation in behavior from Eq. (7) is due to the fact that the soluble component of continental aerosol particles is actually a mixture of different salts. Ionic interactions in a mixed solution increase the solubility of the various ions and result in a reduction in water vapor pressure lowering. Winkler (1973) and Hänel (1970) have derived equations which approximate the observed average growth curves of particles collected near Mainz, West Germany. In the light of Winkler's work, the aerosol particle model described by Eqs. (2)–(7) must be regarded as a special case of mixed nuclei.

The relative humidity in equilibrium with a solution droplet of specified size and composition may be readily computed from Eq. (7). However, the inverse problem of calculating the equilibrium radius of an aerosol particle at a specified humidity is more difficult. One approach is to compute \( S \) as a function of \( r \) from (7) and then interpolate between values. An alternative approach is to expand the two factors on the right in (7), retaining as many terms as are needed to yield the desired accuracy, and to solve the resulting polynomial for \( r \). Calculation of the equilibrium size of aerosol particles by either of these methods can be extremely time consuming.

In the following section, approximation formulas for the equilibrium radius of a solution droplet as an explicit function of the variables \( r_d, S \) and \( \epsilon \) are derived.

3. Approximation formulas

The equilibrium saturation ratio over a solution droplet was computed from Eq. (7) as a function of \( r, r_d \) and \( \epsilon \). Computations were performed for nine different electrolytes serving as the soluble constituent of the particles: (NH\(_4\))\(_2\)SO\(_4\), NaCl, NH\(_4\)NO\(_3\), NH\(_4\)Cl,
CaCl₂, NaBr, NaNO₃, MgCl₂ and LiCl. Large particles of these salts will undergo the transition to completely dissolved droplets at relative humidities ranging from about 15% for LiCl (the most hygroscopic of these substances) to about 81% for (NH₄)₂SO₄. Therefore, at relative humidities greater than 81%, particles of any of these salts will exist as solution droplets. Data on the variation of i, ρ' and ρ with the molality of aqueous solutions of these electrolytes were obtained from Low (1969a) and from the Handbook of Chemistry (Lange, 1961). A temperature of 20°C was assumed in all computations.

In Figs. 1a and 1b we have plotted the equilibrium radius of particles composed of 100% ammonium sulfate and 50% magnesium chloride, respectively, as a function of rd and S. Similar graphs were constructed for the other electrolytes for five values of ε between 0.1 and 1.0. It will be noticed that in the optically important size range of from 0.05 to 5.0 μm, a nearly linear relationship exists between logr and logrd for values of S ≤ 0.995. This suggests an approximation formula of the form

$$r = α r_d^β$$  \hspace{1cm} (8)

where the parameters α and β are functions of relative humidity and aerosol composition.

Log-linear regression curves were computed for the \( r \) vs \( r_d \) relationships in the size range 0.05 ≤ \( r_d \) ≤ 5.0, as shown in Fig. 2 for pure ammonium sulfate particles.
These curves showed, in the case of all the electrolytes in question, that the functional dependence of \( r \) on \( r_d \) and \( S \) can be represented by Eq. (8) to within 5\%, for values of \( S \) in the range 0.81 to 0.995.

The variation of \( \beta \) (the slope of the straight-line fits) with \( S \) for ammonium sulfate particles is presented in Fig. 3. It was found by trial and error that the dependence of \( \beta \) on \( S \) can be described, to within 0.3\% accuracy, by

\[
\beta = \exp\left(\frac{0.00077S}{1.09 - S}\right), \quad 0.81 \leq S \leq 0.995.
\]  

(9)

The value of \( \beta \) is fairly insensitive to both the chemical composition and mass fraction of soluble material in a particle. The maximum error introduced by assuming (9) to be valid for the other electrolytes is less than 3\% when \( \epsilon \geq 0.5 \).

A plot of \( \alpha \) as a function of \( S \) (for \( r \) and \( r_d \) expressed in microns) is given in Fig. 4 for particles composed of two different percentages of ammonium sulfate. The functional dependence of \( \alpha \) on \( S \) (for \( \epsilon = 1 \)) can be expressed, to within 1\%, by

\[
\alpha_1[\text{(NH}_4\text{)}_2\text{SO}_4] = 1.2 \exp\left(\frac{0.066S}{\Phi - S}\right),
\]

(10)

where

\[
\Phi = \begin{cases} 
1.058, & S \leq 0.97 \\
1.058 - \frac{0.0155(S - 0.97)}{1.02 - S^{1.4}}, & 0.97 < S \leq 0.995
\end{cases}
\]

The subscript 1 on \( \alpha \) indicates that the equation applies for a value of \( \epsilon \) of unity.

The ratio \( (\alpha_1/\alpha) \) of \( \alpha \) for particles composed of a fraction \( \epsilon \) of ammonium sulfate to the value of \( \alpha \) for pure ammonium sulfate particles, was calculated as a function of \( \epsilon \) and \( S \). The results are shown in Fig. 5 where second-order polynomials have been fitted to the computed values. The variation of \( \alpha_1/\alpha \) with \( \epsilon \) and \( S \) is described by

\[
\frac{\alpha_1}{\alpha} = 1 - k_1(1 - \epsilon) - k_2(1 - \epsilon^2),
\]

where

\[
k_1 = 10.2 - 23.7S + 14.5S^2
\]

\[
k_2 = -6.7 + 15.5S - 9.2S^2.
\]

The next step is to relate the value of \( \alpha \) for particles composed of ammonium sulfate as the soluble constituent to the \( \alpha \) values for partially soluble particles of the electrolytes NH4NO3, NaCl, CaCl2, NH4Cl, NaBr, LiCl, MgCl2 and NaNO3. For each electrolyte, the ratio \( \alpha[\text{electrolyte}]/\alpha[\text{(NH}_4\text{)}_2\text{SO}_4] \), was computed as a function of \( \epsilon \) and \( S \). In all cases, this ratio did not vary by more than 10\% over the range 0.81 \leq S \leq 0.993 and \( \epsilon \geq 0.6 \). Table 1 lists the mean value of the \( \alpha \)-ratio for each electrolyte.

The results presented thus far may be summarized as follows: For values of relative humidity between 81 and 99.3\%, the equilibrium radius of a solution droplet, formed by a particle composed of greater than 60\% by mass of any of the electrolytes listed in Table 1 and having a dry radius in the range 0.05 to 3.0 \( \mu m \), may be computed from Eq. (8) to within 5\%. The value of the parameter \( r \) in (8) is obtained by multiplying the product of Eqs. (10) and (11) by the appropriate value from Table 1. The parameter \( \beta \) is calculated from
Table 1. The ratio of the value of $\alpha$ for various electrolytes to that for ammonium sulfate.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$\alpha_{\text{electrolyte}}$</th>
<th>$\alpha_{\text{(NH}_4\text{)}_2\text{SO}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>1.23</td>
<td>1.29</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>NaBr</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td></td>
<td>1.54</td>
</tr>
<tr>
<td>LiCl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Eq. (9). The accuracy of these approximation formulas decreases rapidly for values of $r_d$, $\epsilon$ and $S$ outside the above stated limits.

4. Particle size at 100% relative humidity

As is discussed in most cloud physics texts, Eq. (1) yields a simple, approximation equation for the equilibrium radius, at 100% relative humidity, of a solution droplet formed by a totally soluble nucleus. A similar expression for the radius of a partially soluble aerosol particle in equilibrium with a saturated environment can be obtained from Eq. (7). For a dilute solution droplet it is sufficiently accurate to retain only the first two terms in the series expansion of the two factors on the right-hand side of (7) and to neglect $\rho' r^2 (1-\epsilon)$ and $\rho_0 \rho \beta'$ compared to $\rho' r^3$. With these approximations, and with $S$ set equal to unity, Eq. (7) yields

$$r_{100} = \left( \frac{i \epsilon M_o R_o T^1}{2 \sigma M_o} \right) r^3.$$

To simplify further, the surface tension $\sigma_o$ of pure water may be substituted for $\sigma'$ in (12). Also, when the degree of dissociation of water-soluble material approaches unity, as in very dilute solutions, the van't Hoff factor is nearly equal to the number of moles $\eta$ of ions formed by the dissociation of one mole of electrolyte. Eq. (12) shows that $r \propto r_d^{1/3}$, i.e., $\beta = 1.5$, when $S = 1$. If we ignore the temperature dependence of $\sigma'$, Eq. (12) also predicts that $r_{100} \propto T^1$.

For the values $\epsilon = 1.0$ and $r_d \geq 0.05 \, \mu m$, the error incurred in computing $r_{100}$ from (12) [with $i$ equated to $\eta$] is less than 3% for all the electrolytes examined except ammonium sulfate. In the case of ammonium sulfate the error is 12% for $r_d = 0.05 \, \mu m$ and decreases to less than 3% for $r_d > 0.1 \, \mu m$. The larger error in the case of ammonium sulfate is due to the fact that, with decreasing molality, the van't Hoff factor of an aqueous ammonium sulfate solution does not approach $\eta$ as rapidly as in the case of the other electrolytes. The accuracy of (12) decreases as $\epsilon$ decreases. For a value of $\epsilon$ of 0.5, Eq. (12) is accurate to within 5% (except for ammonium sulfate) over the size range of interest.

5. Effect of relative humidity on the size distribution of a chemically homogeneous aerosol

The formulas just derived may be applied to investigate the effect of relative humidity on the size distribution of a chemically homogeneous aerosol. It is well established that, in the range $0.1 \leq r_d \leq 5.0 \, \mu m$, the size distribution of natural aerosols obeys the power law (Junge, 1963)

$$\frac{dN(r_d)}{d \log r} = cr_d^{-\nu},$$

where $N(r_d)$ is the number of particles per unit volume which have a radius $\leq r_d$. Most aerosols are characterized by a value of $\nu$ between 2.5 and 3.5. Integration of (13) yields

$$N(r_d) = N_i - \frac{c}{2.3\nu} r_d^{-\nu},$$

where $N_i$ is the total number of particles per unit volume.

For a chemically homogeneous aerosol, a one-to-one correspondence exists between $r$ and $r_d$. This means that $N(r) = N(r_d)$. Upon combining Eqs. (8) and (14) [with $r_d$ expressed in microns], we obtain

$$N(r) = N_i - \frac{c}{2.3\nu} \alpha^{\nu/\beta} r^{-\nu/\beta}.$$

Differentiation of (15) yields

$$\frac{dN(r)}{d \log r} \beta = -\frac{c}{2.3\nu} \alpha^{\nu/\beta} r^{-\nu/\beta}.$$

Eq. (16), in conjunction with Eqs. (9) and (10), describes, in an approximate manner, the effect of relative humidity on the equilibrium size distribution of an aerosol of uniform composition. Eq. (16) predicts that the slope of the size distribution will decrease slightly, from $\nu$ to about 0.94$\nu$, as the relative humidity increases from 80 to 99%. The shape of the distribution becomes increasingly more sensitive to humidity as saturation is approached. It follows from (12) and (16) that the slope of the size distribution will be 0.67$\nu$ at 100% relative humidity.

6. Summary

Approximation formulas [Eqs. (8)–(11)] for the equilibrium size of soluble and partly soluble (i.e., mixed) particles at relative humidities between 81 and 99.3% are derived. A simple model of a mixed nucleus, in which a particle consists of an insoluble core
surrounded by a shell of a pure salt, is adopted. For particles containing greater than 60% by mass of any one of the electrolytes listed in Table 1 and having a dry radius in the range 0.05 to 3.0 μm, these formulas agree with the exact equations [Eqs. (1) and (7)] to within 5%. The newly derived formulas are used to obtain an expression for the size distribution of a chemically homogeneous aerosol as a function of relative humidity.

REFERENCES


