

CONDENSATION ON AMMONIUM SULPHATE PARTICLES AND ITS EFFECT ON VISIBILITY

J. A. GARLAND

Health Physics and Medical Division, A.E.R.E., Harwell

Abstract—Ammonium sulphate is a frequent and important constituent of the atmospheric aerosol in some areas. Calculations have been carried out to determine, as a function of relative humidity, the size of ammonium sulphate nuclei, and the extinction coefficient (which determines the visibility) of monodisperse ammonium sulphate aerosols. The method for extending the calculations to heterodisperse aerosols is outlined and the results for a Junge type haze distribution and an experimental ammonium sulphate distribution are presented. The critical supersaturation of ammonium sulphate nuclei has also been found.

1. INTRODUCTION

THE work of JUNGE (1954) and more recently of EGGLETON and ATKINS (1969) and HEARD and WIFFEN (1969) has shown ammonium sulphate to be an important constituent of continental atmospheric aerosols. Heard and Wiffen have shown that on many occasions most of the particles in haze conditions are nearly pure ammonium sulphate, while Eggleton and Atkins found a close inverse correlation between

Nomenclature:

- H = relative humidity;
 H' = relative humidity in equilibrium with a flat surface of solution of the same concentration and temperature as the droplet;
 γ = surface tension of the droplet solution;
 ρ = density of the droplet;
 M = molecular weight of water;
 R = the gas constant;
 T = the absolute temperature;
 a = mass of ammonium sulphate dissolved per 100 g of water;
 r = droplet radius;
 m = mass of ammonium sulphate present in the droplet;
 H_c = critical relative humidity;
 S_c = critical supersaturation;
 r_c = critical radius of droplet;
 σ = extinction coefficient;
 N = number of particles per unit volume;
 $K, K(\alpha)$ = the scattering area ratio;
 μ = refractive index of droplet solution;
 λ = wavelength of light;
 α = $2\pi r/\lambda$;
 $K'(r, \mu)$ = the value of K averaged for the response of the eye to daylight to produce a function of r and μ , independent of λ ;
 p = the percentage of ammonium sulphate in the droplet solution;
 $\sigma(m, H)$ = the extinction coefficient of a monodisperse aerosol with mass m of ammonium sulphate per particle or droplet and of unit mass concentration of ammonium sulphate, at relative humidity H ;
 $\bar{\sigma}(H)$ = the extinction coefficient of heterodisperse ammonium sulphate haze of unit mass concentration of ammonium sulphate at relative humidity H .

visibility and the ammonium sulphate content of the atmosphere. In view of these results it is of interest to investigate theoretically the effect of ammonium sulphate particles on visibility, taking into account the effect of varying humidity on the size of the particles. The results of field experiments may then indicate what proportion of the reduction of visibility can be attributed to the ammonium sulphate present, and whether other aerosol species are of importance in this respect.

It is well known that soluble particles suspended in the atmosphere grow in size as the relative humidity increases [e.g. JUNGE (1952), DESSENS (1949)]. KOHLER (1921), WRIGHT (1963), MASON (1957) and several other authors have derived equations relating the particle size to the relative humidity and these have been used to calculate the growth of sodium chloride particles in the atmosphere (MASON 1957). However, in spite of the importance of ammonium sulphate particles in atmospheric aerosols no similar calculations for ammonium sulphate particles appear in the literature. In this paper the variation of size of ammonium sulphate particles with relative humidity will be considered. The results will be used to find the effect of these particles on visibility.

2. DROPLET SIZE AND RELATIVE HUMIDITY

The equilibrium size of droplets of ammonium sulphate solution was found as a function of the mass of ammonium sulphate present and of the relative humidity by solving the following equation:

$$H = H' \exp \left(\frac{2 \gamma M}{\rho R T r} \right). \quad (1)$$

This expression for H differs from those used by previous authors [e.g. MASON (1957)] in use of the term H' rather than a theoretical expression for it. This allowed the use of experimental values found in the literature, avoiding the uncertainty in the van't Hoff's factor, discussed by Mason.

Values of H' , γ , ρ for ammonium sulphate solutions of various concentration and at 10°C were obtained from the International Critical Tables. Approximate linear relationships were fitted to these values and are presented in the Appendix.

The graph (FIG. 1) shows the value of H for various values of r and several values of the mass of ammonium sulphate, m g, present in the droplet. Note that values above 100 per cent relative humidity are shown on a logarithmic scale.

3. CRITICAL SUPERSATURATION FOR AMMONIUM SULPHATE PARTICLES

The critical values of the supersaturation and droplet diameter can be deduced from information collected for the above calculation. They are included here for completeness, though they are not essential to the main argument. These are the co-ordinates of the maxima in the curves of FIG. 1 and are important in condensation phenomena since a droplet will grow indefinitely once this supersaturation is exceeded.

At the critical supersaturation $\frac{dH}{dr} = 0$. Let a be the concentration of ammonium sulphate in the droplet (i.e. the mass of the salt per 100 g water). Then for a given drop-let r is a function of a only, and at the critical supersaturation $\frac{dH}{da} = 0$. Hence from

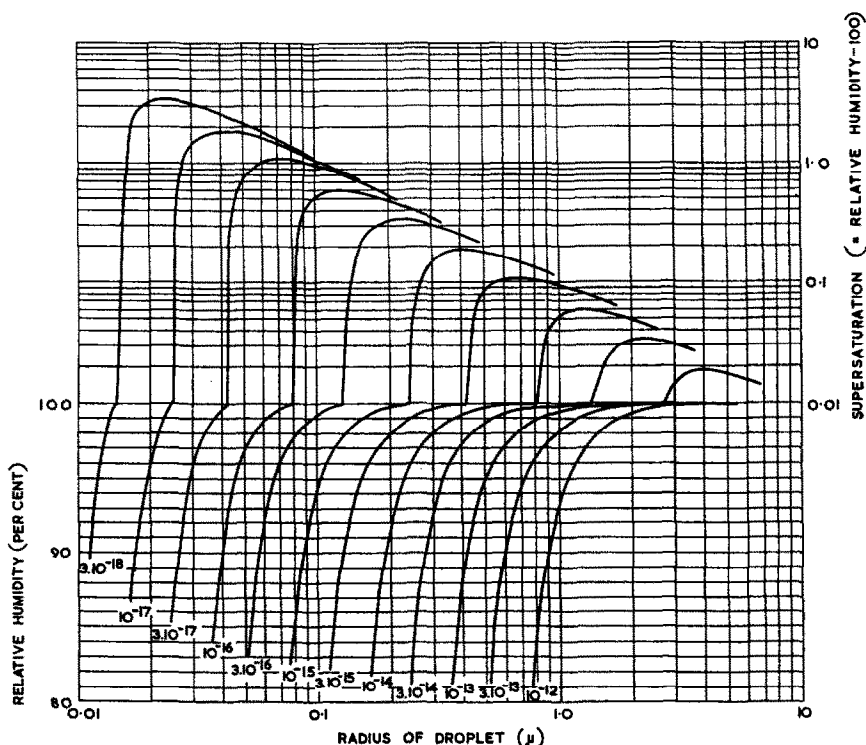


FIG. 1. Size of droplets of ammonium sulphate at different relative humidities. Each curve is labelled with the mass of ammonium sulphate in grammes. Note that above 100% relative humidity the supersaturation is plotted on a logarithmic scale.

equation (1)

$$\frac{dH'}{da} \exp\left(\frac{2\gamma M}{\rho RTr}\right) + H' \frac{d}{da}\left(\frac{2\gamma M}{\rho RTr}\right) \exp\left(\frac{2\gamma M}{\rho RTr}\right) = 0$$

$$\text{or} \quad \frac{1}{H'} \frac{dH'}{da} = -\frac{d}{da}\left(\frac{2\gamma M}{\rho RTr}\right)$$

The group $\frac{2\gamma M}{\rho RTr}$ can be written in the form $\left(\frac{a}{m}\right)^{\frac{1}{3}}(C + Da \dots)$ and its derivative $\frac{1}{3} \frac{a^{-\frac{2}{3}}}{m^{\frac{1}{3}}}(C + 4Da \dots)$. In the neighbourhood of the maximum Da can be shown to be

negligible compared with C . The approximate relationships shown in the Appendix were used to evaluate C and the critical values of a , the radius and supersaturation could then be found. The critical supersaturation S_c and radius r_c were found to be

$$S_c = (H_c - 100) = 6.00 \times 10^{-9}/m^{\frac{1}{3}}$$

and

$$r_c = 1.26 \times 10^7 m^{\frac{1}{3}} \text{ microns}$$

where m is in g.

Values obtained from these equations agree well with the co-ordinates of the maxima in FIG. 1, showing that it is valid to neglect all but the first term in the expansion above.

4. EXTINCTION COEFFICIENT AND VISIBILITY IN MONODISPERSE AMMONIUM SULPHATE AEROSOLS

The extinction coefficient, σ , was also calculated for air containing 10^{-6} g/m³ of ammonium sulphate present as particles of various sizes. The extinction coefficient is related to the visibility by the Koschmieder relationship

$$\text{Visual range} = 3.91/\sigma \quad (\text{MIDDLETON (1952), p. 105})$$

and it was calculated from the formula

$$\sigma = NK\pi r^2 \quad (\text{MIDDLETON (1952), p. 29})$$

where N = the number of particles per unit volume,

r = the droplet radius,

and K = the scattering area ratio.

Here, K is a function of the ratio of particle radius to wavelength, and of refractive index. It is usually tabulated against the variable $\alpha = 2\pi r/\lambda$. There is some difficulty in choosing the appropriate value since the human eye responds to a range of wavelength and the refractive index varies with concentration, so the following procedure was adopted.

Values of $K(\alpha)$ for $\mu = 1.33$, due to LA MER and SINCLAIR (1949) and HOUGHTON and CHALKER (1952), listed in MIDDLETON (1952, p. 30) were used. For each of several values of r , values of K appropriate to a range of wavelengths in the visible spectrum were obtained by interpolation and averaged using as weights the eye's response to daylight tabulated on p. 50 of MIDDLETON (1952). Thus, a function $K'(r, \mu)$ was obtained for $\mu = 1.33$.

As no useful data were found in the literature the refractive indices of nine ammonium sulphate solutions, ranging from 2 to 36 per cent by weight were measured at 10°C. The results fitted the linear relationship,

$$\mu = 1.3337 + 0.00156 p.$$

The particle radius for each ammonium sulphate aerosol considered at each relative humidity was obtained by solving equation (1) numerically by computer. The percentage of ammonium sulphate in the droplets was also found so the refractive index could be found. PENNDORF (1958) showed that for values of μ from 1.33 to 1.5, K can be expressed approximately as a function of $r(\mu - 1)/\lambda$ only. It follows that

$$K'(r, \mu) \approx K' \left(r \frac{(\mu - 1)}{(\mu_1 - 1)}, \mu_1 \right)$$

This relationship made it possible to estimate K' for any value of μ using the values for $\mu_1 = 1.33$.

The value of N was calculated from the particle mass m to correspond to 10^{-6} g/m³.

Thus the extinction coefficient was found as a function of the mass of ammonium sulphate per particle for nine values of the relative humidity. The results are plotted in FIG. 2. The 70 per cent and 80 per cent relative humidity curves pertain to droplets of supersaturated solutions. These points may have some relevance since DESSENS (1949) has observed that droplets may remain supersaturated for considerable periods of time. However, the physical properties needed for the calculations can not be measured readily for supersaturated solutions and were therefore extrapolated from the sub-saturated region. The results may therefore be inaccurate.

5. EXTINCTION COEFFICIENT IN ATMOSPHERIC HAZES

The calculations discussed in Section 4 relate to monodisperse ammonium sulphate aerosols. The results can be used to estimate the extinction coefficient in real hetero-disperse hazes due to ammonium sulphate particles if the size distribution is known. The extinction coefficient per microgram per cubic metre is found as

$$\bar{\sigma}(H) = \frac{\sum \sigma(m_i, H) \times \Delta M_i}{\sum \Delta M_i} \quad (2)$$

Here $\sigma(m_i, H)$ is the extinction coefficient of a monodisperse ammonium sulphate aerosol of concentration $1 \mu\text{g}/\text{m}^3$ with particle mass m_i and relative humidity H , and

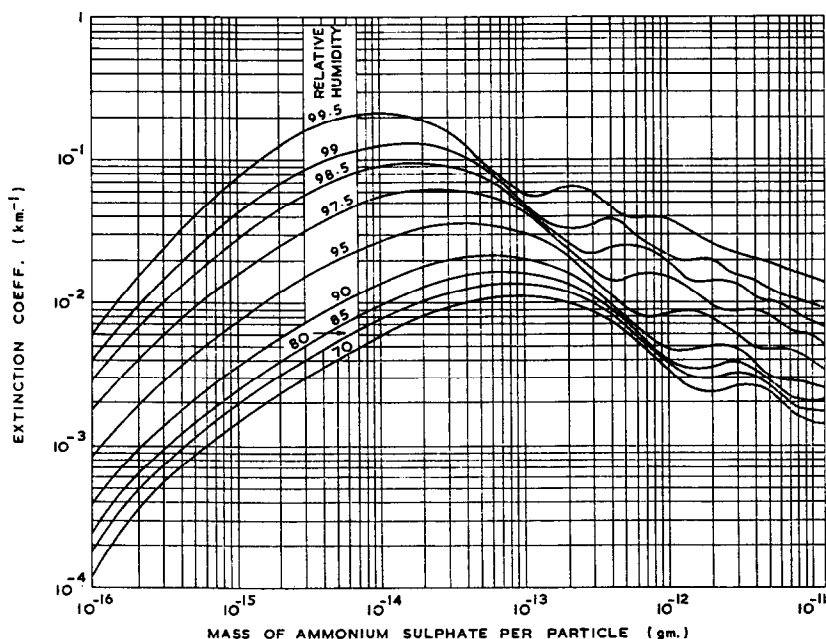


FIG. 2. Extinction coefficient of an atmosphere containing $1 \mu\text{g}/\text{m}^3$ ammonium sulphate as a function of the mass of ammonium sulphate per particle for several values of the relative humidity.

may be read from FIG. 2. ΔM_i is the mass of ammonium sulphate particles in the i 'th size interval, with particle mass m_i .

For illustration this calculation has been carried out for two size distributions and a range of relative humidities, and the results are plotted in FIG. 4.

The first distribution chosen is one of the type reported by JUNGE (1963). Junge found that the distribution frequently follows the relationship $\frac{dN}{d \log r} \propto \frac{1}{r^3}$ from less than 0.1μ to 1μ or 10μ radius. The simple model shown in FIG. 3, is probably reasonably representative of his results and is convenient for calculation. The mass median diameter for this distribution is 0.42μ , corresponding to a particle mass of $6.7 \times 10^{-14} \text{ g}$

and the extinction coefficient for a monodisperse aerosol of this size is plotted for comparison. This is seen to be about twice the value for the Junge distribution except at very high relative humidities. The result for the Junge distribution is sensitive to the limits chosen for the distribution. If the limits are extended the total mass of particles increases more rapidly than the total extinction coefficient (i.e. the denominator in equation 2 increases more rapidly than the numerator). Thus if the upper limit is raised from $1\ \mu$ to $10\ \mu$ radius, the mass increases by 60 per cent while the total extinction

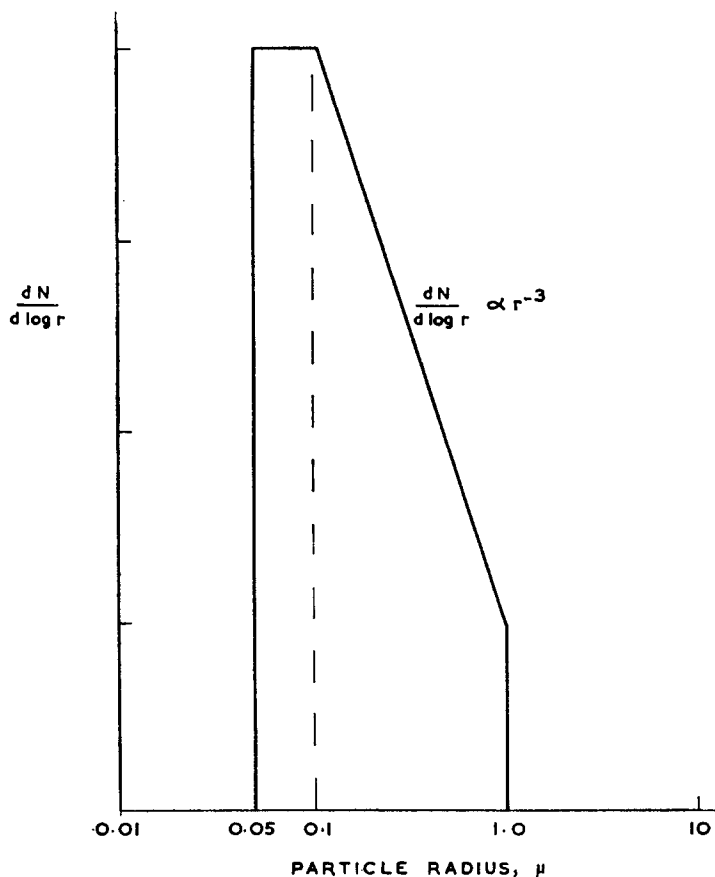


FIG. 3. Simplified size distribution, after Junge, used in the calculations.

coefficient increases only 5 or 10 per cent. Hence $\bar{\sigma}(H)$ is reduced by a factor of about 0.67.

Very few size distributions relating to ammonium sulphate particles in the atmosphere have been measured. Thus MÉSZÁROS (1968) has measured the distribution of ammonium ions and sulphate ions with particle size and WAGMAN (1967) and CORN (1965) measured the distribution of sulphate ions. These measurements were made without drying the natural aerosol and at unknown relative humidity, so that there is some uncertainty in relating the size of particles sampled to the ammonium sulphate particle mass. Moreover the distributions may be distorted by the presence of a few large particles, other than ammonium sulphate, containing one or other of the ions

detected. HEARD (1969), however, collected particles after drying the air and identified ammonium sulphate particles in the electron microscope. On this occasion over 90 per cent of the particles consisted of rather pure ammonium sulphate. His size distribution, tabulated below, was therefore chosen as the second example. In this case the size distribution was much narrower than the distribution of the Junge type discussed above. Consequently the agreement shown in FIG. 4. with the median size (0.6μ), is rather closer, and $\bar{\sigma}(H)$ is rather higher for humidities up to 98 per cent since most of the particles have particle masses lying near the main maximum exhibited by the curves of FIG. 2.

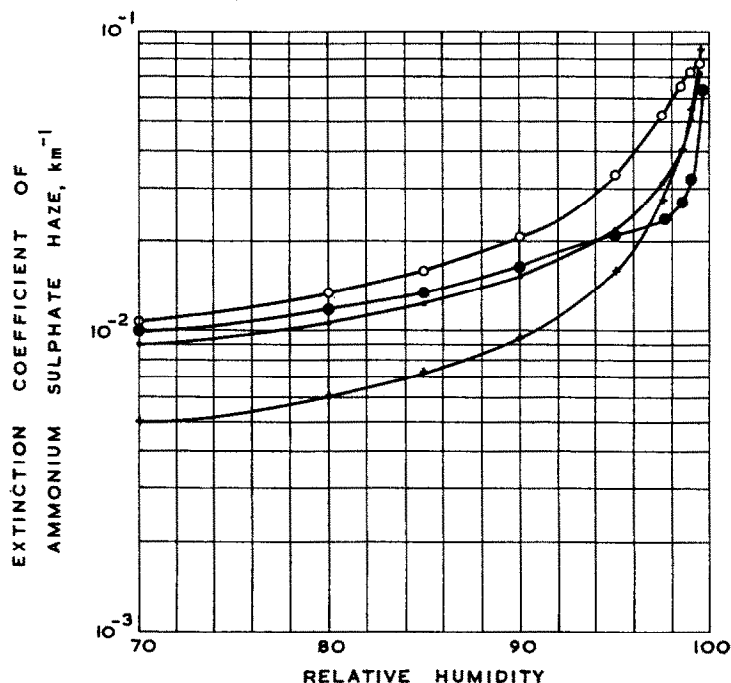


FIG. 4. The extinction coefficient of an atmosphere containing $1 \mu\text{g}/\text{m}^3$ of ammonium sulphate with the following size distributions:

+ distribution of the Junge type illustrated in FIG. 3.

○ monodisperse aerosol at the mass median diameter, 0.42μ , of the Junge distribution.

● distribution measured by Heard and Wiffen.

⊗ monodisperse aerosol at the mass median diameter, 0.6μ , of Heard and Wiffen's distribution

APPENDIX

The following linear relationships were found to represent the values of vapour pressure, surface tension and density given in the International Critical Tables and were used in the calculations.

$$H' = 100 - 0.2533 a.$$

$$\gamma = 74.22 + 0.1635 a.$$

$$\rho = 0.9997 + 0.0060 p \text{ for } 0 < p < 16.$$

$$\rho = 1.0049 + 0.0057 p \text{ for } 16 < p < 32.$$

$$\rho = 1.0087 + 0.00558 p \text{ for } p > 32.$$

In these formulae

a = mass of ammonium sulphate dissolved in 100 g water.

p = percentage of ammonium sulphate in the solution.

TABLE 1. THE SIZE DISTRIBUTION OF AMMONIUM SULPHATE PARTICLES IN THE ATMOSPHERE ON 23.8.67, REPORTED BY HEARD AND WIFFEN

Diameter (μ)	Average mass of ammonium sulphate per particle (g)	Percentage of total mass in size interval (%)
0.12-0.21	4.3×10^{-15}	1.4
0.21-0.29	1.45×10^{-14}	5.3
0.29-0.37	3.43×10^{-14}	6.6
0.37-0.46	6.7×10^{-14}	14.1
0.46-0.54	1.16×10^{-13}	12.65
0.54-0.62	1.84×10^{-13}	16.75
0.62-0.70	2.74×10^{-13}	20.0
0.70-0.79	3.9×10^{-13}	14.2
0.79-0.87	5.36×10^{-13}	9.75

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