

Lecture 16: Aerosol Light Scattering and Cloud Nucleation

Required Reading: FP&P Section 9.A.4 and 9.C.1.d

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Jose-Luis Jimenez

Outline of Lecture

- We study aerosols because of effects on:
 - Health
 - Ecosystems (acid rain)
 - Visibility
 - Climate
- Today
 - Aerosol light scattering
 - Aerosol water uptake
 - Subsaturated
 - Influence in light scattering
 - Supersaturated: cloud formation

Health Effects of Particles

From FP&P

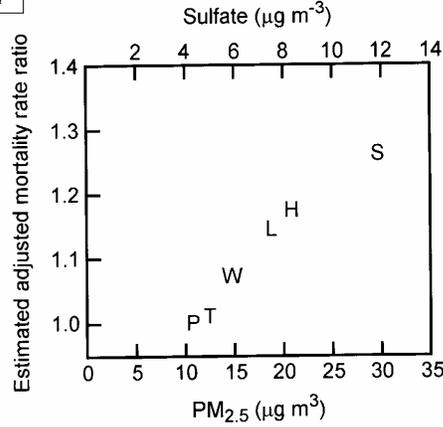
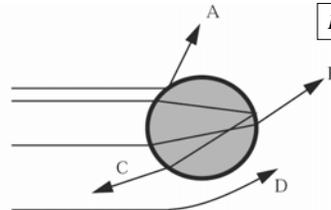


FIGURE 2.14 Estimated adjusted mortality rate ratios, taking the least polluted city, Portage, Wisconsin (P), as 1.0. T = Topeka, Kansas; W = Watertown, Massachusetts; L = St. Louis, Missouri; H = Harriman, Tennessee; S = Steubenville, Ohio. (Adapted from Dockery *et al.*, 1993.)

- “Harvard six-city study” (1993)
- Mortality increases with fine particle concentration
- Disputed for a decade, now considered proven
 - New Dutch study shows even greater risk
- Mechanism still uncertain

Visibility Degradation I

- Particles can scatter and absorb radiation
- These effects limit atmospheric



From Jacob

Figure 8-3 Scattering of a radiation beam: processes of reflection (A), refraction (B), refraction and internal reflection (C), and diffraction (D).

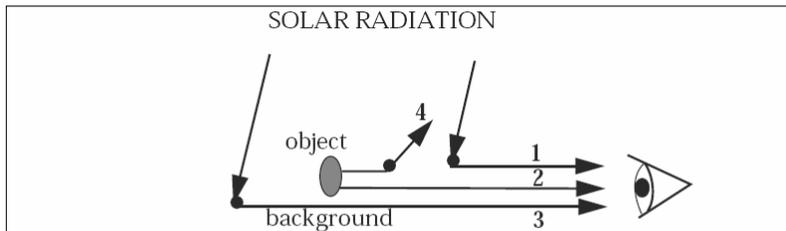
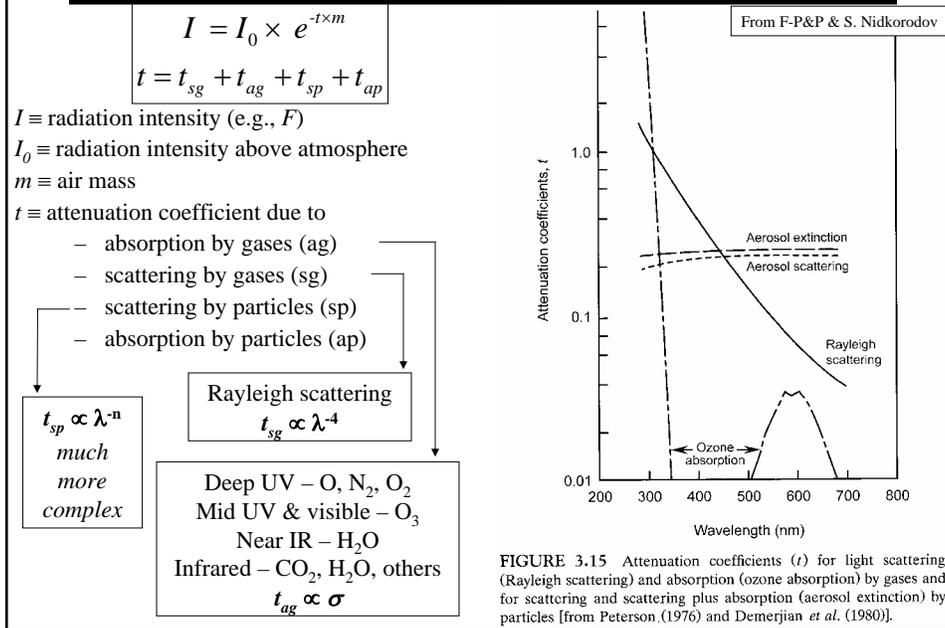


Figure 8-5 Reduction of visibility by aerosols. The visibility of an object is determined by its contrast with the background (2 vs. 3). This contrast is reduced by aerosol scattering of solar radiation into the line of sight (1) and by scattering of radiation from the object out of the line of sight (4).

Direct Attenuation of Radiation



Scattering by Gases

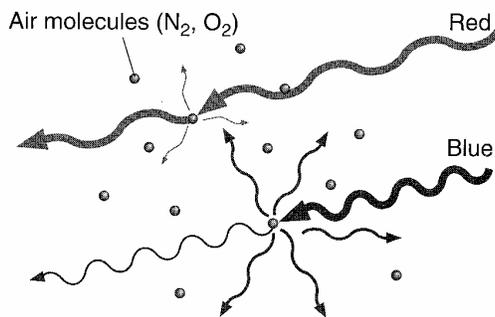


Figure 3.11 Light scattering by air molecules. According to the Rayleigh scattering law, blue light, which has shorter wavelengths than red light, is scattered more effectively by air molecules. Hence the clear sky illuminated by the sun takes on the blue color of the scattered light.

From Turco

- Purely physical process, not absorption
- Approximation:

$$t_{sg} = 1.044 \cdot 10^5 \cdot (n_{0\lambda} - 1)^2 / \lambda^4$$

- Strongly increases as λ decreases
- Reason why “sky is blue” during the day

Gas vs. Particle / Scat. Vs. Abs.

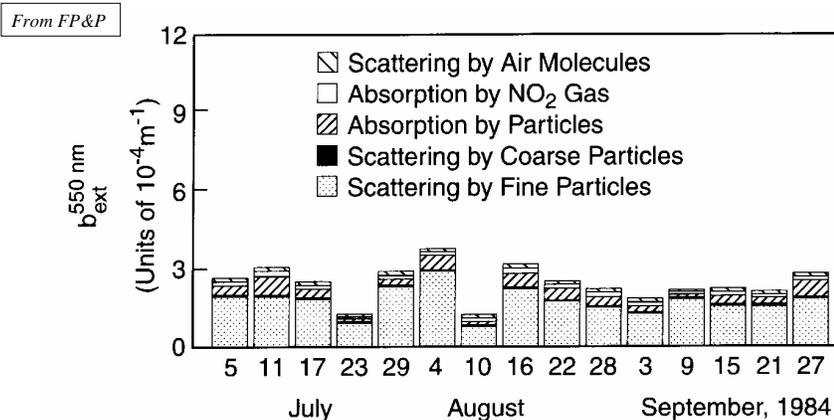


FIGURE 9.17 Individual contributions of scattering and absorption of light at 550 nm by gases and particles in Pasadena, California, during the summer of 1984 (adapted from Larson and Cass, 1989).

- Denver Brown Cloud (late 70's): 7% NO₂, 93% particles

Light Scattering by Particles

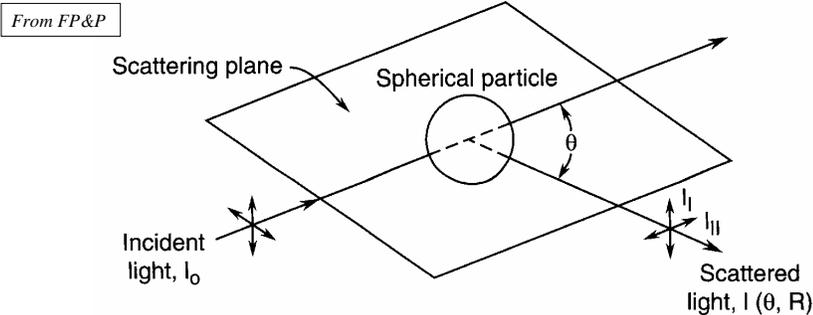


FIGURE 9.18 Diagram showing scattering angle, scattering plane, and the polarized components of scattered light. (From Hinds, W. C. *Aerosol Technology*. Copyright © 1982 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

Rayleigh scattering:	$D_p \ll \lambda$
Mie scattering:	$D_p \approx \lambda$
Geometric scattering:	$D_p \gg \lambda$

Size Parameter

$$\alpha = \frac{\pi D}{\lambda}$$

Nephelometer

From FP&P

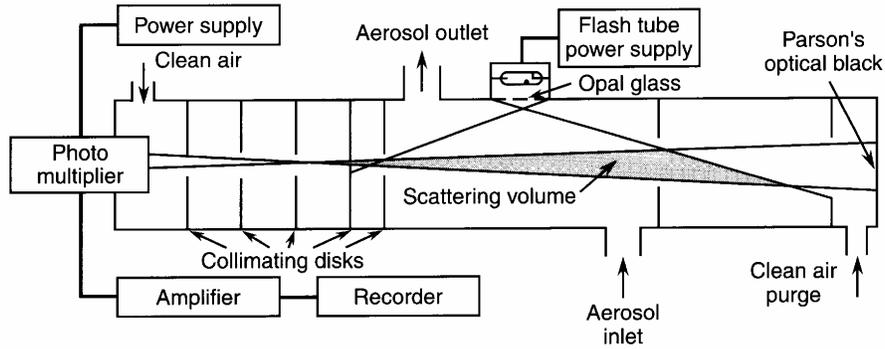


FIGURE 9.21 Schematic diagram of an integrating nephelometer (from Charlson *et al.*, 1967).

TABLE 9.6 Index of Refraction at 589 nm for Some Species Found in the Atmosphere or Used for Instrument Calibration^a

Species	Index of refraction
Vacuum	1.0
Water vapor	1.00025
Air	1.00029
Water (liquid)	1.333
Ice	1.309
Rock salt	1.544
Sodium chloride	1.342–1.378 ^b
in aqueous solutions	
Sulfuric acid	1.339–1.437 ^c
in aqueous solutions	
Benzene	1.501
α -Pinene	1.465
<i>d</i> -Limonene	1.471
Nitrobenzene	1.550
Diethyl phthalate	1.49
Oleic acid	1.46
Polystyrene latex	1.59
Carbon	1.59–0.66 ^{d,f}
Iron	1.51–1.63 ^d
Magnetite (Fe ₃ O ₄)	2.58–0.58 ^e
Copper	0.62–2.63 ^d

^a Data from the *Handbook of Chemistry and Physics*, unless otherwise noted (~20–25°C).

^b For solution densities from 1.035 to 1.189.

^c For solution densities from 1.028 to 1.811.

^d From Hinds (1982).

^e From Huffman and Stapp (1973).

^f At $\lambda = 491$ nm.

From FP&P

Mie Scattering I

$$I(\theta, R) = \frac{I_0 \lambda^2 (i_1 + i_{11})}{8\pi^2 R^2}$$

- i_1 and i_{11} are “Mie intensity parameters”
- Functions of α , θ , & m
- m : refractive index = c/v
- Imaginary part of m represents absorption

Absorption by EC

From FP&P

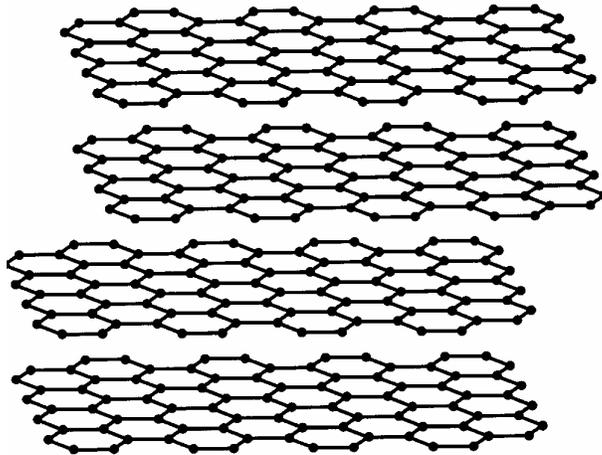


FIGURE 9.29 Structure of elemental carbon.

Relative Importance of Abs. vs. Scat.

From FP&P

TABLE 9.8 Contribution of Light Absorption to Total Light Extinction Due to Particles in the Troposphere^a

Type of atmosphere	Location	b_{ap} (m^{-1})	$b_{ap} / (b_{ap} + b_{sp})$	Reference
Remote	Mauna Loa, Hawaii	6×10^{-8}	0.069	Clarke and Charlson, 1985
Rural	Allegheny Mts./Laurel Hill	1.9×10^{-5}	0.13	Japar <i>et al.</i> , 1986
	Shenandoah Valley/Blue Ridge Mts.	1.0×10^{-5}	0.051	Ferman <i>et al.</i> , 1981
	Off East Coast of U.S. (Virginia)	$(0.01-1.0) \times 10^{-5}$	0.029-0.24	Novakov <i>et al.</i> , 1997 ^b
Urban/residential	Denver, Nov/Dec. 1978	6.6×10^{-5}	0.42	Groblicki <i>et al.</i> , 1981
	Detroit, July 1981	2.4×10^{-5}	0.13	Wolff <i>et al.</i> , 1982a,b
	Houston, Sept. 1980	3.0×10^{-5}	0.18	Dzubay <i>et al.</i> , 1982
	Los Angeles Basin, Oct. 1980	6.4×10^{-5}	0.25	Pratsinis <i>et al.</i> , 1984

^a From Japar *et al.* (1986).

^b At altitudes from 0.2 to 3 km.

Mie Scattering vs. α

From FP&P

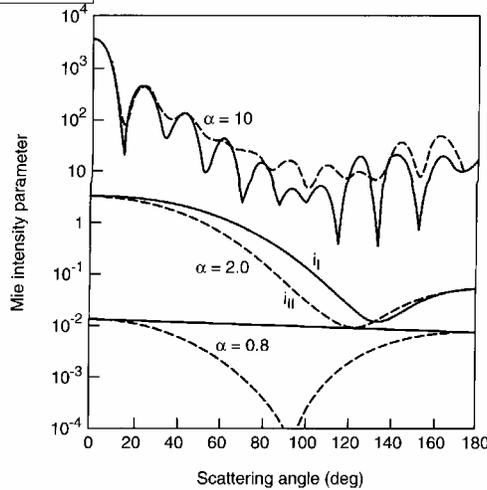


FIGURE 9.19 Mie intensity parameters versus scattering angle for water droplets ($m = 1.333$) having $\alpha = 0.8, 2.0,$ and 10.0 . Solid lines are i_1 , and dashed lines are i_{11} (adapted from Hinds, 1982).

- Visible Mie scattering reaches peak efficiency for particles $\approx 0.30 - 0.70 \mu\text{m}$. Because this is close to typical ambient particle sizes, Mie scattering is the most important in the atmosphere.
- Mie scattering can only be treated analytically for spherical homogeneous particles.
- Mie scattering mostly occurs in forward direction, as opposed to Rayleigh scattering, which is symmetric

From FP&P

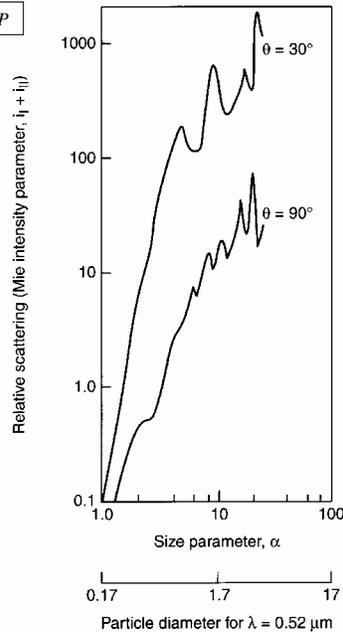


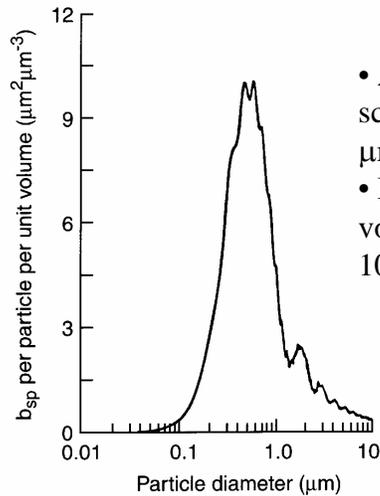
FIGURE 9.20 Relative scattering [Mie intensity parameter ($i_1 + i_{11}$)] versus size parameter for water droplets ($m = 1.33$) at scattering angles of 30° and 90° (adapted from Hinds, 1982).

Mie Scattering vs. size

- This is for a single particle
- Note Rayleigh limit as d^6 at small sizes

Mie Scattering per unit volume

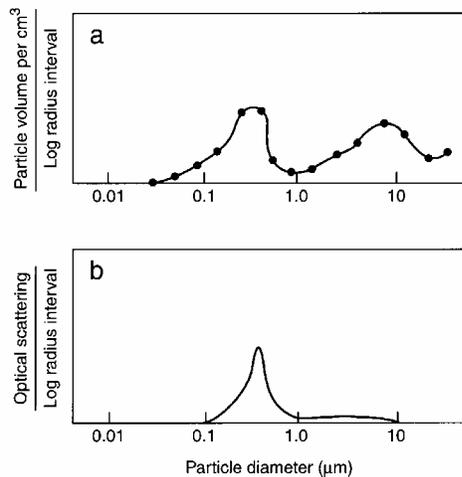
From FP&P



- A single 10 μm particle scatters much more than a 1 μm particle
- But the reverse is true per unit volume (one 10 μm particle vs 1000 1 μm particles)

FIGURE 9.22 Scattering coefficient per particle divided by particle volume plotted as a function of diameter. The particles are assumed to be spheres of refractive index 1.50 and the light has $\lambda = 550 \text{ nm}$ (adapted from Waggoner and Charlson, 1976).

Scattering in Atmosphere



- By coincidence, mass concentration is largest for particles that are most efficient scatterers
- Scattering by fine mode dominates total scattering in most conditions
- Some exceptions such as dust storms

FIGURE 9.23 (a) Aerosol particle size distribution measured at Pomona during the 1972 State of California Air Resources Board ACHEX program. (b) Calculated optical scattering by particles, b_{sp} , for measured size distribution (adapted from Waggoner and Charlson, 1976).

From FP&P

Scattering vs. Fine Particles

From FP&P

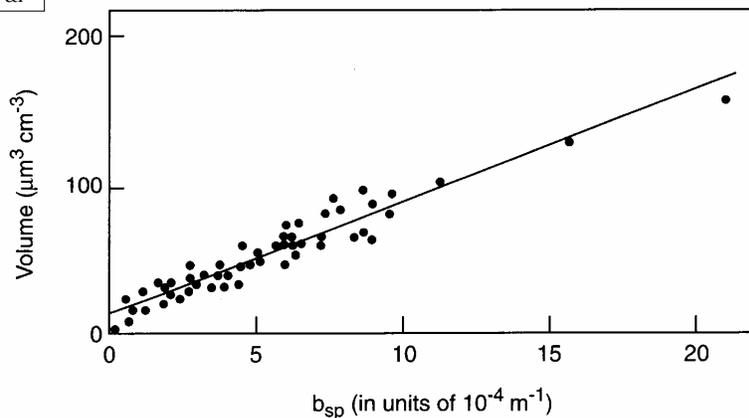


FIGURE 9.24 Plot of measured aerosol fine particle volume (including only those particles of 0.1- to 1.0- μm diameter) versus measured b_{sp} . Measurements were part of the State of California Air Resources Board ACHEX program (adapted from Waggoner and Charlson, 1976; data supplied by Dr. Clark of North American Rockwell).

Scattering vs. Fine & Coarse Part.

From FP&P

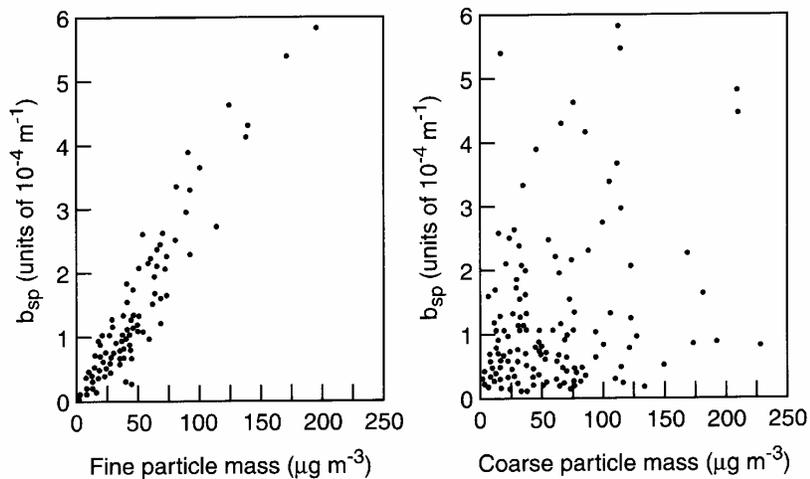


FIGURE 9.25 Correlation of b_{sp} with fine and coarse particulate mass (adapted from Groblicki *et al.*, 1981).

Mass Scattering Efficiencies

From FP&P

TABLE 9.7 Some Reported Values of the Light Scattering Coefficients (a_i) for Common Constituents of Atmospheric Particles^a

Compound	a_i ($\text{m}^2 \text{g}^{-1}$)	Reference
Elemental (black) carbon	0.45–1.4	Petzold <i>et al.</i> , 1997
Sulfate	5.2–13 ^b	Howell and Huebert, 1998
	3–7	McMurry <i>et al.</i> , 1996
	2.1	Eatough <i>et al.</i> , 1996
	2.2–3.2	Hegg <i>et al.</i> , 1995
	3.2–13.5	White, 1986
Nitrate	1.8	Eatough <i>et al.</i> , 1996
	0.5–6.0	White, 1986
Organics	3–7	McMurry <i>et al.</i> , 1996
	1.1	Eatough <i>et al.</i> , 1996
	0–4.6	White, 1986

^a For dry particles unless otherwise specified.

^b At 80% RH.

- Be careful with these as they depend on size dist. & state of mixing

Dependence of Scattering on RH

From FP&P

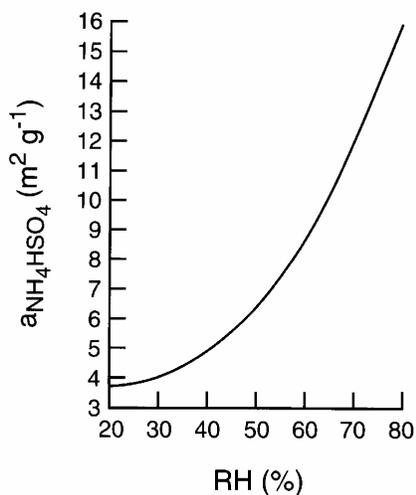


FIGURE 9.26 Calculated light scattering coefficient for NH_4HSO_4 droplets as a function of relative humidity (adapted from Sloane, 1986).

Why Dependence on RH is so Strong

From FP&P

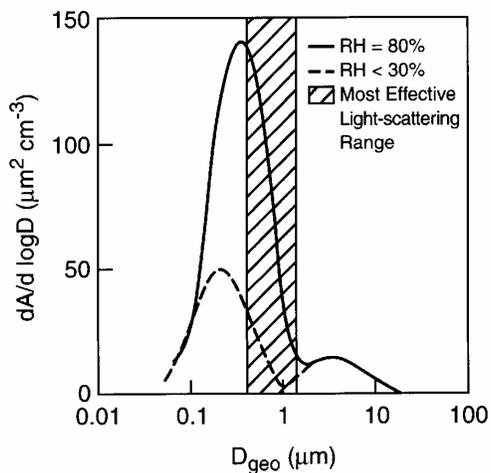
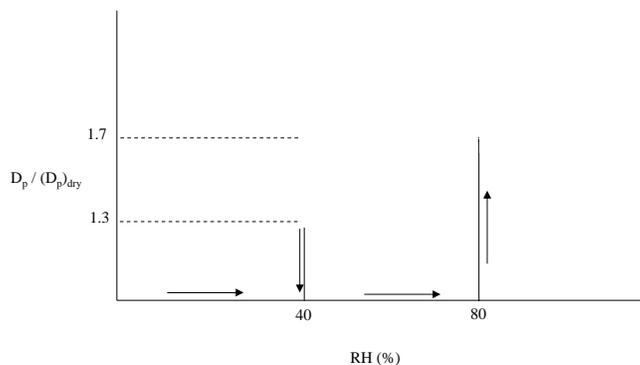


FIGURE 9.28 Size distribution of particle geometric cross section ($dA/d \log D$) as a function of geometric diameter for a typical rural aerosol (adapted from Hegg *et al.*, 1993).

Deliquescence and Efflorescence



Compound	RHC (%)	RHD (%)
$(\text{NH}_4)_2\text{SO}_4$	40	80
NH_4HSO_4	10	40
H_2SO_4	0	0
NH_4NO_3	28	62
NaCl	42	75

From Don Collins
Texas A&M U

Deliquescence for $(\text{NH}_4)_2\text{SO}_4$

From FP&P

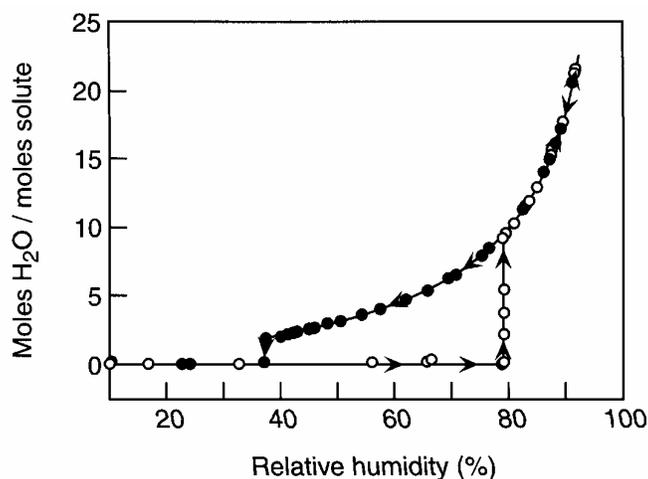


FIGURE 9.41 Uptake of water by $(\text{NH}_4)_2\text{SO}_4$ and its drying as a function of relative humidity at 25°C (adapted from Tang *et al.*, 1995).

Deliquescence Points

TABLE 9.16 Deliquescence Points of Some Salts Commonly Found in Ambient Air at 25°C^a

Composition	Deliquescence Relative humidity (%)
$(\text{NH}_4)_2\text{SO}_4$	79.9
$(\text{NH}_4)\text{HSO}_4$	39.0
$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$	69.0
Na_2SO_4	84.2
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}^b$	93.6
NH_4NO_3	61.8
NaCl	75.3
NaNO_3	74.3
NaCl-NaNO_3	68.0
KCl	84.2
NaCl-KCl	72.7

^a From Tang and Munkelwitz (1993, 1994a, 1994b); note there is a hysteresis so that the RH at which the salts recrystallize as the RH drops (the effluorescence RH) is lower than these values.

^b From Goldberg (1981).

From FP&P

Deliquescence vs. Composition

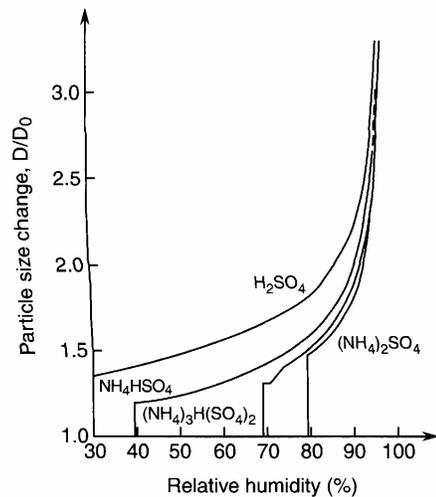


FIGURE 9.40 Calculated changes in particle size as a function of relative humidity at 25°C from particles with four different chemical compositions (adapted from Tang, 1980).

From FP&P

Importance of H_2SO_4 Neutralization

From FP&P

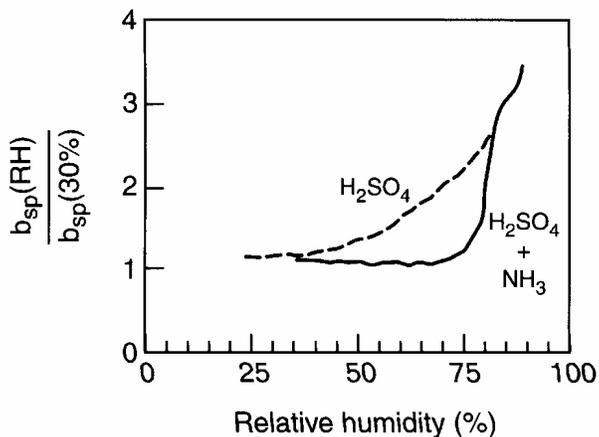


FIGURE 9.42 Humidogram for laboratory H_2SO_4 aerosol (dashed) and for the reaction product of H_2SO_4 and NH_3 (solid) (adapted from Charlson *et al.*, 1974a).

Extension of hygroscopic growth to cloud droplet formation

$$\frac{e_{sd}}{e_s} = \frac{e_{sd}}{e_s} \bigg|_{flat} \frac{e_c}{e_s} \bigg|_{pure} = \gamma_w x_w \exp\left(\frac{4\sigma}{R_w \rho_w T D}\right) = RH \text{ (at equilibrium)}$$

As the RH approaches and exceeds 100%, the solution droplet becomes increasingly dilute \rightarrow γ_w approaches 1.0 and the droplet volume can be directly related to the amount of water.

$$\frac{e_{sd}}{e_s} = \exp\left(\frac{2\sigma}{R_w \rho_w T r} - \frac{3iMW_w m}{4\pi\rho_w MW_s r^3}\right) = \exp\left(\frac{A}{r} - \frac{B}{r^3}\right)$$

$$\frac{d}{dr}\left(\frac{e_{sd}}{e_s}\right) = 0 \Rightarrow r_c = \left(\frac{3B}{A}\right)^{1/2}$$

$$\ln\left(\frac{e_{sd}}{e_s}\right) = \ln(S_c + 1) \approx S_c = \left(\frac{4A^3}{27B}\right)^{1/2}$$

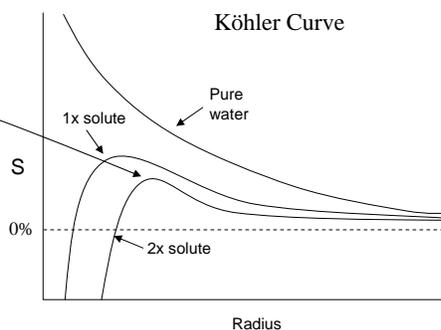
Example: Calculate the critical supersaturation of a 0.08 μm diameter ammonium sulfate particle

$$A = \frac{2\sigma}{\rho_w R_w T} = \frac{2(0.075 \frac{\text{J}}{\text{m}})(\frac{\text{J}}{\text{Nm}})}{(1000 \frac{\text{kg}}{\text{m}^3})(461 \frac{\text{J}}{\text{kgK}})(298 \text{ K})} = 1.0919 \times 10^{-9} \text{ m}$$

$$m_s = \frac{4}{3}\pi\rho_p r_p^3 = \frac{4}{3}\pi(1760 \frac{\text{kg}}{\text{m}^3})(0.04 \times 10^{-6} \text{ m})^3 = 4.7183 \times 10^{-19} \text{ kg}$$

$$B = \frac{3iMW_w m_s}{4\pi\rho_w MW_s} = \frac{3(3)(0.018 \frac{\text{kg}}{\text{mol}})(4.7183 \times 10^{-19} \text{ kg})}{4\pi(1000 \frac{\text{kg}}{\text{m}^3})(0.132 \frac{\text{kg}}{\text{mol}})} = 4.608 \times 10^{-23} \text{ m}^3$$

$$S_c = \left(\frac{4A^3}{27B}\right)^{1/2} = \left(\frac{4(1.0919 \times 10^{-9} \text{ m})^3}{27(4.608 \times 10^{-23} \text{ m}^3)}\right)^{1/2} = 0.00205 = 0.205\% \Rightarrow RH = 1 + S_c = 100.205\%$$



From Seinfeld, J. H., and S. N. Pandis, *Atmospheric Chemistry and Physics*, John Wiley, New York, 1998.

From Don Collins, Texas A&M U.

Example of Activation in a Cloud

- The next set of slides shows the evolution of the size (i.e. water uptake) of two particles of initial dry sizes of 150 and 300 nm.
- As the air rises in the subsaturated atmosphere below the cloud, the absolute humidity stays constant, but RH increases as T decreases. The particles eventually deliquesce and keep taking up water
- When the particles enter the cloud, which is supersaturated in H₂O they keep growing.
- S reaches a point higher than S_{crit} for the larger particle, which leads to activation of that particle
- S always stays below S_{crit} for the smaller particle, so that one remains unactivated throughout the cloud. This is called the “interstitial” aerosol. Typically 10-50% of the particles activate and the rest remain as interstitial.
- Finally, if the air containing the particles goes beyond the top of the cloud, both particles lose most water because the air is again subsaturated
- This animation was prepared by Don Collins at Texas A&M Univ

