Quiz: What is an Aerosol?

Stable suspension of solid or liquid particles in a gas

Gas (molecules)

Particle (a clump of molecules)

Particulate matter (PM) – a clump of particles
# Aerosols, Particles, and PM

**Aerosol**

Stable suspension of solid or liquid particles in a gas

**Particle**

A liquid or solid object 0.001 µm - 100 µm in diameter that can be kept suspended in a gas by Brownian motion or convection for an atmospherically relevant (minutes to years) period of time

**PM**

PM (particulate matter) collection of all particles suspended in a given volume of air (measured in µg/m³)

**Related terms**

Ash, smoke, dust, fog, mist, drizzle, smog, haze, etc.

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**Importance of atmospheric particles:**

- Chemistry (dry and wet deposition, photochemical smog, heterogeneous catalysis, etc.)
- Cloud formation (cloud condensation nuclei)
- Climate (light scattering, light absorption, indirect effect on cloud albedo)
- Health effects (asthma, mortality, lung cancer, depression, …)
Typical Particle Sizes: nm (clusters) to µm (droplets)

- Molecule (0.0001 µm)
- Diesel particle (0.05 µm)
- Typical smog particle (0.5 µm)
- Typical sea-salt spray particle (2.5 µm)
- Typical cloud droplet (100 µm)

(magnified by 25,000×)
Diversity of Aerosol Particles

- Many different types of particles
  - Soot, dust, organic aerosols, ice, ...
- High degree of chemical heterogeneity
- Highly disordered surfaces
  - One “huge surface defect”
- Continuously evolving
  - (as a result of chemical reactions, evaporation and condensation, interactions with clouds, and with solar radiation)
Major Inorganic Aerosol: Sulfates

- **Volcanoes** can emit large amounts of $\text{H}_2\text{S}$ and $\text{SO}_2$ in the air.
- Burning **coal** releases similarly large amounts of $\text{SO}_2$ in the air.
- Sulfur compounds get oxidized to produce aerosol particles rich in sulfuric acid (and sulfates).

$$\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{aerosol} \leftrightarrow \text{clouds}$$

$$\text{NH}_3, \text{amines} + \text{H}_2\text{SO}_4 \rightarrow \text{sulfates}$$
Primary Organic Aerosol (POA)

Natural and anthropogenic sources

TRAFFIC

COOKING

OCEAN
Secondary Organic Aerosol (SOA)

**Natural and anthropogenic sources**

**VOC = Volatile Organic Compounds**

**Oxidized VOC**

**Condensation**

**SOA particles**

**BIOGENIC EMISSIONS**

**INDUSTRY and TRAFFIC**
Biomass Burning Aerosol

Biomass burning refers to fires in forests, grasslands, woodlands, etc. Smoke produced by such fires contains a variety of different kinds of particles, including:

- "Tar balls" and other organic aerosol
- Leaf debris
- Soot / ash

SEM image of a particle sampled from a fire smoke. This particular particle happens to be a fragment of a leaf.

Fire in the wetlands vegetation at the Merritt Island National Wildlife Refuge, Kennedy Space Center, Florida. Even wetlands can catch on fire!
Dust

Dust storms commonly carry large amounts of crustal particles over large distances. It is not uncommon to find dust from Sahara in the air in the middle of US or Europe. Unlike particles produced in biomass and fuel burning, dust particles are relatively harmless. However, dust particles produced in areas with heavy agriculture (e.g., Fresno County in California) are known to amplify symptoms of asthma and related diseases.
Fossil-Fuel Combustion

Several major classes of aerosol particles result from fuel burning:

- Diesel particles - fractal-like agglomerates of 5-10 soot balls that are emitted directly by diesel engines. Compared to other type of PM, diesel PM is especially harmful to health; they are known to cause cancer and asthma.

- Secondary Organic Aerosol (SOA) is produced together with ozone from VOCs (Volatile Organic Compounds) in photochemical smog. Their health effects are not understood.
Biological Aerosols

Airborne spores, pollens, and viruses are frequently found in the air, including cloud and in fog water. Although not scientifically proven, such "bioaerosols" are frequently associated with symptoms of allergy, asthma, and related diseases.

Ragweed pollen

Tuber Rufum spore
Highly Unnatural Particles

The plume of chemicals emitted as a result of the September 11, 2001 terrorist attack in New York contained an array of rather nasty toxins in the form of gases and particles. Certain industrial practices produce unusual aerosols as well (metal oxides, engineered nanoparticles, etc.). Their environmental effects are actively researched at present.
Cigarette Smoke

By far the highest aerosol concentrations encountered in "nature" can be found in smoking bars (> 1000 µg/m³!)
A. Soot aggregates

B. Inorganic salts coated with secondary organic material

C. Soot particles coated with secondary organic material

D. Sea salt particles
Classification of Aerosol Particles

By size

- **Coarse** (diameter > 2.5 µm; usually stopped by the nose)
- **Fine** (PM$_{2.5}$; diameter < 2.5 µm; penetrate into lungs)
- **Ultrafine** (diameter < 0.1 µm; penetrate into blood vessels)

By composition

- Sulfates: H$_2$SO$_4$, NH$_4$HSO$_4$, …
- Nitrates: NaNO$_3$, NH$_4$NO$_3$, …
- Elemental carbon (EC)
- Crustal particles (dust)
- Sea-salt particles
- Organic carbon (OC), including:
  - Primary organic aerosol (POA)
  - Secondary organic aerosol (SOA)
Basics: Knudsen Number (Kn)

If a particle is sufficiently large, the gas surrounding it can be regarded as a continuous medium with a certain viscosity. A good figure of merit is the Knudsen number (Kn) defined as:

\[
Kn = \frac{\lambda_{gas}}{R_p}
\]

- If \( Kn \gg 1 \) ⇒ kinetic regime (or molecular regime)
- If \( Kn \ll 1 \) ⇒ continuum regime (or viscous regime)

In a continuum regime, moving particle experiences friction against gas all the time, whereas in kinetic regime the particle can slip past molecules as if it is in vacuum.

Solve in class: calculate Knudsen number for a particle with 2 \( \mu \)m diameter in a gas at 1 atm with effective collision cross section of 40 Å².

Fig. 8.3 From Seinfeld & Pandis: Mean free path for the US standard atmosphere.
Basics: Stokes' Law

Particle moving with speed \( \nu \) in a continuous medium \((Kn << 1)\) with viscosity \( \eta \) experiences a drag force given by Stokes law.

In molecular regime, Stokes law can still be applied with a slip correction factor, \( C_c \) (also known as Cunningham factor).

Stokes law can be used to predict the terminal speed of motion of a particle under the influence of a constant force (e.g., gravity).

Continuum regime:
\[
F_{\text{drag}} = 6\pi \eta R_p \nu
\]

Molecular regime:
\[
F_{\text{drag}} = \frac{6\pi \eta R_p \nu}{C_c}
\]

Solve in class:
Calculate sedimentation velocity of a 2 \( \mu \)m diameter particle with a unit density at STP \((\eta = 1.5e-3 \text{ g/cm/s})\).
Sedimentation vs. Brownian Diffusion

Collisions with molecules exert randomly oriented forces on the particle resulting in its chaotic Brownian motion that competes with sedimentation under gravity.

Brownian motion wins for particles < 0.1 µm

In the absence of convection, particles larger than 100 µm will quickly sediment from the troposphere (they drop like rocks!)

### TABLE 9.5 Cumulative Deposition of Unit Density Particles onto a Horizontal Surface from Unit Aerosol Concentrations\(^a\) during 100 s by Diffusion and Gravitational Settling\(^b\)

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>Diffusion (number cm(^{-2}))</th>
<th>Settling (number cm(^{-2}))</th>
<th>Ratio diffusion / settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>2.5</td>
<td>6.5 × 10(^{-5})</td>
<td>3.8 × 10(^4)</td>
</tr>
<tr>
<td>0.01</td>
<td>0.26</td>
<td>6.7 × 10(^{-4})</td>
<td>390</td>
</tr>
<tr>
<td>0.1</td>
<td>2.9 × 10(^{-2})</td>
<td>8.5 × 10(^{-3})</td>
<td>3.4</td>
</tr>
<tr>
<td>1.0</td>
<td>5.9 × 10(^{-3})</td>
<td>0.35</td>
<td>1.7 × 10(^{-2})</td>
</tr>
<tr>
<td>10</td>
<td>1.7 × 10(^{-3})</td>
<td>31</td>
<td>5.5 × 10(^{-5})</td>
</tr>
<tr>
<td>100</td>
<td>5.5 × 10(^{-4})</td>
<td>2500</td>
<td>2.2 × 10(^{-7})</td>
</tr>
</tbody>
</table>

\(^a\) This assumes an aerosol concentration of 1 particle cm\(^{-3}\) outside the gradient region.

\(^b\) From Hinds (1982).
Basics: Effective Particle Diameters

Depending on the circumstances, different metrics are used for the particle size:

- **Classical aerodynamic diameter**: diameter of a sphere with density = 1 g/cm³ that has the same terminal velocity in a gravitational field as the particle under consideration.

- **Stokes diameter**: same as above except that density of the reference spherical particle is the same as that for the particle in question.

- **Volume equivalent diameter**: diameter of a sphere with the same density that has the same volume as the non-spherical particle in question.

- **Electrical mobility equivalent diameter**: diameter of a sphere with density = 1 g/cm³ that has the same mobility in electrostatic field as the particle under consideration.

\[
\begin{align*}
\text{Particle in an E-field:} \\
F_{\text{drag}} = q^+ F = qE \\
qE = \frac{6\pi \eta \nu_R E}{C_c} \\
\nu = \left[\frac{C_c}{6\pi \eta R_p}\right] \cdot qE \\
\text{Stokes radius} \\
\text{Electric mobility}
\end{align*}
\]

**Solve in class**: Find volume equivalent diameter of a rod-like virus, which is 1 µm long and 0.1 µm wide. The effective density of the virus is 1.1 g/cm³.

**Solve in class**: Find a relationship between aerodynamic and Stokes diameters.
Effective Particle Diameters

Good reference for this topic:

### Table 1

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Diameter relations</th>
<th>( \rho_p ) and ( \rho_m ) relations</th>
<th>( \chi ) and ( \chi' ) relations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Sphere (no voids)</td>
<td>( d_{me} = d_{ve} ) ( d_m = d_{ve} ) ( \frac{d_{me}}{\rho_p} = d_{ve} )</td>
<td>( \rho_p = \rho_m )</td>
<td>( \chi = \chi' = 1 )</td>
</tr>
<tr>
<td>B Sphere (internal voids)</td>
<td>( d_{me} = d_{me} \cdot \delta ) ( d_m = d_{ve} ) ( \frac{d_{me}}{\rho_p} = d_{ve} )</td>
<td>( \rho_p &lt; \rho_m ) ( \delta \cdot \rho_p = \rho_m )</td>
<td>( \chi = 1 \cdot \frac{C_c(d_{me})}{C_c(d_{me})} ) ( \chi' = \delta \cdot \frac{C_c(d_{ve})}{C_c(d_{me})} )</td>
</tr>
<tr>
<td>C Compact Aggregate (internal voids)</td>
<td>( d_{me} = d_{me} \cdot \delta )</td>
<td>Assume: ( d_m \approx d_{ve} )</td>
<td>( \chi \approx 1 ) ( \chi' = \delta \cdot \frac{C_c(d_{me})}{C_c(d_{me})} )</td>
</tr>
<tr>
<td>D Irregular (no voids)</td>
<td>( d_{me} = d_{ve} ) ( d_m &gt; d_{ve} )</td>
<td>( \rho_p = \rho_m )</td>
<td>( \chi' = \chi &gt; 1 )</td>
</tr>
<tr>
<td>E Aggregate (no voids)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F Irregular (internal voids)</td>
<td>( d_{me} = d_{me} \cdot \delta ) ( d_m &gt; d_{ve} )</td>
<td>( \rho_p &lt; \rho_m ) ( \delta \cdot \rho_p = \rho_m )</td>
<td>( \chi' &gt; \chi &gt; 1 ) ( \chi' = \chi' \cdot \delta \cdot \frac{C_c(d_{me})}{C_c(d_{me})} )</td>
</tr>
<tr>
<td>G Aggregate (internal voids)</td>
<td>( d_{me} = d_{me} \cdot \delta ) ( d_m &gt; d_{ve} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \lambda \) mean free path of gas molecules

Kn
Knudsen number

\( d_p \) physical or geometric diameter

\( d_{ve} \) volume equivalent diameter

\( d_e \) envelope equivalent diameter (same as \( d_{ve} \))

\( d_{me} \) mass equivalent diameter

\( d_m \) electrical mobility diameter

\( d_a \) aerodynamic diameter (in any flow regime)

\( d_{ca} \) continuum regime aerodynamic diameter

\( d_{ta} \) (Kn) or \( d_{ta} \) transition regime aerodynamic diameter

\( d_{va} \) vacuum aerodynamic diameter (also known as free-molecular regime aerodynamic diameter)

\( d_{adj} \) adjusted sphere diameter (see section “Relationship of \( \chi \) to Flow Regime” below)

\( d_A \) projected area diameter

\( d_{pp} \) physical diameter of a primary particle of an aggregate

\( C_c \) Cunningham slip correction factor

\( \chi \) dynamic shape factor (in any flow regime)

\( \chi_c \) dynamic shape factor (continuum regime limit)

\( \chi_t \) (Kn) or \( \chi_t \) dynamic shape factor (transition regime)

\( \chi_v \) dynamic shape factor (vacuum or free molecular regime limit)
Schematic Particle Size Distribution for Atmospheric Particles

Particle Concentration \( \frac{dN}{Nd_p} \) vs. Particle Diameter, \( d_p (\mu m) \)

- **Ultrafine (<100 nm)**
- **Fine**
- **Coarse**

Growth, Accumulation, Mechanical

PM\(_{2.5}\), PM\(_{10}\)

Figure Adapted from Finlayson-Pitts & Pitts (2000)
Define:
\[ n_N(D_p) \, dD_p = \text{the number of particles per cm}^3 \text{ of air with diameters between } D_p \text{ and } D_p + dD_p \]
\[ N = \int_0^\infty n_N(D_p) \, dD_p = \text{total number of particles per cm}^3 \]
\[ n_N(D_p) = \text{size distribution function} \]

How about volume and area?
\[ n_s(D_p) \, dD_p = \text{the surface area } \Sigma \text{ of particles per cm}^3 \text{ of air with diameters } D_p \div (D_p + dD_p) \]
\[ S = \int_0^\infty n_s(D_p) \, dD_p = \sum \int_0^\infty D_p^2 \cdot n_N(D_p) \, dD_p \]
- total surface area.
\[ V = \int_0^\infty n_v(D_p) \, dD_p = \frac{1}{3} \sum \int_0^\infty n_N(D_p) \cdot D_p^3 \, dD_p \]
- total volume area.

\begin{align*}
[ N ] &= \# / \text{cm}^3 \\
[ S ] &= \mu m^2 / \text{cm}^3 \\
[ V ] &= \mu m^3 / \text{cm}^3
\end{align*}
Particle Size Distribution Continued

more convenient:

\[ n^o_N (\log D_p) \cdot d(\log D_p) \equiv \text{# of particles in cm}^3 \text{ of air with } \log D_p \text{ in the range of } \log D_p \text{ to } (\log D_p + d \log D_p) \]

\[ n^o_S (\log D_p) = \frac{\pi D_p^2}{6} \cdot n^o_N (\log D_p) \]
\[ n^o_V (\log D_p) = \frac{\pi D_p^3}{6} \cdot n^o_N (\log D_p) \]

surface area and volume distribution functions.

similarly:

\[ S = \int_{-\infty}^{\infty} n^o_S (\log D_p) \, d(\log D_p) \]
\[ V = \int_{-\infty}^{\infty} n^o_V (\log D_p) \, d(\log D_p) \]

One can also use the natural logarithm, in which case one gets \( n^o_N (\ln D_p), n^o_S (\ln D_p) \ldots \)

Note: \( n_N(x), n^o_N(x), n^e_N(x) \) - are all different functions!!!
Relating Particle Size Distributions

Solve in class: Based on the distributions shown above, how many particles have diameter = 0.1 µm? (this is a trick question)

How many particles have diameters in the range 0.1 to 0.11 µm? Use both \( n_N(D_p) \) and \( n_N^e(D_p) \) to find your answers.

\[
dN = n_N(D_p) \ dD_p = n_N^e(\ln D_p) \ d\ln D_p
\]

\[
\Rightarrow n_N^e(\ln D_p) = D_p \cdot n_N(D_p)
\]

Note: these are several representations of one and the same distribution!
If a logarithm of something is normally distributed, that something is said to have a log-normal distribution.

Log-normal function was empirically found to match observed size distribution of atmospheric aerosols.

Sometimes a sum of two or three such functions is required (multimodal distribution) to describe ambient aerosols.
Observed size distributions are often multi-modal reflecting different mechanisms of aerosol formation.

FIGURE 9.7 Schematic of an atmospheric aerosol size distribution showing four modes. The original hypothesis of Whitby and co-workers is shown by the solid, trimodal curves, and the fourth, ultrafine particle mode, as well as the two peaks sometimes observed in the accumulation mode are shown by the dashed lines (adapted from Whitby and Sverdrup, 1980).

FIGURE 9.8 Typical size distribution of nitrate in southern California in 1987 fitted by the sum of three log-normal distributions with peaks at 0.2, 0.7, and 4.4 μm (adapted from John et al., 1990).

FIGURE 9.9 Particle number size distributions measured at Cheeka Peak, Washington, in 1991 (adapted from Quinn et al., 1993).
Growth of Particles

Broadly speaking, particles can grow via the following three mechanisms:

- **Homogeneous nucleation**: particle self-assembles from individual molecules under supersaturated conditions.
- **Heterogeneous nucleation**: molecules deposit on a preexisting condensation nucleus.
- **Agglomeration**: two-particles fuse into one bigger particle (rare).

- In homogeneous nucleation case, clusters grow very slowly until they reach a critical size, after which the growth becomes very (almost uncontrollably) fast.
- For binary homogeneous nucleation (growth of two-component particles such as H$_2$SO$_4$-H$_2$O), nucleation usually occurs easier than for either component in isolation.

\[
D_{\text{crit}} = \frac{4 \times \gamma \times V_{\text{monomer}}}{kT \times \ln(S)}
\]

\[
\gamma = \text{surface tension}
\]

\[
V_{\text{monomer}} = \text{volume of a single monomer}
\]

\[
S = \text{supersaturation}
\]

**TABLE 10.1 Critical Number and Radius for Water Droplets**

<table>
<thead>
<tr>
<th></th>
<th>$T = 273 \text{ K}^a$</th>
<th></th>
<th>$T = 298 \text{ K}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^*$ (Å)</td>
<td>$i^*$</td>
<td>$r^*$ (Å)</td>
</tr>
<tr>
<td>1</td>
<td>∞</td>
<td>∞</td>
<td>∞</td>
</tr>
<tr>
<td>2</td>
<td>17.3</td>
<td>726</td>
<td>15.1</td>
</tr>
<tr>
<td>3</td>
<td>10.9</td>
<td>182</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>8.7</td>
<td>87</td>
<td>7.6</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>58</td>
<td>6.5</td>
</tr>
</tbody>
</table>

\[a\sigma = 75.6 \text{ dyn cm}^{-1}; v_1 = 2.99 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1}.
\]

\[b\sigma = 72 \text{ dyn cm}^{-1}; v_1 = 2.99 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1}.
\]

From Seinfeld & Pandis
Gas-Particle Partitioning


• Consider reaction of a single reactive organic gas resulting in many products:
  \[ \text{ROG} + \text{Oxidants} \rightarrow \alpha_1 P_1 + \alpha_2 P_2 + \alpha_3 P_3 + \alpha_4 P_4 + \ldots \]

• In SOA literature it is common to express stoichiometric coefficients \( \alpha_i \) not in mole/mole but rather in \( \mu\text{g/m}^3 \) per \( \mu\text{g/m}^3 \). With this approach, we get the following (\( \Delta \text{ROG} \) is the amount reacted, \( MW \) is molecular weight, \( C_i \) is mass concentration of species \( i \)):

  \[ C_i^{\text{total}} = C_i^{\text{gas}} + C_i^{\text{particle}} = \alpha_i \frac{MW_i}{MW_{\text{ROG}}} \Delta \text{ROG} \]

• The next assumption that is made is to treat the particle phase as a quasi-ideal solution. Raoult’s connects partial pressure of compound \( i \) in equilibrium with the particle (\( p_i \)) with its molar fraction in the mixture (\( X_i \)), activity coefficient (\( \gamma_i \)) and equilibrium vapor pressure of the pure compound (\( p_i^0 \)):

  \[ p_i = \gamma_i X_i p_i^0 \]

• Activity coefficients are not known and usually set to 1. Furthermore, it is assumed that the activity coefficients do not depend on the chemical nature of the organic liquid in the particle. Both assumptions represent a gross oversimplification but there is no easy way to measure them experimentally or predict theoretically.
• As the next step, we use ideal gas law. The units for $R$ and $MW$ as well as the conversion factor are dictated by the choice of units for the concentrations:

$$p_i \text{ (atm)} = \frac{C_i^{\text{gas}} \left( \frac{\mu g}{m^3} \right)}{MW_i \left( \frac{\mu g}{mol} \right)} \times R \left( \frac{atm \times m^3}{mol \times K} \right) \times T(K) = \frac{10^3 \times C_i^{\text{gas}} \left( \frac{\mu g}{m^3} \right)}{MW_i \left( \frac{g}{mol} \right)} \times R \left( \frac{atm \times L}{mol \times K} \right) \times T(K)$$

• Combining it all together with the Raoult’s law, we equilibrium concentration of species $i$ in equilibrium with the aerosol. The quantity $C_i^* (=\text{volatility})$ is the saturation concentration that the pure compound $i$ would have in equilibrium with its pure liquid form.

$$C_i^{\text{gas}} = X_i \frac{\gamma_i p_i^0 MW_i}{10^3 RT} = X_i C_i^*$$

• The molar fraction accounts for molecules produced in the reaction as well as additional particle phase liquids that were there to begin with. We will treat the case when nothing is there to begin with ($C_{\text{initial}} = 0$):

$$X_i = \frac{C_{i, \text{particle}}}{MW_i} \left[ \sum_i C_{i, \text{particle}} + \sum_j C_{j, \text{initial}} \right] \approx \frac{C_{i, \text{particle}}}{MW_i} / \sum_i \frac{C_{i, \text{particle}}}{MW_i}$$

• Usually the inverse of the volatility is defined as an “equilibrium constant” for the uptake of the compound by the particle phase. This especially makes sense when molecular weights of all the aerosol compounds are roughly equal (and cancel out):

$$\text{compound}_i^{\text{gas}} + \text{particle} \rightleftharpoons \text{compound}_i^{\text{particle}} \quad K_i \left( \frac{m^3}{\mu g} \right) = \frac{1}{C_i^*} = \frac{X_i}{C_{i, \text{gas}}} \approx \frac{C_{i, \text{particle}}}{C_{i, \text{gas}} C_{\text{total}}^{\text{particle}}}$$
Gas-Particle Partitioning and Aerosol Yield

- In early experiments on aerosol formation, the aerosol yield \((Y, \text{ the fraction of produced particulate mass with respect to the reacted ROG mass})\) was the primary quantity that was measured:

\[
Y = \frac{C_{\text{particle}}}{\Delta \text{ROG}} = \sum \frac{C_{i}}{\Delta \text{ROG}} = \sum Y_i
\]

\[
Y_i = \frac{C_{i}^{\text{particle}}}{\Delta \text{ROG}}
\]

- Solving the above equations for the yields is not possible without making approximations. Going back to the initial definition of \(\alpha\):

\[
\alpha_i \frac{\text{MW}_i}{\text{MW}_{\text{ROG}}} \Delta \text{ROG} = C_{i}^{\text{particle}} + X_i C_i^* = C_{i}^{\text{particle}} + \left[ \frac{C_{i}^{\text{particle}}}{\text{MW}_i} \left/ \sum \frac{C_{i}^{\text{particle}}}{\text{MW}_i} \right. \right] \times C_i^*
\]

- And assuming that all molecular weights of the molecules residing in the particle are about the same \((\text{MW}_{\text{ROG}} \sim \text{MW}_i \text{ for all } i)\) this results in the following expression for the yield:

\[
Y_i = \frac{C_{i}^{\text{particle}}}{\Delta \text{ROG}} = \frac{\alpha_i}{1 + \frac{C_i^*}{C_{\text{particle}}}} = C_{\text{total}}^{\text{particle}} \times \left( \frac{\alpha_i K_i}{1 + C_{\text{particle}}^{\text{total}} K_i} \right)
\]

- The important result here is that the yield is not a constant but depends on the amount of aerosol we produce! In the limit when \(C^* \ll C_{\text{total}}\), the yield is constant \(Y_i = \alpha_i\) but it is difficult to carry out chamber reactions under these conditions.
Gas-Particle Partitioning – 2-Product Model


- Odum et al. showed that a lot of chamber reactions can be modeled quite well by assuming that only two products from in the oxidation
  \[ \text{ROG} + \text{Oxidants} \rightarrow \alpha_1 \text{P}_1 + \alpha_2 \text{P}_2 \]

- Therefore the entire yield curve can be represented by using just 4 parameters \((\alpha_1, \alpha_2, K_1, K_2)\):
  \[ Y = Y_1 + Y_2 = C_{\text{total}}^{\text{particle}} \times \left( \frac{\alpha_1 K_1}{1 + C_{\text{total}}^{\text{particle}} K_1} + \frac{\alpha_2 K_2}{1 + C_{\text{total}}^{\text{particle}} K_2} \right) \]

**FIGURE 1.** SOA yields for \(m\)-xylene as a function of \(M_0\). Values used to generate the two-product model line are 0.03, 0.167, 0.032, and 0.0019 for \(\alpha_1, \alpha_2, K_{\text{om},1},\) and \(K_{\text{om},2}\), respectively.

**FIGURE 2.** SOA yields for 1,2,4-trimethylbenzene as a function of \(M_0\). Values used to generate the two-product model line are 0.0324, 0.166, 0.053, and 0.002 for \(\alpha_1, \alpha_2, K_{\text{om},1},\) and \(K_{\text{om},2}\), respectively.
Gas-Particle Partitioning – VBS


- Donahue et al. took these ideas further by developing Volatility Basis Set (VBS), now widely used in the aerosol literature. Starting from the previously derived equation for the volatility of a given compound ($C_i^*$), they define a fraction of the compound that sits in the particle

$$C_i^* \approx \frac{C_i^{\text{particle}}}{C_i^{\text{total}}}$$

$$\xi_i = \frac{C_i^{\text{particle}}}{C_i^{\text{particle}} + C_i^{\text{gas}}} = \frac{C_i^{\text{particle}}}{C_i^{\text{particle}} + \frac{C_i^{\text{particle}}}{C_i^{\text{total}}} C_i^*} = \left(1 + \frac{C_i^*}{C_i^{\text{particle}}} \right)^{-1}$$

- Forgetting about the stoichiometric coefficients $\alpha_i$ altogether (which makes sense since reactions leading to aerosols are rather complex, so the coefficients are empirical) they divide all products into “volatility bins” on a logarithmic scale. In other words, their product “basis set” consists of a set of products with volatilities spanning the range:

$$\{C_i^*\} = \{...,10^{-3},10^{-2},10^{-1},1,10,100,10^3,...\} \frac{\mu g}{m^3}$$

- The formulation makes it possible to represent both the gas-phase and particle-phase products of reaction on the same graph
FIGURE 1. (a) Partitioning of a collection of semi-volatile compounds, with total loadings (in $\mu g \ m^{-3}$) shown with full bars and the condensed-phase portion with filled (green) bars. Compounds are distributed according to their mass-equivalent effective saturation concentration ($C^*$, also in $\mu g \ m^{-3}$), which is presented as a logarithmically distributed basis set. $C_{OA} = 10.6 \ \mu g \ m^{-3}$, shown with an arrow, and so that bin is evenly split between the two phases. (b) Semi-volatile emissions as they might appear near the output of a primary source, before substantial dilution into the background atmosphere (only enough dilution to cool the emissions to ambient temperature is assumed). The high loading leads to partitioning well into the high $C^*$ end of the distribution, as shown in brown. Note the scale of the $y$ axis (mg m$^{-3}$), which is a factor of 1000 greater than the scale on the other figures. (c) The effect of dilution by pure air on the emissions depicted above. The dilution factor of 1000 is indicated with a horizontal black arrow. Dilution by a factor of 1000 reduces the aerosol mass by a factor of 4000 because of repartitioning into the vapor phase. (d) The effect of dilution, as depicted in panel b above but now into background air represented in panel a above. The partitioning of the background organic material and the fresh emissions are kept separate, in green and brown, only for illustrative purposes. The vapor portions of the background and the fresh emissions are also separated, though each is shown with a white bar. Note that both the background and fresh emissions are partitioned more toward the condensed phase than in panels a or d, instead of 12.4 $\mu g \ m^{-3}$ there are 14.1 $\mu g \ m^{-3}$ and the condensed-phase mass due to the fresh emissions is almost doubled.
Recently, a number of studies questioned the equilibrium assumptions made by Pankow, Donahue, and others. Some of the recent papers challenging the equilibrium theories:

“Annoying” Complications


- $F_i$ = particle phase concentration
- $M$ = total particulate mass concentration
- $A_i$ = gas phase concentration
- We would expect $F_i/M = K_i \times A_i$ if the equilibrium holds – not true for SOA!

\[
F_i = \text{particle phase concentration} \\
M = \text{total particulate mass concentration} \\
A_i = \text{gas phase concentration} \\
\text{We would expect } F_i/M = K_i \times A_i \text{ if the equilibrium holds – not true for SOA!}
\]
Kelvin Effect: Aerosols as CCN

Vapor pressure over a droplet is higher than over a flat surface

**Kelvin equation** describes a *metastable* (not true) equilibrium

Clouds will form easier on pre-existing aerosols (Cloud Condensation Nuclei)

\[
N_T = N_1 + N_2
\]

\[
N_1 - \text{molecules still in gas-phase} \\
N_2 - \text{molecules in the droplet}
\]

\[
\Delta G = \left( N_1 \cdot \overline{G}_{\text{gas}} + N_2 \cdot \overline{G}_{\text{liq}} + 4\pi R_p^2 \gamma \right) - N_T \cdot \overline{G}_{\text{gas}}
\]

\[
\Delta G = \left( \overline{G}_{\text{liq}} - \overline{G}_{\text{gas}} \right) \cdot N_2 + 4\pi R_p^2 \gamma
\]

From thermo:

\[
\overline{G}_{\text{liq}} - \overline{G}_{\text{gas}} = -kT \ln \frac{P}{P_0}
\]

\[
S = \frac{P}{P_0}
\]

\[
S > 1
\]

\[
S < 1
\]

\[
R_{\text{crit}} = \frac{2\pi V_{\text{monomer}}}{kT \ln S}
\]

\[
P = P_0 \exp \left( \frac{2\pi V_{\text{monomer}}}{kT R_p} \right)
\]
What if water droplets contain solutes?

- $x_1$ = mole fraction of $H_2O$
- $x_2$ = mole fraction of solute

\[ P = x_1 \cdot P_0 \cdot \exp \left( \frac{2 \cdot \gamma \cdot V_{monomer}}{kTRp} \right) \]  

- Kelvin law
- Raoult's law

Suppose the amount of solute in the droplet is fixed: 

\[ n_2 = \text{const.} (\ll n_1) \]

\[ x_1 = \frac{n_1}{n_1 + n_2} \approx 1 - \frac{n_2}{n_1} \]

because \[ n_1 = \frac{4\pi \cdot R_p^3}{3 \cdot V_{monomer}} \]

we get:

\[ P = P_0 \left( 1 - \frac{b}{R_p^3} \right) \exp \left( \frac{2 \gamma \cdot V_{monomer}}{kTRp} \right) \]

(meta-stable) equilibrium pressure of $H_2O$ (solvent) over a droplet containing some involatile solute.

**FIGURE 14.38** (a) Schematic diagram of traditional Köhler curve, where $S = P_A/P_A^s - 1$ is the supersaturation and $r$ is the radius of the droplet. (b) Köhler curves for 30-nm dry particle of (NH$_4$)$_2$SO$_4$: (1) traditional curve; (2) for a 500-nm CaSO$_4$ particle (slightly soluble) and (NH$_4$)$_2$SO$_4$ as for curve 1; (3) as for curve 2 but in the presence of 1 ppb HNO$_3$, which is taken up by the particle (adapted from Kulmala et al., 1997).
Particle Phase Transitions

**Deliquescence:** solid $\Rightarrow$ liquid phase transition occurring upon absorbing moisture from air

**Efflorescence:** liquid $\Rightarrow$ solid transition occurring when particles dry out

- At high relative humidity most particles will grow because of the water uptake
- Using differences in deliquescence behavior, one can distinguish pure $\text{H}_2\text{SO}_4$ aerosols from $(\text{NH}_4)_2\text{SO}_4$ aerosols.

**FIGURE 9.40** Calculated changes in particle size as a function of relative humidity at $25^\circ\text{C}$ from particles with four different chemical compositions (adapted from Tang, 1980).

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

- **Direct Effects**
  - Scattering of incoming solar radiation back to space
  - Absorption of incoming solar radiation

- **Indirect Effects**
  - More particles ⇒ longer precipitation lifetimes of clouds
  - More particles ⇒ higher reflectivity (albedo) of clouds

**Fine particles account for more than 50% of light scattering and absorption in a typical urban atmosphere!**
Direct Effect of Particles

- **Light Absorption → heating**: Photon is taken up and converted into heat by particle. Soot particles efficiently absorb all visible light.

- **Light Scattering → cooling**: Photon is taken up but immediately re-emitted in a different direction. Blue light is scattered more efficiently than red.
  - Rayleigh scattering (particle size \(<<\lambda\)) ⇒ fairly isotropic; all angles
  - Mie scattering (particle size \(~\lambda\)) ⇒ complicated function of scattering angle (see next slide)
  - Geometric scattering (particle size \(>>\lambda\)) ⇒ mostly forward
  - Geometric reflection (cloud droplets) ⇒ reflected as if by a curved mirror
Mie scattering is quite significantly polarized and also depends strongly on the particle size.

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

\[ \Delta F = -\frac{1}{4} F_0 \cdot (1 - A) \left[ 2 T^2 (1 - R_s)^2 B \right] \alpha \]

- **cooling**
- **solar constant** = 1368 W/m²
- **fraction covered by clouds**
- **surface reflectivity**
- **fraction scattered up**
- **loading of sulfate aerosols**

**FIGURE 14.29** Calculated direct radiative forcing due to sulfate aerosol particles (adapted from Penner et al., 1998).
Indirect Effect of Particles

Particle → Cloud → Climate

From 2007 IPCC Fourth Assessment Report
http://www.ipcc.ch/
Indirect Effect on Climate

Positive values: surface heating  
Negative values: surface cooling

- IPCC – summary for policy makers
- IPCC – full reports
Aerosol Techniques

Particle Generation

- Atomization (nebulization)
- Electrospray assisted atomization
- Mechanical suspension
- Gas-to-particle condensation

Jet Nebulizer (Atomizer)

- Jet (Collision) nebulizer creates a polydisperse aerosol of high concentration
- Bernoulli effect sucks the liquid up the capillary
- As it enters the gas stream, the liquid is broken up into droplets, which then dry into aerosol

Glass nebulizer for making aerosols for ICP (Inductively coupled plasma)

TSI model 3076 atomizer
VOAG

- Vibrating orifice aerosol generator (VOAG)
- Piezoelectric crystal vibrates
- Liquid is forced through 10µm orifice
- Vibrations break liquid up into droplets of identical size
- These are especially useful for studies where monodisperse particles are needed:
  - Rate of particle growth and shrinkage in chemical reactions
  - Hygroscopic growth
Gas-to-Particle Condensation

- Vaporize a solid/liquid by heating: it will form submicron particles upon cooling (vaporization – condensation)
- Gas phase species may react to form non-volatile species that condense into liquid or solid phase
  - $\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$
  - $\text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{SO}_4(l)$
  - Ozone$_{(g)}$ + terpene$_{(g)} \rightarrow \text{SOA}_{(l \text{ or } s)}$

![Diagram showing gas-to-particle condensation process](image)
Electrospray Aerosol Generator

- Liquid (e.g., NaCl solution) pumped through a capillary
- The tip of the capillary has high voltage applied
- Taylor cone is formed at the tip of the capillary
- Liquid flies apart into (charged) aerosol droplets
- Droplets get neutralized, and then dry out into particles

\[ q_i \rightarrow \text{(wet highly charged droplets)} \rightarrow \text{Neutralization}^{\text{85Kr}} \rightarrow q_f \]

\( (~10^6 \text{ fold conc. vs. MS}) \)

HV (~3kV)
Collection of Particles

Particles are usually extracted from the atmosphere using filtration. There are different kinds of filters which use sedimentation, inertial impactation, diffusion, electrostatic precipitation and other mechanisms to grab particles out of the air. It is important to realize that almost any kind of filter will fail to catch particles outside a certain size range. Once the particles are collected on filters, they are brought to the lab to be analyzed for their mass content and average composition.

<table>
<thead>
<tr>
<th>Method</th>
<th>Approximate range of diameters(^a) ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filters</td>
<td>&gt;0.03</td>
</tr>
<tr>
<td>Sedimentation collectors</td>
<td></td>
</tr>
<tr>
<td>Gravitational</td>
<td>≥10</td>
</tr>
<tr>
<td>Centrifugal</td>
<td>0.1–10</td>
</tr>
<tr>
<td>Impactors</td>
<td></td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>≥0.5</td>
</tr>
<tr>
<td>Low pressure</td>
<td>≥0.05</td>
</tr>
<tr>
<td>Precipitators</td>
<td></td>
</tr>
<tr>
<td>Electrostatic</td>
<td>0.05–5</td>
</tr>
<tr>
<td>Thermal</td>
<td>0.005–5</td>
</tr>
</tbody>
</table>

\(^a\) The upper size ranges are usually related to inlet losses that prevent large particles from reaching the sampling surface.

FIGURE 11.56 Schematic of Hi-Vol particulate sampler (adapted from Lawrence Berkeley Laboratory, 1979).
Collection with Impactors


![Diagrams of inertia impactor](image)

**Figure 1.** Three types of inertial impactors: (a) plate (or jet) impactor, (b) virtual impactor, and (c) body impactor.

Impactors collect aerosol particles based on their inertia

Smaller particles have less inertia and are swept around the bend

Larger particles carry on to hit the impactor plate

Typical impaction substrates for the collection are:
- Aluminum foil
- Teflon filter
- Optical window
- TEM grid

Impactation probability \( \propto \frac{D^2 \times \text{Velocity} \times \text{Particle density}}{\text{Gas Viscosity} \times \text{Inlet Diameter}} \)
MOUDI Impactor

- Micro-orifice Uniform Deposit Impactor
- Several impaction stages with progressively smaller orifices
- Stages rotate to deposit particles uniformly on foil substrate
- Used for segregating particles by size before their analysis
Measuring Particle Sizes

• MOUDI – very crude
• Aerodynamic Particle Sizer (> 0.5 µm)
  – Particles are accelerated by expansion into a low pressure region
  – Particle acceleration depends on size (air resistance)
  – The terminal velocity can be converted into size
• Scanning Mobility Particle Sizer (< 1.0 µm)
  – Particles are charged with charger/neutralizer
  – Particle mobility in electrostatic field is measured
  – Concentration at each size can then be measured by a particle counter

Sheath flow

Aerosol

Small particle with a high mobility is deflected and removed
Intermediate particle goes through
Large particle is too heavy and is lost with the sheath flow
Shapes of Particles and Mobility Diameters

this is what the particles are actually like

\[ d_m \]

\[ \text{H}_2\text{O(g)} \]

\[ d_{ve} \]

A sphere with an equivalent volume

Hypothetical Experiment:
2 equal mass particles of different shape

Fixed HV

Cubic particle experiences more drag and appears to be larger in terms of mobility

therefore \( d_m > d_{ve} \) for irregular particles;

Need to correct for this effect with a **shape factor**

Differential Mobility Analyzer (DMA)

- Particle flow is injected around the edge \( (F_{\text{aerosol}} = 0.3 \text{ SLM}) \)
- Much larger sheath flow \( (F_{\text{sheath}} = 3 \text{ SLM}) \) is injected in the center of the column
- Particles move through the sheath flow toward the center rod with voltage \( V_{\text{applied}} \)
- Depending on the applied rod voltage, different mobility-equivalent particle sizes come out

\[
Z_p^* = \frac{F_{\text{sheath}}}{2\pi V_{\text{applied}} L} \ln \left( \frac{r_2}{r_1} \right) 
\]  
(electrical mobility)

\[
d_m = \frac{neC_c}{3\pi \eta_{\text{gas}} Z_p^*} 
\]  
(mobility diameter)

\[
R = \frac{\Delta Z_p^*}{Z_p^*} = \frac{F_{\text{aerosol}}}{F_{\text{sheath}}} 
\]  
(resolving power)

Nice historic perspective on this topic:
Condensation Particle Counter (CPC)

- Particles move through chamber with supersaturated butanol vapor
- Particles quickly uptake butanol to grow to several microns in diameter
- Particles are counted by light scattering
Measuring Particle Mobility Diameter ($d_m$)

Scanning Mobility Particle Sizer (SMPS)

DMA platform (Model 3080)

Differential Mobility Analyzers (DMA)

Ultrafine Condensation Particle Counter (CPC)
Tandem DMA Analyzers


Nanoparticle Generation and Drying

- Syringe pump
- MFC
- Dry air
- 85Kr neutralizer
- CCD camera
- Vent
- HV

Size Selection

- MFC
- Fixed HV
- DMA 1
- Dry air
- Vent
- DAQ board
- Computer
- Particle Detection

DMA 2

- RHP
- Humid air
- Nafion
- Varying HV

Particle Condition and Hygroscopic Growth

- MFC
- Humid air

Particle Detection

- CPC
- Vent
Hygroscopic Growth Experiments

- 3.1% RH: ~30% of mass exposed to vapor phase
- 73.2% RH: addition of 3 - 4 monolayers of H₂O
- 79.6% RH
- 86.6% RH: DRH

Particle concentration (#/cm³)

Diameter (nm)

- 10.8 nm
- 11.4 nm
- 11.7 nm
- 16.8 nm
- 18.3 nm
Aerosol Particle Mass Spectrometry

PALMS designed by Dan Murphy at Aeronomy Lab
http://www.al.noaa.gov/PALMS/.

Particle mass-spectrometers use lasers or heat to vaporize individual particles and analyze their compositions with either quadrupole or TOF MS. They provide valuable information about size distribution and composition of atmospheric aerosols. Jose-Luis Jimenez (CU Boulder) created an excellent compilation of existing aerosol mass spectrometers at http://cires.colorado.edu/~jjose/ams.html

Figure 11.71 Typical laser ionization positive ion mass spectra of single particles in rural Colorado (adapted from Murphy and Thomson, 1997a,b).
Field Workhorses: AMS and HR-ToF-AMS


**HR-ToF-AMS instrument with TOF analyzer:** DeCarlo et al. (2006), *Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer*, Analyt. Chem., 78(24), 8281-8289.

**APES software (ToF-AMS High Resolution Elemental Analysis software):**
Primary Component Analysis with AMS


\[
\text{Signal} \left( \frac{m}{z} \right) = \sum_i \alpha_i \times \text{[Mass Spectrum of Component } i] 
\]

Components:
- **HOA** = "hydrocarbon-like" organic aerosol (related to POA), identified primarily by large signal at \( m/z = 57 \) (\( \text{C}_4\text{H}_9^+ \))
- **OOA** = oxygenated organic aerosol (related to SOA), identified primarily by large signal at \( m/z = 44 \) (\( \text{CO}_2^+ \))
- Later split into **LV-OOA** (low volatility OOA), **SV-OOA** (semivolatile OOA), **BBOA** (biomass burning organic aerosol), and other factors.

Aerosol Analysis by AMS

Figure 1. Location of the AMS datasets analyzed here (data shown in Table S1 in the auxiliary material). Colors for the study labels indicate the type of sampling location: urban areas (blue), <100 miles downwind of major cites (black), and rural/remote areas >100 miles downwind (pink). Pie charts show the average mass concentration and chemical composition: organics (green), sulfate (red), nitrate (blue), ammonium (orange), and chloride (purple), of NR-PM$_1$.


AMS is insensitive to particles above 50 nm in size. Jim Smith's and Fred Eisele's research group at NCAR constructed a very nice desorption chemical ionization mass spectrometer, which is capable of chemical analysis of particles as small as few nanometers in diameter!
Ambient mass spectrometry methods analyze aerosol samples without any special preparation steps. EXAMPLES:

**Desorption electrospray ionization mass spectrometry (DESI)** – makes it possible to analyze aerosol filter samples without a need for pre-extraction of the collected filter material. Key reference:

**Extractive electrospray ionization spectrometry (EESI)** – a related method for ionizing aerosols directly by a crossed electrospray:
High Resolution Mass Spectrometry Methods

Advantages of High Resolution in Mass

Negative ion
m/z = 299.259

$R = 100$
$\Delta m/z = 0.3$

Matches 37 different formulas
$C_xH_yO_z^-$ (with valence rules observed)

Negative ion
m/z = 299.259

$R = 100,000$
$\Delta m/z = 0.003$

Only ONE possible match = $C_{18}H_{35}O_3^-$

$R = 100,000$ is sufficient to unambiguously assign formulas to m/z<500 molecules containing C, H, O atoms
### Resolving Power Limitations

<table>
<thead>
<tr>
<th>Add</th>
<th>Remove</th>
<th>Δm/z</th>
<th>R required (at m/z 500)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>O</td>
<td>0.03639</td>
<td>14,000</td>
</tr>
<tr>
<td>C₄</td>
<td>O₃</td>
<td>0.01526</td>
<td>33,000</td>
</tr>
<tr>
<td>S</td>
<td>O₂</td>
<td>-0.01776</td>
<td>28,000</td>
</tr>
<tr>
<td>N₂</td>
<td>CO</td>
<td>0.01123</td>
<td>45,000</td>
</tr>
<tr>
<td>SH₄</td>
<td>C₃</td>
<td>0.00337</td>
<td>150,000</td>
</tr>
<tr>
<td>N</td>
<td>¹³CH</td>
<td>-0.00815</td>
<td>61,000</td>
</tr>
<tr>
<td>NaH</td>
<td>C₂</td>
<td>-0.00237</td>
<td>210,000</td>
</tr>
</tbody>
</table>


- R = 100,000 is adequate for molecules containing C, H, O atoms; also works for most N-containing species
- Positive ion mode (Na adducts) may require higher R
- Adding heteroatoms (S, P, etc.) may require higher R
Novel Mass Spectrometry Tools for Droplets