INTRODUCTION

Atmospheric nanoparticles are of growing interest to many investigators for two main reasons. First, nanoparticles are important precursors for the formation of larger particles, which are known to strongly influence global climate, atmospheric chemistry, visibility, and the regional and global transport of pollutants and biological nutrients. Second, atmospheric nanoparticles may play critical roles in the deleterious human health effects associated with air pollution. In addition to these two well-recognized roles, nanoparticles may also significantly influence the chemistry of the atmosphere. Because their composition and reactivity can be quite different from larger particles, the presence of nanoparticles may open novel chemical transformation pathways in the atmosphere. There is possibly also an important role for nanostructures within larger particles, which often contain nanoscale features such as mineral grain agglomerates, soot spherules, or layer coatings of sulfates and nitrates. These complex morphological features likely influence a number of properties. For example, nanostructures probably affect water uptake via capillary condensation and nanoscale aqueous surface films may provide a medium for heterogeneous chemistry. In addition, nanoscale active sites on surfaces may influence particle phase transitions through heterogeneous nucleation. However, with a few notable exceptions, the potential roles and implications in atmospheric chemistry for nanoparticles and nanostructures have not been quantitatively examined.

The goal of this chapter is to provide a survey of what is currently known about nanoparticles in the atmosphere, especially in terms of their formation and growth, number concentrations and chemical composition, and chemical, physical, and mechanical properties. Although combustion sources are important sources of nanoparticles, we do not discuss the special conditions (e.g., in terms of particle dynamics) encountered in combustion plumes. This chapter complements two recent journal issues, one focused on nano- and ultrafine particles in the atmosphere (Philosophical Transactions of the Royal Society of London A, vol. 358, no. 1775, 2000) and the other containing papers related to nanoparticles in technology and in the atmosphere (Journal of Aerosol Science, vol. 29, no. 5-6, 1998). Given the mineralogy context of the volume in which this chapter appears, we also provide a general introduction to the occurrence and physicochemical properties of atmospheric particles.

At the outset of this chapter, one point of distinction is necessary regarding the term “nano” in the context of atmospheric particles. In contemporary scientific usage in many fields such as materials science, chemistry, and physics, nanoscale is understood to mean
at a lengthscale where properties diverge from the bulk. In this chapter, we also adopt this
definition on occasion. However, there is a second usage employed by aerosol scientists,
who in recent years have pushed the detection limits of their instrumentation to particles
as small as 3 nm. In this framework, a nanoparticle is defined solely by size. A common
contemporary understanding is that a nanoparticle has a diameter under 50 nm, and we
will generally use this definition in this chapter. The exact usage in each case should be
clear from its context.

As this review will show, much must still be elucidated in the field of atmospheric
nanoparticles and many important unknowns remain. However, a recent surge of research
activities in this area should greatly contribute to our knowledge in the coming years.

BACKGROUND CONCEPTS

This section provides a general overview on the physicochemical properties of
atmospheric aerosols. An aerosol is defined as a suspension of solid or liquid particles in
a gas, though sometimes the term is used in the vernacular to refer solely to the
suspended particles or particulate matter. Excellent references on atmospheric aerosols
include Finlayson-Pitts and Pitts (2000), Seinfeld and Pandis (1998), Kreidenweis et al.
(1999), and Friedlander (2000).

Size distributions of atmospheric particles

Atmospheric particles have spherical equivalent diameters ($D_p$) ranging from 1 nm
to 100 $\mu m$. Plots of particle number concentration (as well as surface area and volume) as
a function of particle size usually show that an atmospheric aerosol is composed of three
or more modes, as illustrated in Figure 1. By convention, particles are classified into
three approximate categories according to their size: Aitken (or transient) nuclei mode
($D_p < 0.1\ \mu m$), accumulation mode ($0.1 < D_p < 2.5\ \mu m$), and coarse mode ($D_p > 2.5\ \mu m$)
(Seinfeld and Pandis 1998). Particles smaller than 2.5 $\mu m$ are generally classified as fine.
The terms PM$_{2.5}$ and PM$_{10}$ refer to particulate matter with aerodynamic equivalent
diameters under 2.5 and 10 $\mu m$, respectively. These terms are often used to describe the
total mass of particles with diameters smaller than the cutoff size.

In addition to the three modes described above, recent measurements have shown
that there is often a distinct particle mode under 10-nm diameter (Fig. 2). There is no
current agreement for the name of particles in this mode, which are interchangeably
called ultrafine particles, nanoparticles, or nucleation mode particles. There are also
alternative definitions for these terms, which can be a source of confusion. For example,
the term ultrafine particles is sometimes employed to refer solely to particles with $D_p = 3 -10$ nm (e.g., in nucleation studies) or to all particles with $D_p < 100$ nm (e.g., in health
and emission studies). Similarly, the term nanoparticles is sometimes employed as a
description for all particles of $D_p < 50$ nm (regardless of mode), sometimes for particles
of 10-nm diameter or less, and occasionally for any particle with $D_p < 1 \ \mu m$. In this
review we use the common current definitions of ultrafine particles as those with
$D_p < 100$ nm and nanoparticles as those with $D_p < 50$ nm.

The different size modes reflect differences in particle sources, transformations, and
sinks (Finlayson-Pitts and Pitts 2000). For example, coarse particles are generated by
mechanical processes such as wind erosion of soil, wave action in the oceans, and
abrasion of plant material. In contrast, many of the fine particles in the atmosphere are
produced from either primary emissions from combustion sources or via atmospheric
gas-to-particle conversions (i.e., new particle formation). The relative and absolute sizes
of particle modes, as well as the number of modes, can vary greatly in different locations
and at different times. In addition, the chemical composition of particles within one size
Figure 1. Number ($\Delta N/\Delta \log D$), surface area ($\Delta S/\Delta \log D$), and volume ($\Delta V/\Delta \log D$) distributions for a typical urban aerosol. The solid lines are the size distributions, while the dashed lines show the tails between intersecting modes. The total number concentration, surface area, and volume equal the areas under the curves of each mode. From Finlayson-Pitts and Pitts (2000). Used by permission of Academic Press.

Figure 2. Trimodal structure of the submicron particle number size distribution observed at a boreal forest in Hyytiälä, Finland on June 17, 1996, 08:09-08:19. The total particle number concentration of the submicron aerosol is 1011 particles cm$^{-3}$. From Mäkelä et al. (1997). Used by permission of the American Geophysical Union.
mode often differs considerably from those in other size modes. Even within one size mode, there is often a wide variety of particle compositions, i.e., the aerosol is externally mixed (Noble and Prather 1996). The opposite situation, where all particles have the same composition, is called an internally mixed aerosol.

As shown in Figure 1, within an atmospheric aerosol the smallest particles usually dominate the total number of particles, while the accumulation and coarse modes often determine the total surface area and volume (i.e., mass), respectively. For example, Figure 3 shows results from a study in Atlanta where nanoparticles (\(D_p = 3\text{-}10 \ \text{nm}\)) and nano- and ultrafine particles (\(D_p = 10\text{-}100 \ \text{nm}\)) contributed approximately 30 and 60%, respectively, to the total particle number concentration (\(D_p \leq 2 \ \text{μm}\)). However, in terms of particle mass, the accumulation mode particles were dominant, and nanoparticles with \(D_p < 10 \ \text{nm}\) contributed insignificantly.

**Sources and sinks of atmospheric particles**

Atmospheric particles are classified as primary when they are emitted directly into the atmosphere and as secondary when they form in the atmosphere from reactions of atmospheric gases. The dominant particle sources by mass are mineral dust from wind-blown soils and sea-salt particles from wave breaking (Table 1). These primary sources produce high numbers of coarse particles that dominate the mass distribution of the aerosol, but measurements during the last decade show that these sources can also produce appreciable numbers of nanoparticles. The dominant sources of fine particles include anthropogenic primary emissions from combustion processes and secondary aerosol formation from the oxidation of species such as gaseous SO\(_2\) or organic compounds (Table 1). The estimates in Table 1 show that anthropogenic emissions of particles and their gaseous precursors have more than doubled the flux of fine particles into the atmosphere. This fact suggests that the burden of nanoparticles in the atmosphere has also greatly increased because of anthropogenic emissions.

There are three major sinks that act to remove particles from the atmosphere: diffusion (Brownian motion), wet deposition, and gravitational settling. The relative importance of each mechanism depends primarily upon particle size (Seinfeld and Pandis 1998; Kreidenweis et al. 1999; Friedlander 2000). As shown in Figure 4, diffusion is the

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**Figure 3.** Percent of total (\(D_p \leq 2 \ \text{μm}\)) particle number and volume concentrations in three size ranges in Atlanta, Georgia. From Woo et al. (2001). Used by permission of Taylor & Francis, Inc.
Atmospheric Nanoparticles


<table>
<thead>
<tr>
<th>Source</th>
<th>Estimated flux (Tg yr⁻¹)</th>
<th>Particle size category⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
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<tr>
<td>NATURAL</td>
<td></td>
<td></td>
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<tr>
<td>Primary</td>
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<tr>
<td>Soil dust (mineral aerosol)</td>
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<td>3000</td>
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<tr>
<td>Sea salt</td>
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<td>Biological debris</td>
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<td>80</td>
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<tr>
<td>Secondary</td>
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<tr>
<td>Sulfates from biogenic gases</td>
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<td>150</td>
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<td>Sulfates from volcanic SO₂</td>
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<tr>
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<td>650</td>
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<tr>
<td>TOTAL</td>
<td>2500</td>
<td>24000</td>
</tr>
</tbody>
</table>

¹ Coarse and fine size categories refer to mean Dₚ above and below 1 pm, respectively.
² By mass, coarse particles dominate. By number the fine mode may dominate.

Note that sulfates and nitrates are assumed to occur as ammonium salts.
Flux units: 10¹² g yr⁻¹ (dry mass).

dominant removal mechanism for nanoparticles (Dₚ < 50 nm) because of their small sizes. Nanoparticles can be removed by diffusing to the Earth’s surface (dry deposition), diffusing and colliding with larger particles (intermodal coagulation), or by growing out of the nanoparticle size range (through condensation of gases). Nanoparticle residence times thus depend both upon diameter (which affects the diffusion rate) and upon the atmospheric aerosol surface area. Under typical conditions, nanoparticles are believed to have residence times ranging from minutes to a few days. Coarse particles also have atmospheric residence times that vary from minutes to days, but due to their relatively large sizes, gravitational settling is their dominant removal mechanism. Intermediate between these sizes are the accumulation mode particles. These particles are removed efficiently neither by diffusion nor by settling, and thus they tend to have the longest atmospheric lifetimes (typically days to weeks). The dominant sink for accumulation
mode particles is generally removal by precipitation, either as rain-out or wash-out (Finlayson-Pitts and Pitts 2000).

Visibility reduction

One of the most widely recognized aspects of atmospheric pollution is reduced visibility, which is due primarily to light extinction by particles. A common measure of visibility is visual range ($V_R$), which is defined as the maximum distance at which a black object can be seen against the horizon, as follows:

$$V_R = \frac{\ln(C/C_0)}{b_{ext}}$$

where $C/C_0$ is the contrast that can be discerned by an observer (typically 0.02-0.05) and $b_{ext}$ is the extinction coefficient (units of length$^{-1}$) (Pilinis 1989; Finlayson-Pitts and Pitts 2000). Thus regions with greater extinction coefficients have lower visual ranges and visibility. Four components contribute to $b_{ext}$: scattering of light by particles ($b_{sp}$), absorption of light by particles ($b_{ap}$), scattering by gases ($b_{sg}$), and absorption by gases ($b_{ag}$).

In areas with reduced visibility, scattering of light by particles is usually the dominant extinction term. Typical values of $b_{sp}$ are $10^{-5}$ to $10^{-3}$ m$^{-1}$ (Mathai 1990; Sloane et al. 1991; Eldering et al. 1994; Finlayson-Pitts and Pitts 2000; Pryor and Barthelmie 2000). Light scattering is conveniently classified into three regimes based on the size parameter, $\alpha$, expressed as $\alpha = 2D_p/\lambda$ where $\lambda$ is the wavelength of light. Rayleigh scattering occurs for small $\alpha$, Mie scattering for $\alpha \sim 1$, and geometric scattering occurs for large $\alpha$ (Friedlander 2000; Finlayson-Pitts and Pitts 2000). For visible wavelengths, which are relevant for visibility reductions as well as the direct climate effects discussed.
Atmospheric Nanoparticles

Light scattering per unit volume of aerosol material ($G$) as a function of particle diameter ($d_p$), integrated over the wavelengths 360-680 nm for a refractive index of 1.5. The curve is independent of the particle size distribution. From Friedlander (2000) © by Oxford University Press, Inc. Used by permission.

below, Mie scattering is typically the most important mechanism for scattering by atmospheric aerosols. In this regime accumulation mode particles are the most efficient at scattering visible light (Friedlander 2000), as shown in Figure 5. Because of this, and because accumulation mode particles typically dominate fine particle mass, values of $b_{\text{ext}}$ for atmospheric aerosols often correlate well with the mass of the fine particle fraction (Finlayson-Pitts and Pitts 2000). Fine particulate components such as sulfate, nitrate, and organic carbon often contribute significantly to $b_{\text{sp}}$ (Pilinis 1989; Eldering et al. 1994; Pryor and Barthelmie 2000). In contrast, ultrafine and nanoparticles make small contributions to the scattering of visible light (cf. Fig. 5) (Friedlander 2000).

Absorption of light by particles ($b_{\text{ap}}$) is sometimes an important contribution to the value of $b_{\text{ext}}$. In urban areas, $b_{\text{ap}}$ can account for approximately 13-42% of the total extinction coefficient (Finlayson-Pitts and Pitts 2000). The chemical components that contribute most substantially to $b_{\text{ap}}$ are soot, organic carbon, and soil dust (Finlayson-Pitts and Pitts 2000). It is unclear whether nano- and ultrafine particles contribute significantly to light absorption by particles. On the one hand, these particle sizes account for an appreciable number fraction of the soot emitted from combustion sources such as diesel engines. On the other hand, unless the particles are highly absorbing, light absorption scales with particle mass, which for atmospheric aerosol contains an insignificant contribution from nanoparticles.

Radiative forcing and climate change

Over the course of the past century, human activities have significantly changed the composition of the atmosphere, which in turn has apparently altered the Earth’s climate (IPCC 2001). For example, anthropogenic emissions of long-lived greenhouse gases, such as CO$_2$, have made the atmosphere less transparent to longwave radiation. Consequently, the atmosphere more efficiently traps longwave radiation emitted by the Earth, which is expected to lead to increased surface temperatures (Crowley 2000; IPCC 2001). However, it is unclear to what extent this increase in temperature might be damped, or possibly enhanced, by climate feedbacks involving clouds, desertification, or changes in ocean circulation. Overall, anthropogenic increases in directly emitted greenhouse gases since pre-industrial times have caused a global-mean radiative forcing
Figure 6. Estimates of globally averaged radiative forcings at the tropopause as a result of changes in greenhouse gases, aerosol particles, and solar activity from pre-industrial times to the present. From Buseck et al. (2000). Used by permission of the editor of *International Geology Review*.

of ca. +2.5 W m\(^{-2}\) (Fig. 6). According to most current models, this greenhouse gas forcing is primarily responsible for the globally averaged 0.6°C increase in temperature that has occurred over the past century (Barnett et al. 1999; Crowley 2000; IPCC 2001).

Based on our current understanding, this greenhouse warming would have been larger if not for the effects of atmospheric particles (IPCC 2001). Anthropogenic increases in atmospheric particle loadings have provided a net cooling effect as a result of both direct (i.e., backscatter of incoming solar radiation to space) and indirect effects (i.e., by their effects on clouds) (Boer et al. 2000a,b; Schwartz and Buseck 2000; IPCC 2001). One of the most investigated direct effects is the scattering of incoming solar radiation by sulfate particles. This scattering is believed to cause a negative radiative forcing of approximately -0.5 W m\(^{-2}\), though the exact value is uncertain (Fig. 6) (Penner et al. 1998; Harvey 2000; Kiehl et al. 2000). Anthropogenic sulfate particles are derived primarily from fossil fuel combustion, which releases SO\(_2\) that is subsequently oxidized in the atmosphere to H\(_2\)SO\(_4\) (Finlayson-Pitts and Pitts 2000). The combustion of fossil fuels, especially coal, has approximately doubled the mass of sulfate particles in the atmosphere (Table 1).

Other types of particles also contribute significantly to changes in radiative forcing (Fig. 6). Carbonaceous aerosols from biomass burning are thought to cause a net negative forcing due to scattering from organic components. In contrast, soot from fossil fuel combustion is believed to have a net positive forcing because of light absorption (Penner et al. 1998). Recent work by Jacobson (2001) estimates the forcing from soot particles to be +0.55 W m\(^{-2}\). This value is much larger than previously thought (e.g., Fig. 6) and arises from the internal mixing of soot with other particle types such as sulfate. It has been suggested that this atmospheric warming by soot particles could reduce cloud cover (Ackerman et al. 2000). However, modeling by Lohmann and Feichter (2001) indicates
that on a global scale this ‘semi-direct’ effect is small compared to the indirect effects of aerosols.

Another important particle type is mineral dust. The atmospheric loading of mineral dust is increasing due to land-use changes accompanying anthropogenic activities. These particles may have significant climatic effects, though the sign and the magnitude of this forcing are not known (Fig. 6) (Buseck and Pósfai 1999; Buseck et al. 2000). This uncertainty arises because mineral dusts both scatter incoming solar radiation (a negative forcing) and absorb solar and longwave radiation (a positive forcing) (Miller and Tegen 1998; Buseck and Pósfai 1999).

In addition to their direct effects, particles also affect climate indirectly by modifying the optical properties, frequencies, and lifetimes of clouds (IPCC 2001). This indirect effect is estimated to have a very large negative forcing, though the magnitude of the effect is highly uncertain (Fig. 6). The indirect effect is a result of anthropogenic increases in the number of cloud condensation nuclei (CCN), which are hygroscopic particles that serve as centers for water condensation and thus the formation of cloud droplets (Finlayson-Pitts and Pitts 2000). For a fixed cloud liquid water content, an increase in the number of CCN yields smaller cloud drops. This causes an increase in the albedo (reflectivity) of the cloud and thereby enhances its efficiency for scattering incoming solar radiation (Twomey 1977; Charlson et al. 1992). In addition, clouds with smaller drops precipitate less frequently and thus have longer lifetimes, which amplifies the climatic impact (Albrecht 1989; Borys et al. 2000; Rosenfeld 2000). Because nanoparticles are important precursors for CCN, there is much current research activity aimed at understanding how nanoparticles form and grow into CCN.

Health effects

Epidemiologic analyses link ambient atmospheric particles with acute and chronic adverse health effects, including respiratory disease, reduced lung function, cardiovascular effects, and mortality (Pope et al. 1995a; Pope 2000; Schlesinger 2000). The associations found in these analyses are particularly strong for susceptible populations such as the elderly, children with asthma, and others with pre-existing respiratory problems (Utell and Frampton 2000). There is no consensus on what types or sizes of atmospheric particles are most responsible for these effects. While a number of epidemiological studies find that fine particle mass (i.e., PM$_{2.5}$) is strongly associated with adverse health effects (Dockery et al. 1993; Pope et al. 1995b; Brunekreef 2000; Pope 2000), other studies indicate coarse particles (e.g., PM$_{10}$) are more strongly associated (Pope et al. 1995a; Pekkanen et al. 1997; Brunekreef 2000; Loomis 2000). In addition, a few epidemiological studies have shown that impairment in pulmonary function is best correlated to the number of ultrafine (D$_p$ < 100 nm) particles (Peters et al. 1997; Hauser et al. 2001).

There are numerous hypotheses–but few definitive results–as to what physicochemical characteristics of atmospheric particles are responsible for adverse health effects (Samet 2000; Schlesinger 2000). Hypotheses include general properties such as mass, surface area, or size, as well as more specific chemical properties such as acidity or elevated concentrations of transition metals (Dreher et al. 1997; Samet 2000). For example, it has been suggested that particulate iron is toxic due to its ability to generate the strongly oxidizing hydroxyl radical through the Fenton reaction (Ghio et al. 1996; Smith and Aust 1997; Donaldson et al. 1998; van Maanen et al. 1999):

$$\text{Fe(II)} + \text{HOOH} \longrightarrow \text{Fe(III)} + \cdot \text{OH} + \cdot \text{OH}$$

(2)
In biological systems the hydroxyl radical can lead to damage such as lipid peroxidation and DNA breakage (van Maanen et al. 1999). In support of this hypothesis, iron is often the most abundant transition metal in atmospheric particles, and there are numerous reports that particulate Fe(III) can be reduced to Fe(II) as a result of atmospheric reactions (Faust 1994).

Animal studies provide additional evidence that ultrafine or nanoparticles might be at least partially responsible for the health effects associated with atmospheric particles. For example, for the same mass of particles instilled into rat lungs, TiO₂ nanoparticles (Dₚ = 20 nm) yield a greater inflammatory response compared to that from fine TiO₂ particles (250 nm) (Oberdörster 2001). However, when the doses are normalized to particle surface area, the inflammatory response is the same, suggesting that surface reactions might have been responsible for the observed effects. These results also indicate that there is no special reactivity for the TiO₂ nanoparticles compared to the larger particles. In contrast, Donaldson et al. (2000) suggest that, in terms of adverse health effects, nanoparticle surfaces might be more active than the surfaces of larger particles. A number of other studies show that inhaled or instilled nanoparticles give a greater inflammatory response and cause more oxidative stress than fine particles, though the confounding role of surface area is not evaluated (Donaldson et al. 1998, 2000, 2001). Not all studies, however, show that nanoparticles cause measurable responses. For example, in one study rats and mice exposed to nanoparticles of black carbon (Dₚ ~ 40 nm; 10⁵-10⁶ cm⁻³) show no signs of lung injury, while those animals exposed to greater masses of fine particles (Dₚ ~ 400 nm; 10⁴-10⁵ cm⁻³) show some adverse effects (Arts et al. 2000).

In addition to the greater surface area discussed above, a number of other hypotheses have been presented as potential explanations for the possibly greater toxicity associated with nano- and ultrafine particles. First, these particles could have increased toxicity because of their high number concentrations in the atmosphere and significant deposition in the lungs. Hughes et al. (1998) have estimated that ca. 10¹¹ ultrafine particles are deposited daily in the lungs of a typical person in the Los Angeles area during winter. Ultrafines are efficiently deposited in human lungs (e.g., 40-50% deposition fraction for inhaled 40-nm particles (Jaques and Kim 2000)), and a large fraction of this deposition occurs in the alveoli (i.e., the deepest reaches of the lungs) (Oberdörster 2001). By contrast, accumulation mode particles typically have lower number concentrations, a lower overall lung deposition rate, and a smaller fraction deposited in the alveoli (Oberdörster 2001). Second, there is some evidence that nanoparticles inhibit or overwhelm phagocytosis, perhaps because of their great numbers, and thus decrease the ability of alveolar macrophages to clear out foreign particles (Donaldson et al. 2001). This causes an increased contact time between particles and lung epithelial cells (Donaldson et al. 1998). In conjunction with the small size of nanoparticles, this might allow these particles to cross the alveolar epithelial barrier and enter interstitial spaces (Donaldson et al. 2001). Subsequent transport to other organs could then be possible (Oberdörster 2001). Finally, at least one study indicates that nanoparticles act synergistically or additively with ozone to cause adverse health effects, especially in older rats and mice pre-treated with endotoxin to simulate the compromised lungs of susceptible groups (Elder et al. 2000). This result suggests that health effects from particles are strongly tied with co-exposure to other pollutants (Samet 2000; Oberdörster 2001).

The evidence of adverse health effects from respirable particles, and perhaps nanoparticles in particular, raises the question of what regulatory strategy would be most effective to protect human health. In response to the epidemiological evidence linking
fine particles with adverse health effects, the EPA in 1997 proposed a new mass-based PM$_{2.5}$ standard for ambient air quality (Seinfeld and Pandis 1998). However, in light of the limited evidence that nanoparticles in particular, and perhaps particle number in general, are more important components of particle toxicity, there is concern that the PM$_{2.5}$ standard is not the most effective or economic regulatory approach to protect human health. This is because most of the PM$_{2.5}$ mass results from the larger accumulation mode particles, but most of the aerosol particle number generally results from the nano- and ultrafine particles. The result is that particle number and mass are expected to generally be unrelated (Fig. 7) (Keywood et al. 1999; Woo et al. 2001). Thus control of fine particle mass is likely to have little effect upon nanoparticle number concentrations in the atmosphere. Similarly, a mass-based standard is unlikely to be effective or economic if specific chemical species within atmospheric particles are responsible for the observed adverse health effects.

![Figure 7. Relationship between volume and number concentrations for particles with D$_p = 3$ nm to 2 $\mu$m in Atlanta, Georgia, during August 1998 through August 1999. From Woo et al. (2001). Used by permission of Taylor & Francis, Inc.](image)

**Chemical reactions of atmospheric particles**

Reactions involving atmospheric particles have significant effects upon the composition of the atmosphere (Andreae and Crutzen 1997). Perhaps the most well known example is the particle-catalyzed springtime destruction of stratospheric ozone over the Antarctic. Particle reactions in the troposphere are also significant and affect concentrations of important gaseous pollutants such as ozone, nitric acid, and sulfur dioxide. These reactions often alter the composition of the particles as well, which can alter the ability of particles to act as cloud condensation nuclei, change their efficiency for scattering and absorbing light, and perhaps influence their health effects.

Three examples of chemistry occurring on or in atmospheric particles are provided below. These examples demonstrate how particulate-based chemical reactions can alter the composition both of particles and of the gas phase. However, the examples are by no means comprehensive of all chemical processes that occur in the troposphere. The particles involved in these examples are generally accumulation or coarse mode, though
in some cases similar reactions on nanoparticles of the same material might also occur. The chemistry of nanoparticles is discussed separately later in this chapter.

**Mineral dusts.** The northern African and Gobi deserts are large sources of mineral dusts (Pye 1987; Charlson and Heintzenberg 1994; Prospero 1999a), which are regularly carried by atmospheric circulation patterns to the eastern USA and Brazil as well as the Pacific Ocean (Swap et al. 1992; Leinen et al. 1994; Prospero 1999a). The dusts are monitored both by analysis of collected aerosol particles (Prospero 1999b) and by satellite observations (Husar et al. 1997; Herman et al. 1997; Chiapello et al. 1999) (Fig. 8). In addition to these global sources, there are also regional emissions of mineral dusts. In total, nearly one-third of the Earth’s land surface is arid and hence a possible dust source (Tegen and Fung 1994), and land use changes associated with human activities are expected to increase the global burden of mineral dusts (Tegen and Fung 1995; Tegen et al. 1996). In addition to the chemistry described below, mineral dusts are also important as an essential component of open ocean fertility, primarily as a source of iron (Duce et al. 1980; Martin and Gordon 1998; Boyd et al. 2000).

**Figure 8.** Radiatively equivalent aerosol optical thickness (EAOT \(\times 1000\)) over the oceans derived from NOAA AVHRR satellites for summer. Darker shades indicate greater values of EAOT. Adapted from Husar et al. (1997). Used by permission of the American Geophysical Union.

The mode of the number size distributions of mineral dusts outside of source regions (i.e., after long-range transport) is approximately 100 nm, though the mass mode typically lies between diameters of 2 to 5 μm (D’Almedia and Schütz 1983). The small particles usually arise from submicron clay particles that are initially attached to larger mineral grains but break free during the abrasive events of a dust storm. Analysis of mineral dust indicates the particles are largely composed of silicates (clay minerals, feldspars, and quartz) and occasionally carbonates and sulfates (Schütz and Sebert 1987; Schütz 1989, 1997; Merrill et al. 1994; Claquin et al. 1999). Dominant clays are illite and kaolinite with contributions by smectite (montmorillonite) and chlorite. Iron and aluminum oxides and hydroxides also contribute, especially as surface coatings, which then dominate the surface chemistry of agglomerated mineral particles (Dixon and Weed 1989). On average, dust composition reflects that of the Earth’s crust, though northern Saharan dust contains an unusually high proportion of calcite and gypsum. Submicron
dust arises from heavily weathered soil components.

During their residence time in the atmosphere, mineral dusts become coated by sulfates, nitrates, and other species (Dentener et al. 1996; Buseck and Pósfai 1999; Zhang and Carmichael 1999; Song and Carmichael 1999; Buseck et al. 2000). These coatings are formed through chemical reactions such as the oxidation of SO$_2$ and NO$_2$ at the gas-solid interface, as well as by condensation of sulfuric and nitric acids. Once coated, the hygroscopic dusts act as cloud condensation nuclei and further oxidation reactions can take place in the aqueous medium (Wurzler et al. 2000). Subsequent evaporation of the cloud droplet yields a coated particle.

Recent work has investigated whether surfaces of mineral dusts may provide stoichiometric or catalytic reaction centers that are significant enough to perturb important gas-phase cycles (Dentener et al. 1996; Zhang and Carmichael 1999; Song and Carmichael 1999; de Reus et al. 2000a). For example, the kinetics of the oxidation of SO$_2$ and NO$_2$ in the atmosphere may be enhanced by mineral surface reactions. Compared to the gas-phase oxidation of SO$_2$ and subsequent formation of new submicron sulfate particles, the scavenging of SO$_2$ by mineral surfaces reduces the climate cooling effect of sulfate aerosol by reducing particle number. In addition, interactions of O$_3$, HNO$_3$, and HO$_2$•-radicals with mineral surfaces may perturb the photooxidant cycle downwind of dust sources and lead to reduced levels of tropospheric ozone. A number of studies have examined the uptake of HNO$_3$ and O$_3$ on mineral dusts or surrogate surfaces (Fenter et al. 1995; Dentener et al. 1996; Goodman et al. 2000; Hanisch and Crowley 2001; Underwood et al. 2001). In some cases values range widely, as discussed by Underwood et al. (2000) and Hanisch and Crowley (2001). The uptake coefficients for NO$_2$ reaction on alumina and other crustal constituents are regarded as too low to have an impact on gas-phase NO$_2$, HNO$_3$, or O$_3$ (Borensen et al. 2000; Underwood et al. 2001), though coating of mineral surfaces may still be significant. The uptake coefficients for low molecular weight organic molecules such as acetaldehyde, acetone, and propionaldehyde have been measured on SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$, and CaO. Model results with these uptake values suggest that heterogeneous loss of these organics to mineral dusts is comparable to their loss by direct photolysis or through reaction with hydroxyl radical (•OH) in the middle to upper troposphere (Li et al. 2001). In contrast to nitrate, a critical unknown is the rate of SO$_2$ uptake (and oxidation) on mineral surfaces. More laboratory work is necessary to reduce these uncertainties; current modeling studies must employ assumed values.

**Polar stratospheric clouds.** During winter over the polar regions of the Earth, temperatures are cold enough that polar stratospheric cloud (PSC) particles composed of sulfuric and nitric acids and water are present (Peter 1997, 1999; Zondlo et al. 2000). The PSC particles form on background H$_2$SO$_4$ particles, which have diameters of approximately 50 nm, and grow by condensation of gaseous H$_2$O and HNO$_3$ to form particles with diameters of up to several micrometers. Particles as large as 25 μm have recently been reported (Fahey et al. 2001). The chemical constituents of PSC particles may be arranged in several possible phases, including aqueous, ice, and hydrates of sulfuric and nitric acid (Kolb et al. 1995; Martin 2000). Common hydrates include H$_2$SO$_4$·4H$_2$O (sulfuric acid tetrahydrate, SAT), HNO$_3$·2H$_2$O (nitric acid dihydrate, NAD), and HNO$_3$·3H$_2$O (nitric acid trihydrate, NAT).

A critical step in the annual depletion of polar ozone is the activation of chlorine on the surface of PSC particles, i.e., the conversion of non-ozone-destroying chlorine forms such as ClONO$_2$ into reactive, ozone-destroying chlorine compounds (Abbatt and Molina 1993; Anderson 1995). Critical heterogeneous reactions, for example, are:
HClO and Cl₂ both rapidly photolyze during polar spring to yield Cl radicals which catalytically destroy O₃. In addition, the HNO₃-containing PSC particles sediment out of the stratosphere, thus removing HNO₃ and serving as a sink for NOₓ (i.e., NO and NO₂). This denitrification contributes to sustaining Cl as an active radical because it slows several important chlorine deactivation pathways such as:

\[
\begin{align*}
\text{ClO} + \text{NO}_2 \xrightarrow{\text{PSC}} & \text{ClONO}_2, \\
\end{align*}
\]

One critical research question relates to the kinetics of PSC formation (e.g., nucleation rates of ice and the various acid hydrates) from supercooled aqueous droplets of sulfuric and nitric acids (Tolbert and Toon 2001). Nucleation rates measured in the laboratory appear too slow in many cases to explain the occurrence of PSC particles observed in the polar stratosphere. The obvious hypothesis, that the particles contain heterogeneous nuclei, has not found support because of the low occurrence of nuclei in the stratosphere and the low activity of candidate materials tested in the laboratory. An active area of research remains investigating mechanisms that could explain the formation of PSCs.

**Sea-salt particles.** Particles formed from sea spray initially have a composition that is similar to bulk seawater but with enhanced levels of organic compounds. The inorganic species in sea-salt particles are chiefly Na⁺ and Cl⁻ with contributions from SO₄²⁻, Ca²⁺, Mg²⁺, and K⁺ (Holland 1978). The organics include surfactants and other compounds that are enriched in the surface layer of the ocean. It has been suggested that these compounds form organic layers on the surfaces of sea-salt particles that might impede the transport of gases to and from the largely inorganic core (Ellison et al. 1999). Although most sea-salt particle mass occurs in the coarse mode, there are also significant numbers of sea-salt particles at sizes below 100 nm (Gong et al. 1997). For example, Berg et al. (1998) report the occurrence of sea-salt particles in the smallest size mode (35 nm) of their measurements.

Atmospheric processing alters the chemical composition of sea-salt particles, for example by increasing the amounts of SO₄²⁻ and NO₃⁻ and depleting Cl⁻ (Duce, 1969; Finlayson-Pitts et al. 1989; Chameides and Stelson 1992; McInnes et al. 1994). One pathway in this processing is:

\[
\text{NaCl(s,aq)} + \text{HNO}_3(g) \longrightarrow \text{NaNO}_3(s,aq) + \text{HCl(g)}
\]
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(RH), crystalline phases precipitate from the aqueous droplets (Martin 2000). Solid formation during the evaporation of relatively large volumes of seawater begins with CaSO₄·2H₂O, which is followed by NaCl and finally Na₂Ca(SO₄)₂ at lower RH (McCaffrey et al. 1987; Marion and Farren 1999). However, at the smaller volumes characteristic of atmospheric particles, significant supersaturation is possible and even likely according to laboratory studies (Tang et al. 1997). A critical uncertainty in the laboratory work to date, especially for aerosols, is that ambiguity remains as to which phases nucleate rapidly and thus crystallize in atmospheric sea-salt particles and in what relative order they do so. It is not known, for example, if CaSO₄·2H₂O is the first salt to crystallize. It is important to emphasize that laboratory studies on NaCl surfaces indicate that several monolayers of water coat the surface even at low RH (Barraclough and Hall 1974; Peters and Ewing 1997a; Hemminger 1999). Thus chemical transformations of gas-phase species at the surfaces of crystalline sea-salt particles usually have reactivity and pathways similar to an aqueous environment (Finlayson-Pitts and Hemminger 2000). However, the optical properties of these particles are described well by consideration of the crystalline core, which is much more massive than the aqueous surface coating.

NUCLEATION

The formation of nanoparticles from gaseous precursors is the dominant mechanism for new particle formation in the atmosphere. Secondary mechanical effects, such as shattering of ice or rain particles or abrasion of mineral dust, also lead to increases in particle number density but at sizes larger than the nanoparticle range. As illustrated in Figure 10, the first step in nanoparticle formation is generally the oxidation of precursor gases such as SO₂ or

Figure 9. TEM images of sea salt. (a and b) Subhedral halite (NaCl) and euhedral sulfate crystals. The particle in b belongs to the smallest sea-salt particles that occur in the ACE-1 samples (Southern Ocean, Cape Grim, ACE-1); (c) Halite particles in various stages of conversion to sulfate and nitrate. Grain A is partly converted, whereas C has been completely converted to nitrate and grains B to sulfates. (Azores, North Atlantic, ASTEX/MAGE.) Images by Mihaly Pósfai. Figure adapted from Buseck and Pósfai (1999). Used by permission of the editor of Proceedings of the National Academy of Sciences, USA.
organic compounds to form low-volatility products such as H$_2$SO$_4$ or polar organics. At sufficient supersaturations, these products condense to form a critical germ (also called a critical nucleus), which is a polymeric unit just sufficient in size to begin growth into a larger particle. Growth of the critical germ by condensation of low-volatility gases yields a nanoparticle (diameter of ~1 nm). These fresh nanoparticles can eventually join the accumulation mode via further growth, e.g., through continued condensation of vapors.

Nucleation is the science investigating the kinetics and thermodynamics of the formation of a new phase of a material at a size just sufficient to be stable. In addition to their role in new particle formation, nucleation processes are also critical to an accurate understanding of a number of other atmospheric events, including cloud droplet activation on CCN, ice formation, and the deliquescence/efflorescence of particles. In this section we focus on the nucleation of new particles through homogeneous nucleation, i.e., from gaseous precursors. The theoretical treatment of new particle nucleation, as well as field and laboratory measurements of nanoparticle formation, are addressed.

**Theoretical treatment of critical germ formation**

The process of new particle formation is a first-order transition from a disordered to
Gas-to-liquid and liquid-to-crystalline conversions both proceed via first-order transitions, which require activated nucleation. Although the overall transformation is favored by a negative change in the Gibbs free energy, each microscopic step along the route is not. Thermal fluctuations in the medium must assist in overcoming the positive free energy change in a microscopic region. As an example, liquid water has a driving force to freeze below 273 K, but in fact submicron droplets readily supercool to 233 K. Liquid water monomers are dynamically associating in larger polymeric networks resembling ice. Most of these networks dissipate, however, without forming ice because the surface free energy of small networks exceeds the volume free energy. At this microscopic step in the freezing process (i.e., the \( n \)-mer or cluster level), the Gibbs free energy change is positive and unfavorable. However, the liquid is incessantly exploring possible configurations of its spatial and energy coordinates through thermal fluctuations, and at some time point an \( n \)-mer forms that is large enough such that the negative volume free energy just offsets the positive surface free energy. This large \( n \)-mer, called a critical germ, then grows freely into a large crystal. These ideas have been developed quantitatively by classical nucleation theory and more recently by density functional theory and cluster kinetic theory (Laaksonen 1995; Kusaka et al. 1998a,b, 1999; Bowles et al. 2000).

Classical homogeneous nucleation theory is widely employed to describe the formation of new particles in the atmosphere (Pruppacher and Klett 1997; Seinfeld and Pandis 1998). The free energy of germ formation, \( \Delta G_{\text{germ}} \), in classical homogeneous nucleation theory is described as follows:

\[
\Delta G_{\text{germ}} = \frac{16 \pi \sigma_{\text{germ}}^3}{3kT \ln S} 
\]

(7)

where \( \nu \) is the molecular volume, \( \sigma_{\text{germ}} \) is the surface tension of the germ in the medium, \( k \) is the Boltzmann constant, \( T \) is temperature, and \( S \) is the saturation ratio of a metastable phase with respect to a stable phase. The third-order dependence on \( \sigma_{\text{germ}} \) makes this term a critical factor in calculations. The volume nucleation rate, \( J \), is as follows:

\[
J = \frac{n kT}{h} \exp \left( -\frac{\Delta G_{\text{germ}}}{kT} \right) 
\]

(8)

where \( n \) is the molecular concentration in the liquid phase and \( h \) is the Planck constant. The probability, \( P \), of a chemical system forming a critical nucleus after time \( t \) is:

\[
P(t) = 1 - \exp(-JVt) 
\]

(9)

where \( V \) is the system volume.

Nucleation of an ordered phase is often favored when there is an available surface of foreign matter. The free energy of germ formation is then reduced by a favorable interaction of the critical germ with the foreign surface. Classical heterogeneous nucleation theory provides the surface nucleation rate as follows:

\[
j = n_s \frac{kT}{h} \exp \left( -f(m) \frac{\Delta G_{\text{germ}}}{kT} \right) 
\]

(10)

where \( n_s \) is the number of monomer units per unit surface area. An important assumption inherent in this theory is an undifferentiated surface (i.e., a large terrace structure). \( f(m) \) describes the favorability of the interaction between the germ and the foreign surface, as
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follows:

\[ f(m) = \frac{(2 + m)(1 - m)^2}{4} \]  

(11)

The term \( m \) follows from \( m = \cos \theta \) where \( \theta \) is the contact angle, as given by the surface tension relationships of Young’s equation. Because \(-1 \leq m \leq 1\), it follows that \( 1 \geq f \geq 0 \).

The probability of a chemical system forming a critical nucleus is:

\[ P(t) = 1 - \exp(-jAt) \]

(12)

where \( A \) is the area of the foreign surface.

**Chemical composition of critical germ**

The chemical composition of a critical germ often differs significantly from both the constitution of the supersaturated mother liquor and the equilibrium composition of the stable phase. For example, for \( J = 1 \) cm\(^{-3}\) s\(^{-1}\) at 298 K, 2.2 \times 10^9 molecules H\(_2\)SO\(_4\) cm\(^{-3}\) and 4.2 \times 10^{17} \) molecules H\(_2\)O cm\(^{-3}\) (50% RH) in the gas phase are calculated to yield a critical germ containing 39 molecules and a H\(_2\)SO\(_4\) mole fraction of 0.205, in contrast to the gas-phase H\(_2\)SO\(_4\) mole fraction of 5.0 \times 10^{-9} (Jaecker-Voirol and Mirabel 1988). The chemical composition of the germ depends on the details of the energy surface, as specified by \( \Delta G(n_1, n_2, \ldots, n_i) \) for an \( i \)-component system (e.g., \( i = 2 \) for H\(_2\)SO\(_4\)/H\(_2\)O) where \( n_i \) denotes the number of molecules in a candidate germ. Experimental studies on cluster formation are useful in elucidating the shape of the energy surface (Jaecker-Voirol et al. 1987; Mirabel and Ponche 1991; MacTaylor and Castleman 2000). Movement across the surface from monomers to a macroscopic particle requires surmounting an activation barrier denoted by \( \Delta G_{\text{germ}}(n_1^*, n_2^*, \ldots, n_i^*) \), where \( n_i^* \) is the number of molecules of component \( i \) in the critical germ. The height of the barrier is specified by the condition:

\[
\left( \frac{\Delta G_{\text{germ}}}{n_i^*} \right)_{n_i;j \neq 1} = \left( \frac{\Delta G_{\text{germ}}}{n_2^*} \right)_{n_2;j \neq 2} = \ldots = \left( \frac{\Delta G_{\text{germ}}}{n_i^*} \right)_{n_i;j \neq i} = 0
\]

(13)

Experimental data of the dependence of \( J \) on concentration can yield an estimate of \( n_i^* \), especially for the conversion of vapors to condensed phases. The essential relation is provided in the nucleation theorem, as follows (Oxtoby and Kashchiev 1994):

\[
\frac{\partial \Delta G_{\text{germ}}}{\partial \mu_{o,i}} = -\Delta n_i^*
\]

(14)

This equation states that the change in the free energy of the critical germ with the chemical potential \( \mu_{o,i} \) per molecule of species \( i \) in the original phase (i.e., the mother liquor) equals the negative of the excess number \( \Delta n_i^* \) of molecules of type \( i \) in the nucleus over that present in the same volume of original space. The nucleation theorem is independent of the model and of the transition: it holds true for classical nucleation theory, density functional theory, or cluster kinetic analysis and for gas-to-liquid or liquid-to-solid conversions.

In the particular case of gas-to-condensed-phase transitions, Equations 8 and 14 can be developed together to yield the following accurate approximation for isothermal binary nucleation (e.g., for H\(_2\)SO\(_4\)/H\(_2\)O):

\[
\Delta n_i^* = \frac{\partial (kT \ln J)}{\partial \mu_{o,i}} - \delta
\]

(15)
where $\delta$ is a small correction factor (typically between 0 and 1) related to the dependence of the preexponential factor on chemical potentials (i.e., usually small). The chemical potential relates to chemical composition by $\mu_{i,j} = \mu_{o,j}^{0} + kT \ln f_{i}x_{o,i}$, where $f_{i}$ is the activity coefficient and $x_{o,i}$ is the mole fraction composition. When the activity coefficient is unity or otherwise ignored, Equation (15) yields:

$$\dot{c}(\ln J) = (\Delta n_{i}^{*} + \delta)\dot{c}(\ln x_{o,i})$$  \hspace{1cm} (16)

Under the assumption that $\Delta n_{i}^{*}$ is independent of $x_{o,i}$, the slope of a log-log plot of the experimental dependence of $J$ on the composition of component $i$ in the mother liquor yields the composition of the germ component $i$. It should be emphasized that $\Delta n_{i}^{*} = f(x_{o,1}, x_{o,2}, \ldots, x_{o,i})$, which is factorable as $\Delta n_{i}^{*} = N_{i}f(x_{o,1}, x_{o,2}, \ldots, x_{o,i-1})$ under the assumption of independence in $x_{o,i}$. The point is that $\Delta n_{i}^{*}$ has a specific value $N_{i}$ when $x_{o,1}, x_{o,2}, \ldots, x_{o,i-1}$ are held constant. When these values vary, $N_{i}$ also varies.

Employing Equation (16), Ball et al. (1999) analyze their data of particle formation rates from vapors of H$_2$SO$_4$/H$_2$O to determine that there are 13 H$_2$SO$_4$ monomers in a critical germ at $2 \times 10^{9}$ molecules H$_2$SO$_4$ cm$^{-3}$ and 2.3% RH at 295 K. As RH increases to 15.3%, the number of H$_2$SO$_4$ monomers drops to 7. While the H$_2$SO$_4$ monomers drop from 13 to 7, the H$_2$O monomers in the critical germ increase from 4 to 6, and the acid mole fraction in the critical germ shifts from 0.76 to 0.53. In breakthrough work, Eisele and Hanson (2000) succeed in directly measuring H$_2$SO$_4$/H$_2$O clusters containing 3 to 8 H$_2$SO$_4$ molecules by mass spectrometric techniques. The measurements are under conditions where new particle formation is not rapid, i.e., the dynamic cluster distribution is being observed. Kulmala et al. (1998a) provide a parameterization, which is convenient for inclusion in computer codes, of the mole fraction composition of the critical germ and the nucleation rate of new particles from H$_2$SO$_4$/H$_2$O gases.

In the Ball et al. (1999) work mentioned above, addition of NH$_3$ at levels of tens of parts per trillion by volume (pptv) increases the particle nucleation rate and at 15% RH reduces the number of H$_2$SO$_4$ monomers in the critical germ from 8 to 5. It would be desirable in future studies to extend this experimental work to higher RH values because the strongly nonlinear dependencies make extrapolations very uncertain, although modeling work by Korhonen et al. (1999) suggests the nucleation rate from H$_2$SO$_4$/H$_2$O/NH$_3$ could be approximately independent of RH under atmospheric conditions. According to this model description (Korhonen et al. 1999), a critical germ contains 8 H$_2$SO$_4$, 4 NH$_3$, and 6 H$_2$O molecules at 298 K, 52.3% RH, 5 pptv NH$_3$, and $10^{8}$ molecules H$_2$SO$_4$ cm$^{-3}$. In this model the presence of NH$_3$ increases the nucleation rate by several orders of magnitude.

Equations 15 and 16 develop Equation (14) for gas-to-condensed-phase transitions. It would also be desirable to develop Equation (14) for liquid-to-crystalline nucleation to assign physical meaning to $\Delta n_{i}^{*}$. However, development of Equation (14) is difficult both because $\delta$ can be a large correction factor for liquid/solid interfaces and because the molecular density differences between liquids and solids are smaller than between gases and condensed phases (Kashchiev 1982).

**New particle formation in the atmosphere**

Understanding new particle formation has been a focus of field, laboratory, and modeling efforts in recent years. This research has been driven by observations that rates of new particle production in field studies often exceed modeled rates that are based upon laboratory studies of nucleation (Covert et al. 1992; Weber et al. 1996, 1997, 1998a, 1999; Clarke et al. 1998; Kulmala et al. 1998b).
Nanoparticle formation in the atmosphere is initiated by the process of homogenous nucleation from gas-phase precursors (Eqn. 8). As shown in Figure 10, the first step in this process is the conversion of gases to lower volatility products, via reactions with species such as hydroxyl radical (\(\cdot\)OH). When the resulting partial pressures of low volatility vapors exceed saturation, vapor condensation to form new particles with diameters of approximately 1 nm is thermodynamically favored (Seinfeld and Pandis 1998; Friedlander 2000). However, new particle formation is in competition with scavenging of the low volatility gas by condensation to pre-existing particles (Kulmala et al. 1995; Weber et al. 1997; de Reus et al. 1998; Pirjola and Kulmala 1998; Pirjola et al. 1999; Kerminen et al. 2000; Clement et al. 2001). Thus new particle formation is not constant in time but instead occurs in bursts under conditions where there is little pre-existing aerosol but sufficient concentrations of (generally) photochemically produced low volatility vapors, as illustrated in Figure 11.

**Sulfuric acid.** New particle formation involving \(\text{H}_2\text{SO}_4\) has been investigated most intensively because there is strong evidence that sulfuric acid can be an important particle precursor. Gaseous sulfuric acid is formed via the oxidation of sulfur dioxide (SO\(_2\)) by hydroxyl radical in the following multistep reaction:

\[
\text{SO}_2 + \cdot \text{OH} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \cdot \text{HO}_2
\]

(17)

where the rate-limiting elementary step is the attack of \(\cdot\)OH on SO\(_2\) (Finlayson-Pitts and Pitts 2000). Since hydroxyl radical is primarily formed via reactions that require sunlight,

---

**Figure 11.** Particle size distributions (top panel) and particle number concentrations (bottom panel) at Hyytiäliä, Finland as a function of time of day (Julian day 263.5 = noon on September 19, 1996). Note the burst of nanoparticle nucleation occurring near noon and its subsequent growth. From Clement et al. (2001). Used by permission of the editor of *The Journal of Aerosol Science*. 
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the formation of gaseous H$_2$SO$_4$ (and many other secondary low-volatility gases) has a strong diurnal dependence. Correspondingly, new particle formation also shows a diurnal dependence (e.g., Fig. 11).

The photochemical dependence for the production of •OH, H$_2$SO$_4$, and new particles is apparent in Figure 12 for data from Idaho Hill, Colorado, which is a remote continental site (Weber et al. 1997). As seen in the top panel (a), •OH formation begins at sunrise, and concentrations correlate well with the UV irradiance. H$_2$SO$_4$ concentrations (c) also rise at sunrise and correlate with UV irradiance, which follows from Equation (17). On the other hand, SO$_2$ mixing ratios (b) show no diurnal trends because SO$_2$ has a long lifetime (days) with respect to reaction with •OH. The bottom panel in this sequence (d) reveals that the formation of 3- to 4-nm diameter particles is associated with the photochemical cycle and that the greatest particle number concentrations occur near solar noon. However, the appearance of these particles does not begin until approximately an hour after sunrise. This induction period is attributed to the time required for the initial particle nuclei (D$_p$ ~ 1 nm) to grow to measurable size (3 nm) (Weber et al. 1997).

In the Idaho Hill study described above, measured concentrations of gaseous H$_2$SO$_4$ and H$_2$O are much lower than the levels required for rapid new particle formation based on classical nucleation theory (Weber et al. 1997). Similar results are reported in several other studies (Wiedensohler et al. 1997; Pirjola et al. 1998, 2000; O'Dowd et al. 1999; Weber et al. 1999). These measurements show that homogeneous classical nucleation theory for H$_2$SO$_4$/H$_2$O generally underpredicts measured rates of new particle formation in the boundary layer. In contrast, in studies of high-altitude regions near cloud venting, observed rates of nucleation are similar to those predicted from binary nucleation theory (Clarke et al. 1999; Weber et al. 1999). In addition, a study of polluted air masses with high SO$_2$ concentrations in the Finnish Arctic found that application of classical nucleation theory to H$_2$SO$_4$ and H$_2$O can explain measured new particle formation rates reasonably well (Pirjola et al. 1998). Overall, these results suggest that binary nucleation of H$_2$SO$_4$ and H$_2$O is sometimes responsible for new particle formation in the atmosphere, but that other mechanisms are often more important. However, even in these latter cases there is evidence that sulfuric acid plays a role in nucleation, such as the correlation of gaseous H$_2$SO$_4$ with nanoparticle number concentrations at Idaho Hill (Fig. 12). Despite this evidence, it is also possible that H$_2$SO$_4$ is not a nucleating agent in these studies, but instead that its concentration co-varies with another, as yet unknown, photochemically produced agent (Weber et al. 1999).

Numerous authors suggest that a plausible alternative to H$_2$SO$_4$/H$_2$O binary nucleation is ternary nucleation involving H$_2$SO$_4$, H$_2$O, and NH$_3$ (Coffman and Hegg 1995; Weber et al. 1997, 1999; Kim et al. 1998; Korhonen et al. 1999). Ammonia is a common gas in the troposphere with mixing ratios that are typically under 50 pptv in remote regions and on the order of ppbv (parts per billion by volume) in regions near sources such as animal operations (Finlayson-Pitts and Pitts 2000). The H$_2$SO$_4$ vapor pressure is much smaller over aqueous ammonium sulfate solutions, as compared to over H$_2$SO$_4$/H$_2$O solutions, which suggests that NH$_3$ stabilizes H$_2$SO$_4$-H$_2$O clusters (Martí et al. 1997a). In addition, as described earlier, several recent laboratory and modeling studies show that the presence of pptv levels of NH$_3$ greatly reduces the critical concentration of H$_2$SO$_4$ required to form new particles (Ball et al. 1999; Korhonen et al. 1999; Pirjola et al. 2000). Whether the ternary H$_2$SO$_4$/H$_2$O/NH$_3$ system correctly predicts nucleation rates in a wide range of atmospheric conditions remains to be tested.

Recent work by Kulmala et al. (2000) indicates that the H$_2$SO$_4$/H$_2$O/NH$_3$ ternary nucleation mechanism yields nanoparticle (D$_p$ > 3 nm) concentrations that match field observations at a Finnish study site. In addition, the authors present the interesting
Figure 12. Concentrations of (a) \(^{1}OH\), (b) SO\(_{2}\), (c) H\(_{2}\)SO\(_{4}\), and (d) nanoparticles (D\(_{p}\) = 2.7-4 nm) measured at Idaho Hill, Colorado, from September 5 to 29, 1993, during periods of relatively clean (downslope) air flow. The solid curve on each plot (right axis) is the UV irradiance measured on a clear day (September 26) during the study. The vertical line at approximately 06:15 in each plot indicates sunrise. The second vertical line at approximately 07:30 in plot d indicates the beginning of measurable number concentrations of nanoparticles. From Weber et al. (1997). Used by permission of the American Geophysical Union.
hypothesis that 1- to 3-nm particles (‘thermodynamic stable clusters’) nucleate from \( \text{H}_2\text{SO}_4/\text{NH}_3/\text{H}_2\text{O} \) continuously and are present in the atmosphere undetected. According to this hypothesis, these small particles are formed daily to yield peak number concentrations of approximately \( 10^5 \text{ cm}^{-3} \). However, their growth is slow due to the absence of condensable \( \text{H}_2\text{SO}_4 \). Their lifetime is also relatively short in areas with heavy loadings of larger particles due to intermodal coagulation. A measurement challenge (Eisele and Hanson 2000) remains to observe in situ these thermodynamically stable clusters and thus refute or support the hypothesis.

**Organic compounds.** Low volatility organic gases are also believed to be precursors for the formation of new particles. As in the case of \( \text{SO}_2 \) oxidation to \( \text{H}_2\text{SO}_4 \), the first step in the formation of an organic nanoparticle appears to be the oxidation of a precursor gas to a more polar, lower volatility gas (Fig. 10). While there are thousands of natural and anthropogenic organic gases present in the atmosphere (Graedel et al. 1986), only those that are emitted in significant quantities, react quickly in the atmosphere, and form very low volatility products are expected to be significant in particle nucleation. Examples of these potentially significant precursor gases include biogenic monoterpenes such as \( \alpha \)-and \( \beta \)-pinene (Griffin et al. 1999; Kavouras et al. 1999) and, in urban areas, anthropogenic aromatics such as alkyl benzenes (Odum et al. 1997). Reactions of these organic gases with oxidants, such as \( \cdot \text{OH} \) and \( \text{O}_3 \), yield more oxygenated compounds, such as carboxylic acids and peroxides. These oxygenated species have lower volatilities than their parent compounds and thus increase the likelihood of forming new particles (e.g., Forstner et al. 1997; Barthelmie and Pryor 1999; Tobias and Ziemann 2000). The critical germs in these cases probably contain several different types of interacting organic species.

The Idaho Hill study discussed earlier also assesses the possible roles of biogenic terpenes and anthropogenic organic gases in nucleation (Weber et al. 1997; Marti et al. 1997b). The conclusions reached are that \( \text{H}_2\text{SO}_4 \) is generally a more important nucleating species than the measured organic gases but that there are possibly a few events where organics participate in nucleation. There is indirect evidence from other field studies that organic compounds at times lead to new particle formation in the boundary layer. For example, several studies find new particle formation in forests under conditions where organic species should be abundant (Mäkelä et al. 1997; Kulmala et al. 1998b; Becker et al. 1999; Kavouras et al. 1999). In addition, species such as carboxylic acids from terpene oxidation have been measured in accumulation mode or larger particles in forested regions (Kavouras et al. 1999; Yu et al. 1999). However, the most abundant secondary organic compounds in accumulation mode particles are likely to be the compounds condensed during particle growth, rather than any putative organics contributing to the critical germ (Kerminen et al. 2000). Thus while organic compounds are a major component of ultrafine particles in the atmosphere (Cass et al. 2000), much more work remains to identify and to evaluate the organic compounds that might serve as nucleating agents.

**Primary emissions**

In addition to the formation of new secondary nanoparticles, there are also primary emissions of nanoparticles to the atmosphere, most importantly from high temperature combustion. While there are no published emissions inventories specifically for nanoparticles, Cass et al. (2000) estimate that approximately 85% of the mass of primary ultrafine particles (Dp < 100 nm) in the Los Angeles area is emitted from combustion sources. On-road vehicles are estimated to account for approximately 40% of ultrafine particle mass. Similar results are reported for the United Kingdom, with a somewhat greater contribution (60% of total) from vehicles (Harrison et al. 2000). Observations in
Birmingham, where the number of nanoparticles decreases rapidly with distance from roads, also suggest that vehicles are an important source of primary nanoparticles (Shi et al. 1999).

Diesel engines are a particular research focus because they emit approximately 10-100 times more particles by mass than spark-ignition (gasoline) engines (Kittelson 1998). As shown in Figure 13, particulate matter from diesel engines generally contains both a nanoparticle mode ($D_p < 50$ nm) as well as an accumulation mode ($D_p = 100-300$ nm) (Kittelson 1998; Collings and Graskow 2000). The nanoparticle mode typically accounts for more than 90% of the total number of particles emitted from diesel engines, but less than 20% of the total particle mass (Kittelson 1998). The nanoparticle number size distributions recorded in laboratory measurements of vehicle emissions depend strongly upon the dilution process of the exhaust prior to analysis (Kittelson 1998; Shi and Harrison 1999; Collings and Graskow 2000). Even so, chase-car roadway measurements of particles reveal number size distributions similar to the laboratory measurements shown in Figure 13 (Collings and Graskow 2000). In an attempt to reduce diesel particle emissions in the United States, the EPA has enforced a series of increasingly strict mass-based standards (Kittelson 1998). It is unclear whether these regulations will impact the number of particles emitted from diesel engines. In fact, initial evidence suggests that new diesel engines designed to reduce emissions of particle mass might emit higher number concentrations of nanoparticles (Bagley et al. 1996; Kittelson 1998).

![Figure 13](image.jpg)

**Figure 13.** Particle number distributions for a diesel engine (2.5 L displacement, direct injection, 4-cylinder, 1500 rpm, 7.5 kW) run with 300 ppm sulfur content diesel fuel. Distributions are measured using a dilution tunnel with conditions simulating those expected in the environment (final dilution ratio of approximately 100:1). From Collings and Graskow (2000). Used by permission of the Royal Society.

Most of the nanoparticles emitted from diesel vehicles appear to nucleate from sulfuric acid and water during the cooling and dilution of the exhaust with ambient air (Kittelson 1998; Shi and Harrison 1999; Collings and Graskow 2000; Tobias et al. 2001). However, based on results from Shi and Harrison (1999), the measured rate of particle formation in diesel exhaust is much greater than the rate calculated from binary
homogeneous nucleation of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$. The implication is that other species are also participating. As the vehicle exhaust further cools, unburned fuel and lubricating oil condense upon the sulfuric acid nucleus, increasing its size and changing its composition (Burtscher et al. 1998; Kittelson 1998; Tobias et al. 2001). The organic composition of diesel nanoparticles varies with particle size, with a higher proportion of larger and less volatile organics present in the smaller particles (Tobias et al. 2001).

The accumulation mode of diesel particles consists primarily of elemental carbon in addition to significant amounts of organic carbon (including PAHs), sulfate, nitrate, ammonium, chloride, and sodium (Kittelson 1998; Schauer et al. 1999; Kleeman et al. 2000; Richter and Howard 2000). Many other species are also present in trace amounts, including Si, Fe, Ti, Zn, and Al (Schauer et al. 1999; Kleeman et al. 2000). Based on extrapolation of the size-resolved chemical composition measurements for particles with $D_p > 50$ nm (Kleeman et al. 2000), it appears that many of these same accumulation mode components are also present in diesel nanoparticles.

In addition to diesel vehicles, gasoline (spark ignition) vehicles also emit significant numbers of nanoparticles (Burtscher et al. 1998; Kittelson 1998; Kleeman et al. 2000). Although the total mass emission rate of particles from diesel engines is much greater than from gasoline engines, under highway cruise conditions diesel and gasoline engines have similar nanoparticle emission rates (Kittelson 1998). Other combustion sources of primary nanoparticles include the burning of coal and fuel oil (Huffman et al. 2000; Linak and Miller 2000; Senior et al. 2000; Fan and Zhang 2001; Zhuang and Biswas 2001), combustion of wood and other biomass (Rogge et al. 1998; Kleeman et al. 1999), aircraft (Brock et al. 2000; Kärcher et al. 2000), meat charbroiling (Rogge et al. 1991; Kleeman et al. 1999), and cigarettes (Rogge et al. 1994; Kleeman et al. 1999). The particles produced from these processes contain elemental carbon as well as a complex suite of organic compounds and numerous trace metals.

**GROWTH**

This section provides a conceptual framework and several examples of modeling and fieldwork on the growth of atmospheric nanoparticles. The growth of nanoparticles is an important source of Aitken mode and accumulation mode particles, including cloud condensation nuclei, especially in remote regions with few primary particle sources. For more quantitative descriptions of growth processes, as well as their parameterizations in models, see Kulmala (1993), Kulmala et al. (1993), Kerminen et al. (1997), Mattila et al. (1997), Vesala et al. (1997), Seinfeld and Pandis (1998), and Friedlander (2000).

The processes involved in nanoparticle growth are depicted in Figure 10. Phenomenological descriptions of early growth are presently limited because the formation of new nanoparticles, which have diameters of around 1 nm, cannot be detected by current state-of-the-art field-deployable instruments, which can measure particles with diameters of 3 nm and above. Model descriptions, however, indicate that growth is accomplished through one of three pathways: the condensation of low volatility gases such as sulfuric acid, coagulation with other newly formed nanoparticles (i.e., intramodal coagulation), or surface or bulk reactions that increase particle mass (i.e., reactive condensation) (Kerminen 1999). The growth of nanoparticles changes their chemical composition, especially at the surface, and therefore likely alters their health effects and chemical reactivity.

The rates and relative importance of condensation and intramodal coagulation depend upon the number concentration and size of nanoparticles, the partial pressures of condensable gases, and the accommodation coefficients of the gases onto the particles.
While intramodal coagulation can be important under some conditions (e.g., in regions with very high nanoparticle number concentrations), condensation is the dominant growth mechanism under typical atmospheric conditions (Wexler et al. 1994; Kerminen et al. 1997). In addition, the growth of nanoparticles is influenced by the presence of larger particles in the aerosol due to collisions with these particles (i.e., intermodal coagulation) and a competition between the nanoparticles and larger particles in scavenging the condensable gases. All other factors being equal, the vapor pressures of chemical species over nanoparticles are greater than over larger particles due to the Kelvin effect. The Kelvin effect states that the vapor pressure over a curved surface, $P$, increases relative to that over a flat surface, $P^0$, as follows: $P = P^0 \exp(4\sigma \nu k T D_p)$, where $\sigma$ is the surface tension and $\nu$ is the condensed-phase molecular volume (Seinfeld and Pandis 1998). The overall effect of these factors is that insignificant growth, and possibly even evaporation, of nanoparticles occurs in the presence of high number concentrations of larger particles. The third growth mechanism, reactive condensation, is important for the growth of accumulation mode particles through reactions such as the aqueous oxidation of SO$_2$ by HOOH or O$_3$ (Finlayson-Pitts and Pitts 2000). However, these same reactions are calculated to be too slow to be significant for nanoparticle growth (Kerminen et al. 1997; Kerminen 1999).

In the remaining part of this section we focus on nonreactive condensation because this process usually contributes more to nanoparticle growth than does intramodal coagulation (except perhaps in urban environments). In most field studies, observed nanoparticle growth rates are much faster than can be explained by the condensation of H$_2$SO$_4$ and H$_2$O (Weber et al. 1997, 1998a; O'Dowd et al. 1999; de Reus et al. 2000b). Models yield similar results, especially for conditions where particle formation occurs via H$_2$SO$_4$/H$_2$O/NH$_3$ ternary nucleation (Kerminen et al. 1997; Kulmala et al. 2000). In contrast to its effect on nucleation, the presence of NH$_3$ has little effect on growth rates in the H$_2$SO$_4$/H$_2$O system (Kerminen et al. 1997; O'Dowd et al. 1999). Model results reveal that the addition of HNO$_3$ or HCl to the ternary H$_2$SO$_4$/H$_2$O/NH$_3$ system greatly enhances growth rates under conditions found in continental regions, though not at the lower levels of gas-phase HNO$_3$ and HCl found in remote marine systems (Kerminen et al. 1997).

Several lines of evidence suggest that organic compounds play a significant role in nanoparticle growth. For example, terpenoic acids and other terpene oxidation products are present in accumulation mode particles in forested regions (Kavouras et al. 1999; Yu et al. 1999). In addition, Marti et al. (1997b) report that measured total particle surface areas and volumes ($D_p < 500$ nm) at a remote continental location roughly correlate with the estimated rates of formation of condensable products from terpene oxidation. Finally, measurements at two field sites where biogenic organic gases are likely prevalent (namely, a boreal forest in Finland during spring and summer (Kulmala et al. 1998b) and a coastal site during low tide (O'Dowd et al. 1999)) show that measured growth rates require unidentified condensable species with peak concentrations of greater than $10^7$ molecules cm$^{-3}$.

These unidentified species might be organic compounds. Modeling by Kerminen and co-workers shows that condensation of organic gases leads to the growth of 5-nm nanoparticles to CCN size ($D_p > 50$ nm) in under 24 hours. The simulations employ realistic amounts of precursor organic gases and assume that at least some of the organic oxidation products have extremely low saturation vapor pressures on the order of 0.01 pptv or less (Kerminen 1999; Kerminen et al. 2000). These nonvolatile organics are required for the initial stage of growth where the nanoparticle radius is very small and thus the Kelvin effect is very large. As the particle grows, low volatility (rather than nonvolatile) organic gases are increasingly important as particle components, which is a
combined result of a reduced Kelvin effect and the dependence of gas-particle partitioning of organics on particle mass (Kerminen et al. 2000). These results imply that the chemical composition of organic particles changes dramatically during growth and that the composition of the original nonvolatile nanoparticle nucleus is lost as a result of subsequent condensation of other products.

CHARACTERIZATION

Number concentrations

Observations of atmospheric nanoparticle number concentrations have increased greatly during the last five years. This advance has been made possible by new instruments and techniques that can measure particles with diameters as small as 3 nm. The new approaches include pulse height analysis of data from an ultrafine condensation particle counter (UCPC) (Stolzenburg and McMurry 1991; Wiedensohler et al. 1994; Weber et al. 1998b) and the combination of a nano-differential mobility analyzer (nano-DMA) (Chen and Pui 1997; Seto et al. 1997) with a UCPC.

There are large differences in nanoparticle number concentrations between remote and polluted regions: measured values in remote continental and marine areas are typically under 100 cm^{-3} (Weber et al. 1995, 1997; Covert et al. 1996) whereas number concentrations in urban areas are typically 10^{4} cm^{-3} (Shi et al. 1999; McMurry et al. 2000). Higher concentrations (~10^{5} cm^{-3}) occur near roads (Shi et al. 1999) and during bursts of new particle formation (McMurry et al. 2000; Woo et al. 2001). At a given location concentrations of the smallest measurable particles (D_p < 10 nm) are usually highly variable in time, occurring in bursts most commonly seen during periods of high solar radiation (e.g., Figs. 11 and 12). Figure 11 also shows that new nanoparticles (3 nm) grow into larger nanoparticles and nuclei mode particles over the course of several hours when conditions are favorable.

New particle formation in an urban site (Atlanta) is illustrated in Figure 14, which shows an afternoon burst of 3- to 10-nm particles during a period with high levels of SO_2. At its peak, this burst nearly quadruples the total number of particles present at the sampling site (Woo et al. 2001). Overall, number concentrations of the smallest nanoparticles (under 10 nm) are highest in Atlanta during midday, while concentrations of the larger nano- and ultrafine particles (10-100 nm) are typically higher during the morning and evening. These results suggest that vehicular emissions might be a significant source of the larger nanoparticles (Woo et al. 2001). An unexplained observation is that appreciable numbers of 3- to 10-nm particles are present in Atlanta even after sunset (Fig. 14), which is unlike the case for the remote Idaho Hill site (Fig. 12) or the Finnish boreal forest site (Fig. 11). These nighttime particles might be the result of vehicular emissions or other anthropogenic sources of primary nanoparticles in Atlanta.

Particle number distributions over the course of a year in Atlanta are shown in Figure 15. During the period August 1998 to April 1999, the number mode size of the aerosol number distribution typically occurs between 10- and 40-nm diameter. However, during the latter part of this study (April to August 1999), the smallest particles (those under 10 nm) dominate the particle number concentrations. During these months, the number of particles increases with decreasing particle size, suggesting that new particle formation events are common in this region (McMurry et al. 2000; Woo et al. 2001).

Chemical composition

Knowledge of the chemical composition of atmospheric nanoparticles is limited.
Measurements are difficult both because these particles have very little mass and because their composition varies significantly from particle-to-particle, as well as temporally and spatially. As a first step in a description, the chemical composition of new particles should relate directly to their routes of origin and subsequent growth. For example, new
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particles that form from the condensation of \( \text{H}_2\text{SO}_4 \) should clearly contain significant amounts of sulfuric acid as well as any other species involved in the nucleation event (e.g., \( \text{H}_2\text{O} \), \( \text{NH}_4^+ \), and perhaps organic species). Similarly, ammonium nitrate and low volatility organic species, when involved in nucleation, should also be important chemical components of new particles.

For fresh nanoparticles arising from primary emissions, it should be possible to roughly infer their composition based on studies that have characterized fine particles from the same emission source. For example, ultrafine and accumulation mode particles from medium duty diesel vehicles mainly contain elemental and organic carbon (Kleeman et al. 2000). Most individual molecules composing this particulate organic carbon have not been identified, but investigated compound classes include large \( n \)-alkanes, alkanoic acids, and polycyclic aromatic hydrocarbons (Schauer et al. 1999). Though not yet characterized, it is likely that nanoparticles from diesel engines contain similar types of compounds. Likewise, fresh nanoparticles from wood combustion should have compositions somewhat similar to larger wood smoke particles, which contain inorganic compounds as well as hundreds of organic species including levoglucosan, substituted methoxyphenols, and PAHs (Rogge et al. 1998; Simoneit et al. 1999; Nolte et al. 2001; Schauer et al. 2001). One caveat to this argument is that the relatively volatile components (e.g., many of the organics) present in the larger particles should be much less prevalent in nanoparticles from the same source (e.g., Kerminen et al. 2000; Tobias et al. 2001).

As discussed previously, growth and chemical reactions of nanoparticles lead to changes in their compositions. Thus the inferences in composition described above should hold only for fresh nanoparticles; correlations should weaken with atmospheric aging of the particles. It would be desirable to compare these expectations against actual field measurements of particle compositions. However, quantitative measurements of the chemical composition of ambient ultrafine particles are available only for the larger members of this class (\( D_p \approx 50\text{-}100 \text{ nm} \)). Available data, from urban areas in Southern California, indicate that organic compounds represent approximately half of the ultrafine particle mass. The remaining mass is contributed by trace metal oxides, elemental carbon, sulfate, nitrate, ammonium, sodium, and chloride (Cass et al. 2000).

Some examples of the composition of 50- to 100-nm particles from different locations in Southern California are given in Figure 16. These data indicate that the relative amounts of ultrafine particle components vary widely at different locations, a reflection of differences in particle sources and the condensation of low-volatility species. It is unknown what fraction of each chemical component in these samples was present at the point of primary emission (or initial formation) and what fraction resulted from atmospheric aging. Condensation likely contributes most significantly for chemical species that have strong vapor sources, such as organic carbon, sulfate, nitrate and ammonium. In contrast, condensation should contribute insignificantly for nonvolatile components such as metals. As shown in Table 2, Fe, Na, K, and Ti are the most abundant metals in the ultrafine particles measured, and there are also significant concentrations of Cr, Zn, and Ba. These metals are potentially significant because of their possible catalytic chemical activities and potential to contribute to the adverse human health effects associated with particles. Other metals of possible significance, such as Pt, Pd, and Rh, are not determined in the samples because of limitations of the analytical method (Hughes et al. 1998).

Future measurements should greatly increase our knowledge of the chemical composition of nanoparticles. The recent development of a novel laser desorption/ionization single-particle mass spectrometer (RSMS-II) (Carson et al. 1997; Ge et al. 1998; Phares
et al. 2001a) enables real-time measurements of the chemical components of ambient nanoparticles (aerodynamic $D_p \geq 10$ nm). At this time, this instrument does not quantitatively determine chemical composition because the detection of particles, and the efficiency with which they are ablated by the laser, depend upon particle size and composition (Kane and Johnston 2000; Phares et al. 2001a). Even so, the instrument provides insight into the elements and compound classes present in ambient nanoparticles. As configured in the two studies described below, the instrument measures particles in 9 or 13 size bins ranging from $D_p > 1 \mu$m down to nanoparticles as small as 14 nm.

Results are discussed here for the RSMS-II deployed in Atlanta during August 1999 and in Houston during August-September 2000 (Rhoades et al. 2001; Phares et al. 2001b). In the Atlanta study, approximately 16,000 particles, including both nanoparticles and larger particles, are classified into nine major composition classes. Organic carbon is the most abundant class (representing 74% of all particles). Organic particles are even more prevalent among the measured nanoparticles, accounting for 85-90% of the total number of detected particles with diameters under 50 nm (Rhoades et al. 2001). This class of particles is dominated by $C^+$-ions and other carbon fragments, but it
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also includes Si and K ions. These observations are consistent with a high temperature combustion source of primary particles. Given the high biogenic emissions in Atlanta during the summer (Chameides et al. 1988), gas-to-particle conversion of oxidation products from biogenic hydrocarbons also likely contributes to the organic aerosol. Other important particle classes of nanoparticles in Atlanta include potassium (a class with contributions from C, Ca, Na, Si and Al), calcium (with C, Fe, and Si), nitrate (with C, Si, and NH₄⁺), and elemental carbon.

The compositions of nanoparticles in Houston differ markedly from those observed in Atlanta. In particular, the dominant composition in Houston is a Si-based particle rather than an organic type (Phares et al. 2001b). The Si particle type is also prevalent

Table 2.
Concentrations (ng m⁻³-air) of trace metals in ultrafine particles (Dₚ = 50-100 nm)

<table>
<thead>
<tr>
<th>Element</th>
<th>Pasadena, CA ⁹</th>
<th>Central Los Angeles, CA ¹⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Group I and II metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>27.0</td>
<td>0.75 - 34.8</td>
</tr>
<tr>
<td>K</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Cs</td>
<td>0.016</td>
<td>0.0081 - 0.028</td>
</tr>
<tr>
<td>Ba</td>
<td>1.04</td>
<td>bdl - 2.8</td>
</tr>
<tr>
<td>Transition metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>0.0046</td>
<td>bdl - 0.0081</td>
</tr>
<tr>
<td>Ti</td>
<td>7.65</td>
<td>4.07 - 10.2</td>
</tr>
<tr>
<td>V</td>
<td>0.059</td>
<td>bdl - 0.14</td>
</tr>
<tr>
<td>Cr</td>
<td>7.32</td>
<td>bdl - 26.2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.74</td>
<td>bdl - 2.43</td>
</tr>
<tr>
<td>Fe</td>
<td>67.5</td>
<td>bdl - 148.3</td>
</tr>
<tr>
<td>Zn</td>
<td>3.68</td>
<td>bdl - 6.56</td>
</tr>
<tr>
<td>Mo</td>
<td>0.072</td>
<td>bdl - 0.19</td>
</tr>
<tr>
<td>Cd</td>
<td>0.061</td>
<td>bdl - 0.12</td>
</tr>
<tr>
<td>Au</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0052</td>
<td>0.00014 - 0.012</td>
</tr>
<tr>
<td>Lanthanides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>0.11</td>
<td>0.00082 - 0.51</td>
</tr>
<tr>
<td>Ce</td>
<td>0.19</td>
<td>bdl - 0.82</td>
</tr>
<tr>
<td>Sm</td>
<td>0.015</td>
<td>0.00030 - 0.73</td>
</tr>
<tr>
<td>Eu</td>
<td>0.013</td>
<td>bdl - 0.023</td>
</tr>
<tr>
<td>Yb</td>
<td>0.0028</td>
<td>bdl - 0.0059</td>
</tr>
<tr>
<td>Lu</td>
<td>0.00038</td>
<td>bdl - 0.0013</td>
</tr>
<tr>
<td>Actinides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>0.0065</td>
<td>bdl - 0.018</td>
</tr>
<tr>
<td>U</td>
<td>0.0057</td>
<td>bdl - 0.019</td>
</tr>
</tbody>
</table>

bdl denotes ‘below detection limit’  bbl denotes ‘below blank levels’

⁹ Data from Hughes et al. (1998). Used by permission of the American Chemical Society.
¹⁰ Data from Cass et al. (2000). Used by permission of the Royal Society.
among the nanoparticles measured, accounting for approximately 70% and 60% of the number of detected particles with diameters of 35 and 50 nm, respectively. Because atmospheric Si is normally associated with coarse particles derived from crustal material (Finlayson-Pitts and Pitts 2000), the presence of nanoparticulate silica suggests an alternative source, possibly involving high temperature combustion (Wooldridge 1998; Wooldridge et al. 1999). The presence of Si in particles of 35-nm diameter, and perhaps smaller, also lends support to speculation that reactions on silica nanoparticles might occur in the troposphere. Other types of 35-nm particles prevalent in Houston include carbon (including several types of aliphatic amines), iron, mixed organic/mineral, potassium, and aluminum (Phares et al. 2001b). Sea-salt particles of 35-nm diameter are also present in Houston when the wind direction follows from the ocean, in agreement with previous observations of 35-nm diameter sea-salt nanoparticles in the Pacific Ocean (Berg et al. 1998).

**Figure 17.** TEM images of internally mixed terrestrial and marine aerosol particles. (a) Terrestrial smectite with sea-salt particles. The selected-area electron diffraction pattern (upper right) confirms the identification of smectite (Azores, North Atlantic Ocean, ASTEX/MAGE). (b) Fe oxide emitted from coal burning, with Na$_2$SO$_4$ (Sagres, Portugal, ACE-2). Images by Mihaly Pósfai. Figure adapted from Buseck et al. (2000). Used by permission of the editor of *Proceedings of the National Academy of Sciences, USA*.

**Morphology**

The shape of atmospheric particles and the arrangement of chemically distinct components within a single particle have been investigated by sampling onto transmission electron microscopy (TEM) grids followed by imaging in the laboratory (Buseck and Pósfai 1999; Buseck et al. 2000). Figures 9 and 17 provide several examples of inorganic particles collected in different locations. A large inventory of images confirms what these figures suggest, i.e., that atmospheric particles in the large submicron to supermicron sizes are usually composed of grains of material in the nanoparticle regime. Nanoscale sulfate coatings, which are presumed to arise from SO$_2$ oxidation on mineral surfaces or from the condensation of H$_2$SO$_4$, are another common feature. Another particularly good example of morphology at the nanoscale is found in soot particles, which are commonly composed of ca. 50-nm spherical units agglomerated in chains to form larger particles. In situ mass spectrometric analysis of single atmospheric particles also confirms extensive internal mixing of chemical components (Noble and Prather, 2000). An understanding of atmospheric nanoparticles is thus incomplete without recognizing that many, if not most, larger atmospheric particles are agglomerated domains of nanophase materials.

Although environmental TEM instruments are now beginning to come on-line, a drawback of the TEM imaging completed to date is that they required operation at very
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low pressures. Thus the effect of volatile components on particle morphology is unknown; water is of particular importance. Deliquescent components (e.g., NaCl and NaNO₃) likely form an aqueous layer around insoluble minerals (e.g., smectite), at least at some of the higher RH values common in the atmosphere. At lower RH values, complex morphological shapes at the nanoscale increase hygroscopic response by reducing the chemical potentials of aqueous solutions in interstices between particles (Xie and Marlow 1997). Organic surfactant layers may be present in some particles (Gill et al. 1983; Ellison et al. 1999), and one property of this interfacial nanostructure is believed to be a decrease in the water evaporation rate (Xiong et al. 1998).

At sufficiently low RH values, crystallization occurs. The result is rarely nonporous particles of idealized shapes such as spheres or cubes (Charlesworth and Marshall 1960; Leong 1981). Laboratory studies on the morphological characteristics of evaporatively dried salt particles provide some insight into possible processes affecting the morphology of atmospheric particles. Cziczo et al. (1997) and Weiss and Ewing (1999) show from infrared studies that submicron NaCl/H₂O aerosols dried by passage through a diffusion dryer retain nanoscale pockets of water to 0% RH. These studies, however, are unable to provide information on the overall particle shape. Even NaCl particles generated by high-temperature aerosol condensation methods fail to yield nonporous cubic particles. Matteson et al. (1972) report that the density of particles generated by such methods are different from the bulk materials. The differences arise from nanoscale structural features. Craig et al. (1952) and Krämer et al. (2000) report that chain agglomerates of NaCl particles produced by condensation rearrange to cubic particles upon exposure to sub-deliquescent RH values. Although evaporation in diffusion dryers has been modeled, these studies omit the effects of the detailed microphysical structuring of the particles that accompanies drying (Xiong and Kodas 1993). Ge et al. (1996) study multicomponent aerosol crystallization by rapid evaporative drying of particles containing KCl/NaCl/H₂O, KCl/KI/H₂O, (NH₄)₂SO₄/NH₄NO₃/H₂O followed by collection of the mass spectra of the surface layers by single-particle mass spectrometry. They find that nanoscale surface layers are enriched in the minor component. The implication is that the particle morphology consists of some kind of layering with the initially crystallized phase towards the core of the particle and the minor components, which precipitate later, in the surface layers.

The detailed morphology (including overall particle shape, grain sizes and relative juxtapositions, and possible water inclusions) adopted by dried atmospheric particles probably depends on the temperature and the rate of evaporation. For these reasons, it cannot be certain that morphological features observed by TEM for particles dried by exposure to vacuum are the same as those adopted by particles dried by atmospheric processes. A critical need is the development of techniques capable of in situ characterization of particle morphology. Because the particles themselves are often no larger than 1 μm, the heterogeneity of their features occurs on the 10 to 100-nm scale.

**PROPERTIES**

**Motion**

On a large scale, particles (as well as gases) are moved through the atmosphere by advection and turbulence, i.e., horizontal and vertical winds (Wexler et al. 1994; Seinfeld and Pandis 1998). Simultaneous with these large-scale motions are the smaller-scale processes that can transport particles across surface boundary layers (e.g., at the Earth's surface) and thus remove them. As discussed earlier, diffusion is the dominant removal mechanism for small particles because of their high diffusion coefficients and low gravitational settling velocities. Because of their very small sizes, nanoparticles can slip
between gas molecules, with the result that diffusion coefficients for nanoparticles are much larger than predicted based on continuum fluid mechanics (Seinfeld and Pandis 1998; Friedlander 2000). The diffusion coefficient \( D, \text{ cm}^2 \text{ s}^{-1} \) for particles in air is given by:

\[
D = \left( \frac{kT}{3\pi\mu D_p} \right) C_c
\]  (18)

where \( \mu \) is the gas viscosity and \( C_c \) is the Cunningham slip correction factor. The term in parentheses is the Stokes-Einstein relation, which is the diffusion coefficient for particles large enough such that the surrounding gas behaves as a continuous fluid (i.e., \( C_c = 1 \)) (Seinfeld and Pandis 1998).

The Cunningham correction factor has been empirically determined to be (Seinfeld and Pandis 1998):

\[
C_c = 1 + \frac{2\lambda}{D_p} \left[ 1.257 + 0.4 \exp\left( -\frac{1.1D_p}{2\lambda} \right) \right]
\]  (19)

where \( \lambda \) is the mean free path. As shown in Figure 18, \( C_c = 22 \) for a 10-nm particle and is 216 for a 1-nm particle. This slip correction is small (under 1.08) for particles 2 \( \mu \text{m} \) and greater. Limit analysis of Equations 18 and 19 shows that the diffusion coefficient for nanoparticles goes as \( D \propto D_p^2 \).

Figure 18. Cunningham slip correction factors \( (C_c) \) for spherical particles in air as calculated from Equation (19) at 298 K and 1 atm.

Although the terminal settling velocities for nanoparticles are extremely small and of little consequence, it is interesting to note that they are also much faster than predicted from continuum fluid dynamics. As with nanoparticle diffusion, this is a result of particle slip between gas molecules. The terminal settling velocity for particles \( (D_p \leq 20 \mu \text{m}) \) in air is given by the following equation (Seinfeld and Pandis 1998):

\[
v_t = \left( \frac{D_p^2 \rho_p g}{18\mu} \right) C_c
\]  (20)

where \( \rho_p \) is the particle density and \( g \) is the gravitational acceleration (9.8 m s\(^{-2}\)). Thus the terminal settling velocities of nanoparticles are enhanced by the same factor \( (C_c) \) as are their diffusion coefficients.

**Hygroscopic behavior**

The phases of particles (e.g., aqueous or crystalline) affect their roles in atmospheric
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processes (Martin 2000). For example, light scattering is affected by both changes in refractive indices and particle sizes that accompany cycling between aqueous and crystalline states. Heterogeneous chemistry is also strongly influenced by the presence or absence of an aqueous phase. In atmospheric particles, salts comprise one important component in the hygroscopic response, though particulate organics are also increasingly recognized as playing a role (Pitchford and McMurry 1994; Saxena et al. 1995; Cruz and Pandis 2000).

In the lower troposphere, the dominant cycling of the inorganic component of particles is between aqueous and crystalline states as the relative humidity (RH) changes. At sufficiently high RH values, crystalline salts uptake water and deliquesce to form aqueous particles (Martin, 2000). With decreasing RH, crystallization (efflorescence) is often inhibited kinetically and high supersaturations are possible. For example, at 298 K deliquescence of \((\text{NH}_4)_2\text{SO}_4\) particles occurs at 80% RH but crystallization of the \((\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}\) particles via homogeneous nucleation does not occur until 35% RH. Two ongoing research efforts focus on how this hysteresis cycle is altered by the presence of nanosized foreign surfaces such as mineral dusts inside the particle (Han and Martin 1999; Martin et al. 2001) and on how the deliquescence behavior is altered when the salt particles have a significant contribution from surface energies, i.e., nano-sized particles.

**Effect of size on heterogeneous nucleation.** Figure 17 shows an example of a mineral dust particle coated by hygroscopic salts. The deliquescence/efflorescence hysteresis cycle is reduced due to heterogeneous nucleation when foreign material, such

![Figure 17](image-url)

**Figure 19.** RH values observed for the efflorescence of ammonium sulfate (120 sec residence time) by heterogeneous nucleation as a function of mode diameter of the inclusions for corundum (●) and hematite (■). The lines show \(\mathcal{F} = 0.50\) of the optimized fit to the active site model (Eqn. 24). Right axes show saturation ratios, \(S\), of the aqueous phase with respect to crystalline ammonium sulfate and salt mole fractions, \(x\), of the aqueous phase, as calculated from the model of Clegg et al. (1998) when assuming equilibrium between RH and water activity and omitting Kelvin effects. Adapted from Martin et al. (2001). Used by permission of the American Geophysical Union.
as mineral dusts, are present (Han and Martin 1999; Martin et al. 2001). Figure 19 shows that the RH value for (NH₄)₂SO₄ efflorescence increases with the size of submicron hematite and corundum inclusions (Martin et al. 2001). Rationalization of these data based upon changes in surface area is not possible within the framework of classical heterogeneous nucleation theory (Eqns. 10-12) when a reasonable range of physical parameters is employed. According to this theory, the dependence $dR_{\text{Heff}}/dD_p$ is nearly vertical. One critical assumption of classical theory is that the surface is everywhere the same, i.e., an infinitely extending terrace. An alternative theory, based on the occurrence of specific active sites, succeeds in explaining the size-dependence shown in Figure 19. According to the active-site theory (Fletcher 1969; Gorbunov and Kakutkina 1982), a surface is populated by nanoscale step edges, pits, kinks, and so on, of which each is possibly a heterogeneous nucleation center. This chapter follows the development by Han et al. (2001).

The central point of the active-site theory is that the areal density of nanoscale surface features is small and approaches the same scale as individual particle surface areas, especially in the regime of nanoparticles. The probability that a particle bears $i$ active-sites is given by the Poisson distribution, as follows:

$$P_i = \exp(-4\pi R^2 n_0) \frac{(4\pi R^2 n_0)^i}{i!}$$  \hspace{1cm} (21)

where $R$ is the particle radius and $n_0$ is the number of active-sites per unit area (i.e., areal density). For each active-site, the probability distribution of the surface area, $P_s(A)$, is log-normal, as follows:

$$P_s(A) = B \exp\left(-\gamma^2 \left[ \ln \left( \frac{A}{A_0} \right) \right]^2 \right)$$  \hspace{1cm} (22)

where $A$ is the active-site area, $A_0$ is the minimum active-site area, $B$ constrains the integral $\int_{A_0}^{4\pi R^2} P_s(A)dA = 1$, and $\gamma$ is the width of the distribution (Fletcher, 1969). The probability, $P_g(A)$, of a critical embryo forming on an active-site of area $A$ is given as follows:

$$P_g(A) = 1 - \exp\left[-A(j - j_0)\tau\right]$$  \hspace{1cm} (23)

where $j$ (cm$^{-2}$ s$^{-1}$) is the heterogeneous nucleation rate over the active-site (see Eqn. 25), $j_0$ is the heterogeneous nucleation rate over a defect-free portion of the surface (i.e., a terrace as in Eqn. 10), and $\tau$ is the observation time. Based on Equations (21)-(23), Gorbunov and Kakutkina (1982) evaluated the fraction (i.e., probability), $F$, of particles undergoing a phase transition in an ensemble of monodisperse particles, as follows:

$$F = 1 - \exp\left[-4\pi R^2 \left[ j_0 \tau + n_0 \int_{A_0}^{4\pi R^2} P_s(A)P_g(A)dA \right]\right]$$  \hspace{1cm} (24)

For the infrared detection technique employed in Figure 19, the threshold sensitivity to the phase transition is $F = 0.5$. The term $j$ is calculated by a reduction in the free energy barrier due to an improved efficiency over the active site, as follows:

$$j = n \frac{kT}{h} \exp\left(-\frac{f(m)\Delta G_{\text{germ}} - A(m_i - m)\sigma}{kT}\right)$$  \hspace{1cm} (25)

where $\sigma$ is the surface tension of the ammonium sulfate embryo/aqueous solution interface and $m_1$ describes the efficacy of heterogeneous nucleation at the active site (cf.
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We assume perfect active sites (i.e., \( m_1 = 1 \)) as done by Fletcher (1969). The active-site model embodied in Equation (24) rationalizes the data shown in Figure 19 for surfaces described as follows: \( \{<0, 0.4 \pm 0.15, 3 \pm 1 \times 10^{-15} \} \) for \( \alpha\text{-Al}_2\text{O}_3 \) and \( \{0.04, 9.0 \pm 0.2, 0.55 \pm 0.05, 3 \pm 1 \times 10^{-15} \} \) for \( \alpha\text{-Fe}_2\text{O}_3 \) in the format \( \{m, \log_{10} n_0 \text{ (site/cm}^2\text{)}, \gamma, A_0 \text{ (cm}^2\text{)}\} \).

The values for \( \alpha\text{-Al}_2\text{O}_3 \) indicate that the maximum likelihood distribution for 100 particles of 10-nm diameter (Eqn. 21) is that 73 particles have no active sites, 23 have one site, 4 have two sites, and 1 has three or more sites. Each category of particle exhibits strikingly different efficiency as heterogeneous nuclei. Most notable is that those particles having no active sites yield nucleation rates no faster than homogeneous nucleation. In contrast, in a population of 1-μm particles, over 99% of the particles have 3150 ± 100 active sites. The result is a strong nonlinearity in the heterogeneous nucleation properties in scaling from nanoparticles to micron-sized particles.

Figure 19 empirically demonstrates the divergence of nanoparticle properties from bulk properties. At sufficiently large size (i.e., extrapolation beyond the micron), every surface contains a number of active sites and the hysteresis gap between deliquescence and efflorescence approaches a limiting value of zero. However, when the particles move into the nanoregime, the distribution statistics shown by the Poisson distribution in Equation (21) indicate that there are perceptible differences from one particle to the next in terms of how many active sites are on an individual particle. For the smallest particles (e.g., 10 nm), over half of the particles have no active sites at all and are very ineffective heterogeneous nuclei.

**Effect of size on deliquescence relative humidities.** For particle diameters below 1 μm, free energy is affected increasingly by the surface energy contribution. The result is a shift in the deliquescence relative humidity for small particle sizes (Hameri et al. 2000; Mirabel et al. 2000; LM Russell, unpublished results). Work in this area is new, and the experimental and theoretical results have not yet led to agreed-upon conclusions, i.e., whether decreasing particle size leads to higher or lower values of the deliquescence RH (DRH). A theoretical framework can be developed, as follows (Mirabel et al. 2000). The DRH value is the water activity at which the free energies are equal for water and salt molecules arranged as either vapor and crystalline salt or vapor and aqueous salt (Martin 2000). The respective free energy formulations are as follows:

\[
G_{\text{vapor/crystal}} = N_{\text{total}} \mu_{\text{vapor}} + (N_{\text{solute}} \mu_{\text{crystal}} + \sigma_{\text{crystal/vapor}} A_{\text{crystal}})
\]

\[
G_{\text{vapor/aqueous}} = \left(N_{\text{total}} - N_{\text{aqueous}} H_{\text{vapor}}\right) + \left(N_{\text{solute}} \mu_{\text{solute,bulk}}(x) + N_{\text{aqueous}} \mu_{\text{aqueous}}(x) + \sigma_{\text{aqueous/vapor}} A_{\text{aqueous}}(x)\right)
\]

Equation (26) is developed by Mirabel et al. (2000) by assuming that particles are spherical (even when crystalline), that the solute is not volatile, that the vapor phase reservoir of water is infinite, and that all chemical potentials behave ideally with respect to \( x \). Note that the first and fourth approximations are gross.

Figure 20 shows the solution to Equation (26) for several different assumed \( \sigma_{\text{crystal/vapor}} \) values in the NaCl/H_2O system. The y-axis is the ratio of the DRH value anticipated from Equation (26) to the DRH value of a bulk system (DRH_{bulk} = 75% at 298 K) as a function of the number of solute molecules in the particle. In the nanosize regime, the DRH value is predicted to be shifted to much lower values in most cases. This result
is driven primarily by the difference between $\sigma_{\text{crystal/vapor}}$ and $\sigma_{\text{aqueous/vapor}}$ (taken as 70 mJ m$^{-2}$ independent of $x$ in these calculations). Because $\Delta \sigma > 0$ for normally behaving materials (i.e., surface tensions of solids against vapor are greater than liquids against vapor), there is a thermodynamic driving force to favor the aqueous state when sizes are small enough that the surface energy makes a significant contribution to the overall free energy of the particle. In a few cases (e.g., $\sigma_{\text{crystal/vapor}} = 100$ mJ m$^{-2}$), a maximum is seen in Figure 20 where DRH of nanoparticles is greater than the bulk value. This subtle effect, which is explained in detail by Mirabel et al. (2000), arises because H$_2$O is volatile and NaCl is not volatile. In this case, the mole fraction composition of the smallest aqueous droplets are enriched in NaCl because the Kelvin effect drives the evaporation of water. The net effect on the free energies is that DRH increases as compared to bulk values.

Because NaCl is known to adsorb multilayers of water prior to the DRH value, the physical description of the chemical system given by Mirabel et al. (2000) may not be accurate. The multilayer of adsorbed water is believed to be ordered and relatively pure, i.e., free of ions. This interesting phenomenon is under investigation, i.e., pure water whose chemical potential is under unity (Peters and Ewing 1997a,b). The above formulation for the free energy of the system (Eqn. 26) can be revised for a multilayer interface involving the surface tensions of the water layer against the vapor and of the crystal against the water layer, as follows:

$$G_{\text{vapor/adsorbed/crystal}} = \left( N_{\text{H$_2$O, total}} - N_{\text{H$_2$O, adsorbed}} \right) \mu_{\text{H$_2$O, vapor}} + \left( N_{\text{H$_2$O, adsorbed}} \mu_{\text{H$_2$O, adsorbed}} + \sigma_{\text{vapor/adsorbed}} \right) \text{A}_{\text{adsorbed}}$$

$$+ \left( N_{\text{solute, crystal}} \mu_{\text{solute, bulk}} + \sigma_{\text{adsorbed/crystal}} \right) \text{A}_{\text{crystal}}$$

$$G_{\text{vapor/aqueous}} = \left( N_{\text{H$_2$O, total}} - N_{\text{H$_2$O, aqueous}} \right) \mu_{\text{H$_2$O, vapor}} + \left( N_{\text{solute, aqueous}} \mu_{\text{solute, bulk}}(x) + N_{\text{H$_2$O, aqueous}} \mu_{\text{H$_2$O, bulk}}(x) + \sigma_{\text{aqueous/vapor}}(x) \right) \text{A}_{\text{aqueous}}$$

A key point is that both $\sigma_{\text{vapor/adsorbed}}$ and $\sigma_{\text{adsorbed/crystal}}$ are less than $\sigma_{\text{crystal/vapor}}$. Recent work (LM Russell, unpublished results) has shown that for soluble salts that adsorb water below their deliquescence point (including NaCl), the DRH values increase with decreasing particle size for typical values of $\sigma_{\text{vapor/adsorbed}}$ and $\sigma_{\text{adsorbed/crystal}}$. This conclusion differs markedly from the formulation given in Equation (26) and shown in Figure 20, where the limiting value of DRH is zero at small particle sizes. These differences highlight the uncertainty and need for further theoretical and laboratory work on the effect of particle size on DRH values.
Chemical reactivity

Chemical reactions involving atmospheric nanoparticles are potentially important for at least two reasons: (1) reactions might alter the chemical composition and thus the physicochemical properties of nanoparticles and (2) reactions might change the composition of the gas-phase. For example, reactions with O₃ make soot particles more hydrophilic, which should enhance their ability to act as cloud condensation nuclei (Kotzick et al. 1997). Although it has been speculated that nanoparticle reactions also alter gas-phase composition, this is probably quite uncommon except perhaps in aerosols with very high nanoparticle surface areas. Even so, in some specific cases there might be a unique role for nanoparticles in atmospheric chemistry. Such cases could occur, for example, if a nanoparticle reaction is fast compared to the equivalent reaction in the gas-phase or in/on other condensed phases such as cloud drops or larger aerosol particles. Nanoparticles could also significantly alter the composition of the gas phase if the nanoparticle reaction is unique in terms of the reactants destroyed or products produced.

To the best of our knowledge, there are no identified instances of nanoparticle reactions in the atmosphere where either of these two criteria is satisfied. However, this field is largely unexplored at the time of this writing.

As a first step in assessing the potential importance of nanoparticle reactions, we compare the volume and surface areas of these particles with the same values from other condensed phases with known chemical effects. We first consider nanoparticle volumes. As an upper limit, we consider an urban air parcel containing 20-nm diameter nanoparticles at a number concentration of 10⁵ cm⁻³. Under this scenario, the nanoparticle volume is a small fraction (10⁻¹³) of the total air parcel volume. Thus the nanoparticle reaction rate (in units of mol m⁻³-air s⁻¹) would have to be ca. 10¹³ times as fast as the equivalent gas phase reaction (mol m⁻³-air s⁻¹) to have a comparable overall rate in the air parcel. For comparison, clouds typically have liquid water contents of 10⁻⁷ to 10⁻⁶ (volume fraction) and can have significant effects upon atmospheric chemistry (Seinfeld and Pandis 1998). For simplicity of argument, if the medium of the cloud droplets and nanoparticles are assumed similar (e.g., dilute aqueous), then the fundamental rate constants in each medium are similar. Under this condition, reactant concentrations in the nanoparticles would need to be enhanced by 10⁶, as compared to the cloud droplets, to have equal rates. Based on this analysis, it appears unlikely that reactions occurring in the bulk of nanoparticles could affect the composition of the gas phase.

The other possibility is a reaction at the surface of the nanoparticles. For the assumed urban scenario above, the nanoparticle surface area concentration is approximately 100 μm² per cm³-air. At this surface area loading, nanoparticle reactions could plausibly affect the composition of the gas phase. For example, de Reus et al. (2000a) report that plumes of mineral dust particles (primarily in the accumulation mode), with surface area concentrations of ca. 100 μm² cm⁻³, significantly reduce mixing ratios of ozone and nitric acid. While this comparison suggests nanoparticle surface reactions could be significant in urban atmospheres, the conclusion depends on a number of factors, including high particle number concentrations (which are unlikely outside of urban areas), a reactive particle surface with sufficiently high uptake coefficients for trace gases, and surface renewal during the course of the reaction.

In the remaining portion of this section we examine several nanoparticle types and reactions that could potentially be significant in the atmosphere. Of course, until the chemical composition, morphology, and reactivity of nanoparticles are better characterized, it is not possible to assess accurately the significance of these or other reactions.
Concentrated $H_2SO_4$. Sulfuric acid is an important participant in the nucleation and the growth of new particles in the troposphere. The mole fraction acidity (viz. $H_2SO_4$ content) of these particles is believed to be high. It is likely that the presence of this strong sulfate acidity influences the chemistry of nanoparticles because sulfuric acid promotes a number of organic reactions that otherwise either do not occur or occur much more slowly (Liler 1971). We will consider several of these reaction classes here with a focus on those involving organic species common in the atmosphere.

One class of organic reactions in sulfuric acid is hydrolysis, which affects functional groups such as ethers, esters, nitriles, halogenated organics, and converts amides to the corresponding carboxylic acid, as follows:

$$RC(O)NH_2 + H_2SO_4 + H_2O \rightarrow RC(O)OH + NH_4^+ + HSO_4^-$$  

(28)

In addition, concentrated sulfuric acid catalyzes the decarbonylation of aldehydes, aromatic acids, and aliphatic carboxylic acids, such as formic acid:

$$HC(O)OH + H_2SO_4 \rightarrow CO + H_2O + H_2SO_4$$  

(29)

Other classes of reactions are the dehydrations and condensations, such as the conversion of acetone to protonated mesityl oxide, as follows:

$$2 CH_3C(O)CH_3 + H_2SO_4 \rightarrow (CH_3)_2C=CHC(OH^+)CH_3 + H_2O + HSO_4^-$$  

(30)

Finally, a number of commonly occurring atmospheric trace species are converted to reactive electrophiles in concentrated sulfuric acid solutions. For example, nitric acid is converted to $NO_2^+$, which is a potent nitrating agent for aromatic compounds (Liler 1971), and hydrogen peroxide can be converted to peroxymonosulfuric acid (HOOSO$_2$OH), which is a strong oxidant (Mozurkewich 1995; Dalleska et al. 2000).

Studies of these reactions have typically been carried out in very concentrated sulfuric acid solutions (85 to 100 wt % $H_2SO_4$) (Liler 1971). More recent work examines whether similar types of reactions occur at lower sulfuric acid concentrations. Roberts and co-workers, for example, examine the condensation reactions of acetone in thin films of 70 to 96 wt % $H_2SO_4$ at temperatures found in the upper troposphere and lower stratosphere (180-220 K) (Duncan et al. 1998, 1999). According to this work, acetone is protonated in 70 wt % $H_2SO_4$, undergoes condensation to mesityl oxide (Eqn. 30) above 75 wt % $H_2SO_4$, and undergoes further condensation to trimethylbenzene above 85% $H_2SO_4$. Thus acetone condensation to larger carbon products requires quite high acidities. It has not yet been investigated how the rates and extents of the other reactions discussed above vary at lower sulfate acidities.

The weight percent of $H_2SO_4$ in stratospheric sulfuric acid particles is typically between 40 and 80% and stratospheric temperatures are generally between 210 and 240 K (Shen et al. 1995; Tabazadeh et al. 1997, 2000; Finlayson-Pitts and Pitts 2000). On the other hand, tropospheric sulfuric acid particles typically contain less than 75 wt % $H_2SO_4$ (this concentration is in equilibrium with a RH value of less than 1% at 298 K), and temperatures are typically above 230 K. For example, at 298 K pure sulfuric acid-water droplets ($D_p > 100$ nm) contain 42.5 wt % $H_2SO_4$ at a relative humidity of 50% (Seinfeld and Pandis 1998). Thus it is not known whether the reactions mentioned above occur to any appreciable extent in the troposphere or stratosphere. In the troposphere, nanoparticles of sulfuric acid may be much more acidic than larger sulfuric acid particles due to an increase in water vapor pressure with decreasing particle size (i.e., the Kelvin effect) (Fig. 21). For example, at 50% RH the weight percent of $H_2SO_4$ is 1.7 times
greater for a 1-nm particle (72 wt %) as compared to a 100-nm particle (43 wt %). Thus, organic reactions in sulfuric acid, such as those described above, are more likely to occur in nanoparticles and under conditions of low relative humidity. Because some reactions, such as the condensation of aldehydes (e.g., Eqn. 30), produce organic products that are of higher molecular weight and lower volatility than the initial organic compound, these chemical pathways could contribute to the growth of nanoparticles.

**Soot.** Combustion particles containing elemental carbon with variable amounts of organic carbon and trace metals (i.e., soot) consist of 30- to 40-nm diameter nanoparticles agglomerated in chains with typical lengths of a few hundred nanometers (Kennedy 1997; Seinfeld and Pandis 1998; Clague et al. 1999). In the past five years there has been growing interest in atmospheric reactions involving soot. Much of the attention has focused on reactions with O$_3$ and nitrogen oxides (i.e., NO and NO$_2$) because of the importance of these species as air pollutants.

The most significant soot reaction identified to date is the conversion of nitrogen dioxide (NO$_2$) to nitrous acid (HONO) and smaller amounts of nitric oxide (NO) (Ammann et al. 1998; Gerecke et al. 1998; Kalberer et al. 1999; Longfellow et al. 1999; Al-Abadleh and Grassian 2000; Alcala-Jornod et al. 2000; Stadler and Rossi 2000; Saathoff et al. 2001), as follows:

$$
\text{NO}_2 + \text{soot} \rightarrow \text{HONO} + \text{NO}
$$

This reaction is of interest because current models underestimate the production of HONO, which is an important photolytic source of hydroxyl radical (Ammann et al. 1998; Finlayson-Pitts and Pitts 2000). This reaction could also be important as a reductive pathway for nitrogen species in the atmosphere, which is in contrast to most atmospheric reactions which tend to oxidize trace gases (e.g., the conversion of SO$_2$ to H$_2$SO$_4$). Molar yields of HONO via Equation (31) (relative to the moles of NO$_2$ lost) typically range from 50 to 100%, while yields of NO are 4 to 30% (Gerecke et al. 1998; Stadler and Rossi 2000). It appears that the formation of NO results from the secondary reaction of HONO at the surface of the soot (Stadler and Rossi 2000). The mechanism of
this reaction is not known, but water vapor appears to play a significant role (Longfellow et al. 1999). There is also some evidence that the reaction involves organic compounds that can be solvent-extracted from the soot (Stadler and Rossi 2000). There is no consensus on whether this reaction is a significant source of HONO in the polluted troposphere (Ammann et al. 1999; Kalberer et al. 1999; Kirchner et al. 2000; Saathoff et al. 2001) because there is uncertainty whether reactive sites on soot are catalytic (Longfellow et al. 1999) or are deactivated during the reaction (Kalberer et al. 1999; Kirchner et al. 2000).

A number of other atmospheric gases also react with soot. For example, ozone is destroyed on soot to form O₂, CO, and CO₂ (Gao et al. 1998; Kamm et al. 1999), while HNO₃ is reduced either to NO or NO₂ on soot (Choi and Leu 1998; Disselkamp et al. 2000a) or is simply physically adsorbed (Longfellow et al. 2000). In any case, the uptake coefficients for O₃ and HNO₃ are small enough that these soot reactions are not important as sinks for these gases or as a source of NO and NO₂ (Choi and Leu 1998; Gao et al. 1998; Kamm et al. 1999; Disselkamp et al. 2000a, 2000b; Longfellow et al. 2000). There is some evidence that the soot uptake of hydroperoxyl radical (HO₂•), which is a key component of ozone (smog) chemistry in the troposphere, is large enough to reduce O₃ mixing ratios in heavily polluted areas (Saathoff et al. 2001).

Although these O₃ and HNO₃ reactions are not important as sinks for the gases, they are likely important as pathways that chemically transform the surface of soot. For example, exposure of soot to HNO₃ or NO₂ produces surface species such as R-C=O, R-NO₂, R-ONO₂, and R-ONO (Al-Abadleh and Grassian 2000; Kirchner et al. 2000), while exposure to O₃ produces oxygen-containing functional groups such as -OH, R-C=O, and R-C-O (Kotzick et al. 1997; Al-Abadleh and Grassian 2000; Kirchner et al. 2000). These reactions are important because they make the surface of soot particles more polar, which increase soot’s efficiency as a cloud condensation nucleus (Kotzick et al. 1997). These reactions might also affect the toxicity of soot particles. Given that soot is also an important reservoir of atmospheric polycyclic aromatic hydrocarbons (PAHs) (Dachs and Eisenreich 2000), reactions of trace gases such as O₃ with soot may also be important in the transformation and destruction of these toxic molecules (Finlayson-Pitts and Pitts 2000; Poschl et al. 2001).

Although a number of studies have used commercially available carbon black as a surrogate for soot, there are large differences in the composition, and therefore probably in the chemistry, between these two types of materials (Watson and Valberg 2001). Diesel soot, for example, is much more oxygenated, has a more polar surface, and contains higher amounts of trace species such as Fe, S, and Ca than carbon black (Clague et al. 1999). Similarly, even with authentic soots there can be large differences in chemistry, both as a result of different fuels as well as different fuel/air ratios during soot formation (Alcala-Jornod et al. 2000; Kirchner et al. 2000; Stadler and Rossi 2000).

**Metal oxides.** Although most published chemical studies with prepared nanoparticles involve reactants bearing little or no relevance to the atmosphere, there are a number of reports of reactions involving metal or metal oxide nanoparticles that might have analogues in the atmosphere. For example, Klabunde and co-workers report that halocarbons, which are a significant class of anthropogenic atmospheric pollutants, are destroyed by nanoparticles of calcium oxide and magnesium oxide to form products such as CO, CO₂, elemental carbon, and the corresponding metal chloride (Koper et al. 1993, 1997; Li et al. 1994; Koper and Klabunde 1997). However, these reactions are likely insignificant in the atmosphere because they require high temperatures (typically above 600 K). It has also been shown that gases such as NO, HCl, SO₂, and CO₂ adsorb on the surface of MgO and in some cases react at room temperature (Stark and Klabunde 1996;
Stark et al. 1996). However, for these CaO and MgO reactions, the metal oxides are stoichiometrically consumed during the process. Thus even if the reactions could stoichiometrically destroy pollutant gases at atmospheric temperatures, their importance in the atmosphere should be limited by the small available masses of nanoparticulate CaO and MgO.

This stoichiometric constraint on reactivity is eliminated for catalytic or photocatalytic reactions involving nanoparticles. Although no quantitative investigations have yet been performed in either laboratory experiments or modeling, a reasonable speculation is that metals or metal oxides embedded in individual atmospheric nanoparticles might serve as catalysts for oxidation and reduction reactions in the atmosphere, as suggested by José-Yacamán (1998). In support of this view, synthesized nanoparticles containing Fe, Cr, Cu, Ti and other metals are typically very reactive, often catalytically, in reduction and oxidation reactions involving atmospheric pollutants such as CO, CH₄, and larger organic gases (Park and Ledford 1997, 1998; Zhang et al. 1998; Perkas et al. 2001). Furthermore, the rates and the efficiencies of reactions of metal oxide nanoparticles are often enhanced relative to the bulk material due to different surface structures (Stark et al. 1996; Jefferson 2000). However, it is unclear whether the reactivities of nanoparticles used in these studies are comparable to metal and metal oxide nanoparticles in the atmosphere. Moreover, given their small amounts, it is unclear whether reactions involving metal and metal oxide nanoparticles are as significant as similar reactions that might occur on accumulation and coarse mode mineral dusts.

**Electronic.** Several minerals, including oxides of Fe, Si, Ti, or Zn, have been investigated as active heterogeneous photocatalysts in the atmosphere. Gas/solid reactions have been investigated, for example, as tropospheric sinks for chlorofluorocarbons on mineral dusts (Ausloos et al. 1977; Benzoni and Garbassi, 1984; Filby et al. 1981; Zakharenko 1997). Photochemical conversions of aqueous species at the surface of iron oxyhydroxides (e.g., hematite, goethite, lepicrodocite, or ferrihydrite) contained within cloud droplets have also been the focus of considerable study (Sulzberger et al. 1988; Behra and Sigg 1990; Pehkonen et al. 1993, 1995; Litter et al. 1994; Siefert et al. 1994). These reactions favor the formation of oxidized species, both inorganic and organic, within cloud droplets.

The photochemical mechanism is worked out most completely for hematite. This semiconducting mineral generates electron-hole pairs when irradiated with sunlight (Sulzberger 1990; Hoffmann et al. 1995). The valence band holes oxidize adsorbed organics such as oxalate to carbon dioxide and other reduced species such as bisulfite to sulfate. As a by-product, ferrous iron is released to the aqueous solution from the ferric oxide matrix of the mineral. Although the absorption spectrum of hematite is in the red, this color arises mostly from d-orbital transitions in the band structure (2.2 eV) (Finklea 1988). The photoaction spectrum does not show significant activity until 3 eV (Siffert and Sulzberger 1991), which is explained by the band structure. Transitions begin at 3 eV from the occupied O(2p) valence band to the empty conduction band, which is composed of Fe centered d-orbitals. The photochemistry is explained either by hole scavenging by adsorbates or by direct charge transfer from localized orbitals of the oxygen atoms of adsorbed ligands into the conduction band.

The general process of mineral dissolution by photochemical reduction, as well as by pH-dependent non-oxidative thermal dissolution of other minerals in cloud waters (Desboeufs et al. 1999), yields the formation of dissolved aqueous species. Upon cloud droplet evaporation, one reasonable fate we can suggest for these species is reoxidation by abundant atmospheric O₂ followed by recrystallization into nanoparticles (since oxidized ions in general have lower solubility (Stumm and Morgan 1996)). There are two
assumptions inherent in this suggestion: (1) since acidic media dissolve minerals and thus disfavor precipitation of nanoparticles, the acidic cloud drop needs to be neutralized (e.g., by alkaline mineral constituents or ammonia) and (2) mineral precipitation forms new nanoparticles, possibly as accessory minerals, rather than growing material on preexisting surfaces of the same or similar minerals. Furthermore, Ostwald’s rule of stages suggests amorphous phases with less developed band structures would be favored, at least initially, over more crystalline phases (Lasaga 1998). Under conditions favorable with respect to these assumptions, we offer the speculation that nanocrystalline mineral particles crystallize from cloud droplets.

Due to their small size, if these nanoparticles form they should possess altered electronic properties (Brus 1983), including a wider bandgap and thus a blue-shifted photoaction spectrum. Although this effect reduces the sunlight absorbed, the holes formed in the valence band have a higher thermodynamic driving force to promote chemical reactions. Novel chemical channels may then be opened or, alternatively, rates of chemical conversion may be increased for known channels. The idea of the formation of nanocrystalline particles with unique properties within cloud droplets is at best speculative at this time. Even so, it seems appropriate within the aims of this chapter to provide a perspective on possible properties and occurrence of atmospheric nanoparticles with electronic properties different from the bulk. Another occurrence may be in the stratosphere where 50% of the particles are estimated to contain 0.5 to 1 (w/w) iron oxide (Cziczo et al. 2001). It is unknown if the thermodynamics of highly acidic particles (60-80 wt % H₂SO₄) at extremely low temperatures (210-225 K) favors a dissolved or precipitated state for the iron. However, if crystalline, the iron should exhibit size-quantization effects in its band structure.

OUTLOOK

Many critical uncertainties must still be addressed to assess quantitatively the sources and sinks of atmospheric nanoparticles, their physical and chemical evolution during atmospheric aging, their direct and indirect impacts on atmospheric chemistry and physics, and their connections to adverse effects on human health. Several important and complex areas that need much additional study include:

1. New particle formation and growth. These processes are important sources of new particles and CCN, but field observations suggest that current theories relying on H₂SO₄ and H₂O are often inadequate to explain nucleation or growth. The role of NH₃ in a possible ternary nucleation mechanism needs to be examined quantitatively at more field sites. The identities of nonvolatile and low-volatile organic species involved in nucleation and growth should be further examined. To do so, highly sensitive and specific analytical techniques must be developed. In theoretical work, contemporary nonclassical theories of homogeneous nucleation are promising, but they are urgently in need of further data on the kinetics of cluster formation from laboratory studies.

2. Particle composition and morphology. Understanding the adverse health effects and possible chemical reactivity of atmospheric nanoparticles requires knowing their chemical composition and morphology. Quantitative measurements of the composition of ambient nanoparticles, as well as of nanoparticles from emission sources, are needed. Both traditional fine particle emission sources (e.g., combustion) as well as coarse particle emission sources (e.g., oceanic sea-salt and mineral dust) should be examined. Real-time single-particle compositional analysis, albeit still qualitative, has occurred through impressive instrumentation advances in the last few years. These advances highlight the need for commensurate progress in techniques sensitive not
only to overall particle morphology but also to internal structures such as water pockets, grain structures, surfactant layers, or radial compositional layering. In most cases, investigators must be cognizant of the overriding role of relative humidity in affecting morphology.

3. Chemical and photochemical reactions. Evaluating the potential effects of nanoparticles on atmospheric chemistry and composition will require much additional laboratory and modeling work. Experiments need to be performed to measure uptake coefficients, reaction rates, and products formed from the interaction of atmospheric trace gases with authentic or representative nanoparticles. Special attention should be given to important reactions in urban areas (e.g., ozone formation) where nanoparticle concentrations are typically greatest. An additional focus should be to examine reactions with important species that are destroyed only slowly in the gas-phase (e.g., CO or CH₄) since in these cases nanoparticle reactions might be fast enough to compete effectively with the gas-phase reactions. With these data it should then be possible to model atmospheric nanoparticle reactions and their significance.

4. Health effects. More epidemiological and clinical studies are needed to further examine the hypothesis that nano- and ultrafine particles are responsible for adverse human health effects. It will be especially valuable to perform experiments that allow elucidation of the particle properties that are responsible for toxicity, such as number concentration, surface area concentration, or specific chemical species.

5. Unique size-dependent properties. Although it is known that nanosized objects have properties diverging from the bulk, as highlighted in contemporary work on the electronic properties of semiconductors, unique chemical and physical properties in systems relevant to atmospheric nanoparticles are mostly speculative at this time and poorly informed by data. However, further intensive work is warranted based upon available data such as observations that heterogeneous nucleation properties depend on size and reach a critical regime at small size due to the statistics of small numbers, e.g., not every particle has an active site. Deliquescence relative humidities of salts depend critically on size at the nanoscale due to significant contributions of surface energies to the overall free energies. Electronic properties, including photochemistry, of metallic and semiconducting particles present in the atmosphere are strongly altered in nanosized objects. These objects may be spatially separate individual particles or they may instead be a single grain or inclusion embedded within a larger particle. These possible properties and their effects on atmospheric processes need to be investigated through additional laboratory work.

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