5 Physical and Chemical Changes in the Particulate Phase

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INTRODUCTION

Aerosols, by their nature, are somewhat unstable in the sense that concentration and particle properties change with time. These changes can be the result of external forces, such as the loss of larger particles by gravitational settling, or they may be the result of physical and chemical processes that serve to change the size or composition of the particles. This chapter addresses the latter category of processes. They all involve mass transfer to or from a particle. This transfer may be the result of molecular transfer between the particle and the surrounding gas, for example, condensation, evaporation, nucleation, adsorption, absorption, and chemical reaction, or it may result from interparticle mass transfer, such as by coagulation.

Processes that cause physical or chemical changes in the particulate phase influence the particle size distribution of nearly all aerosols. These processes contribute in an essential way to the earth's hydrological cycle. They are involved in the formation of photochemical smog and are key to shaping the atmospheric aerosol size distribution. These processes play a significant role in many occupational aerosol exposures and in the operation of the condensation nuclei counters, described in Chapter 19. They are central to industrial aerosol processing and for the generation of test aerosols.

Condensation, thermal coagulation, and adsorption are related processes that rely on the diffusion of molecules or particles to a particle's surface. Evaporation is the opposite of condensation and is governed by the same laws. Reactions may be nongrowth processes that change the composition or density of an aerosol particle with little or no change in particle size. Because the processes discussed in this chapter are related and may be occurring simultaneously, it is necessary to look at each process separately in order to obtain an accurate picture of the changes that occur. Furthermore, these processes depend on particle size in a complex way, so I adopt a single particle approach for much of the analysis that follows. I rely on the concepts of mean free path and diffusion coefficient, which are defined in Chapter 4.

Definitions

The *partial pressure* of a vapor is a way of expressing the concentration of that vapor in a volume of a gas. It is the pressure the vapor would exert if it were the only component present.

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This pressure, expressed as a fraction of the ambient pressure, is the fractional concentration of the vapor. Air at 293 K [20°C or 68°F] and 50% relative humidity has a partial pressure of water vapor of 1.17 kPa [8.8 mmHg], which means that the air–water vapor mixture is 1.17/101 [= 8.8/760] = 1.2% water vapor on a volume basis.

The *vapor pressure* or *saturation vapor pressure* is a unique property of any liquid at a given temperature. It represents the minimum partial pressure of that liquid's vapor that must be maintained at the gas–liquid interface to prevent evaporation. This is a condition required for mass equilibrium, no net transfer of molecules at the liquid surface, that is, no net condensation or evaporation. Vapor pressure as defined here is for a flat liquid surface, but, as will be explained below, a slightly greater partial pressure is required to maintain mass equilibrium around an aerosol particle. The partial pressure of vapor in a sealed chamber containing a liquid will eventually reach the vapor pressure of the liquid at the temperature of the container.

The vapor pressure of water in kPa and mmHg at a temperature T in K is given by

$$p_s = \exp\left(16.7 - \frac{4060}{T-37}\right)\text{kPa} = \exp\left(18.72 - \frac{4062}{T-37}\right)\text{mmHg} \qquad (5\text{–}1)$$

for T from 273 to 373 K.

For aerosol condensation and evaporation processes, it is the ratio of the partial pressure of vapor to the saturation vapor pressure that is important. This ratio is called the *saturation ratio*, S_R. When the saturation ratio is equal to one, the mixture is described as *saturated*; when it is greater than one, the mixture is *supersaturated*; and when less than one, it is *unsaturated*.

Nucleation or *nucleated condensation* refers to the process of initial formation of a particle from vapor. This process is usually facilitated by the presence of small particles, called *condensation nuclei*, that serve as sites for condensation.

EXAMPLE 5–1

Saturated air coming from the ocean at 293 K [20°C] is carried by air currents up the side of a mountain to an altitude of 1 km. Assuming this represents adiabatic expansion to a pressure of 89 kPa [670 mmHg], what would be the saturation ratio of this air mass if no condensation occurred?

Answer: The absolute temperature of the air mass after an adiabatic expansion of saturated air from p_1 to p_2 is given by

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{0.28} = 293\left(\frac{89.0}{101}\right)^{0.28} = \left[293\left(\frac{670}{760}\right)^{0.28}\right] = 283\,\text{K}$$

At 283 K the saturation vapor pressure for water is given by Eq. (5–1):

$$p_s = \exp\left(16.7 - \frac{4060}{283-37}\right) = 1.22\,\text{kPa} = [9.1\,\text{mmHg}]$$

The saturation ratio is the ratio of the actual partial pressure of vapor, 2.34 kPa [17.6 mmHg] (by Eq. 5–1 at 293 K), to the saturation vapor pressure for the ambient temperature, 1.22 kPa [9.1 mmHg]:

$$S_R = \frac{2.34}{1.22} = \left[\frac{17.6}{9.1}\right] = 1.92$$

Adsorption is the process whereby vapor molecules attach to solid surfaces. It is most important for porous solids, such as activated charcoal, that have large surface areas. *Absorption* refers to the process of vapor molecules transferring from the gas phase to the liquid phase.

For aerosol particles *condensation* occurs when more vapor molecules arrive at a particle's surface than leave. It results in a net growth of the particle. *Evaporation* is the reverse of condensation and results in a net loss of molecules and a shrinkage of the particle.

The Kelvin Effect

Vapor pressure has been defined as the partial pressure required for mass equilibrium (no net evaporation or condensation) for a flat liquid surface. Because liquid aerosol particles have a sharply curved surface, a greater partial pressure is required to maintain mass equilibrium for a droplet than for a flat liquid surface at a given temperature. This increase in partial pressure of vapor required for mass equilibrium increases with decreasing particle size. This effect is called the *Kelvin effect*. The saturation ratio required for mass equilibrium (no net condensation or evaporation) for a droplet of diameter d_p is given by the Kelvin equation:

$$S_R = \exp\left(\frac{4\gamma M}{\rho_p R T d_p}\right) \tag{5–2}$$

where γ, M, and ρ_p are the surface tension, molecular weight, and density of the liquid, respectively, and R is the gas constant. Thus, 0.1 and 0.01 μm diameter water droplets require an environment with a saturation ratio of least 1.022 and 1.24, respectively, to prevent evaporation. Evaporation will occur if the saturation ratio is less than that given by Eq. 5–2, even if the saturation ratio is greater than one. Likewise, if the saturation ratio is greater than that required by the Kelvin equation, then condensation and growth will occur. For a given supersaturation, the minimum droplet size required to prevent evaporation is given by Eq. 5–2 and is referred to as the *Kelvin diameter* for that condition. The Kelvin effect is illustrated by the line labeled "pure water" in Figure 5–1.

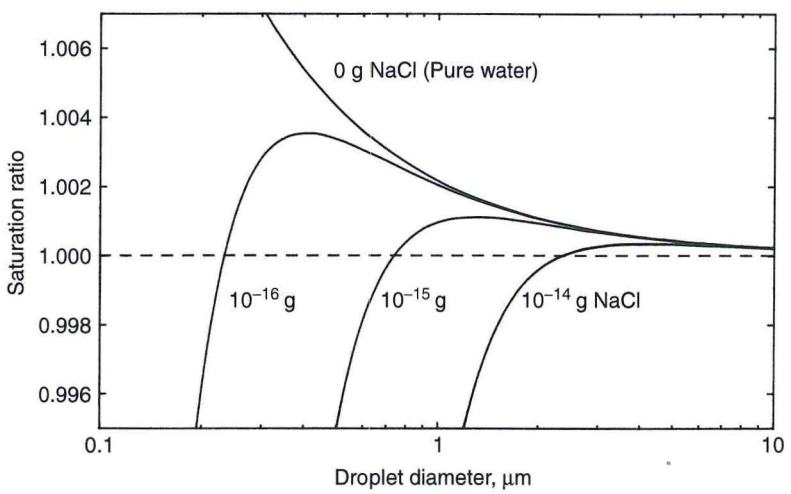

Fig. 5–1. Saturation ratio versus droplet size for pure water and droplets containing the indicated mass of sodium chloride at 293 K [20°C]. (Adapted from Hinds, 1999.)

EXAMPLE 5–2

What saturation ratio is required to prevent growth or evaporation of 0.05 μm pure water droplets?

Answer: Use the Kelvin equation, Eq. 5–2:

$$S_R = \exp\left(\frac{4\gamma M}{\rho_p R T d_p}\right)$$

where $\gamma = 0.0727\,\text{N/m}$; $M = 0.018\,\text{kg/mole}$; $\rho_p = 1000\,\text{kg/m}^3$; $R = 8.31\,\text{J/K·mole}$; $T = 293\,\text{K}$; and $d_p = 5 \times 10^{-8}\,\text{m}$.

Substituting in gives

$$S_R = \exp\left(\frac{4 \times 0.0727 \times 0.018}{1000 \times 8.31 \times 293 \times 5 \times 10^{-8}}\right) = \exp(0.043) = 1.044$$

CONDENSATION

Growth Rate

When a droplet of pure liquid is in a supersaturated environment that exceeds the requirement given by the Kelvin equation, the droplet grows by condensation of vapor on its surface. The rate of growth depends on the saturation ratio and the particle size. It is controlled by the rate of arrival of vapor molecules at the droplet surface. Initially the droplet will usually be less than the mean free path of the surrounding gas λ (0.066 μm at standard conditions; see Chapter 4) and the rate of arrival of vapor molecules is governed by the kinetic theory of gases. The growth rate, the rate of increase in droplet diameter, is given by Hinds (1999) as

$$\frac{d(d_p)}{dt} = \frac{2\alpha_c(p - p_d)}{\rho_p\sqrt{2\pi RT/M}} \quad \text{for } d_p < \lambda \tag{5–3}$$

where α_c is the condensation coefficient, the fraction of arriving molecules that stick, approximately 0.04 (see Barrett and Clement, 1988); p is the partial pressure of vapor in the neighborhood of the droplet; and p_d is the partial pressure of vapor at the droplet surface as given by the Kelvin equation. In the application of Eq. 5–3 to obtain the growth rate in m/s [cm/s] requires that pressure be expressed in Pa[dyn/cm^2] (note that mmHg × 1330 = dyn/cm^2), density of the liquid is in kg/m^3 [g/cm^3], temperature is in K, and molecular weight is in kg/mole [g/mole]. The gas constant R is 8.31 J/K·mole [8.31×10^7 dyn·cm/K·mole].

Once a droplet's size is greater than the mean free path, the rate of arrival of vapor molecules is governed by the rate of molecular diffusion to the droplet surface. Under these conditions the rate of growth is given by

$$\frac{d(d_p)}{dt} = \frac{4D_v M}{\rho_p d_p R}\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right)\phi \quad \text{for } d_p > \lambda \tag{5–4}$$

where D_v is the diffusion coefficient of the vapor molecules, $2.4 \times 10^{-5}\,\text{m}^2/\text{s}$ [0.24 cm^2/s] for water vapor at 293 K [20°C]; the subscript ∞ refers to conditions removed from the particle; and the subscript d refers to conditions right at the particle surface. During rapid condensation ($S_R > 1.05$), the temperature of the droplet T_d will be greater than the

surrounding air due to the release of heat of vaporization. The droplet temperature due to heating during condensation or cooling during evaporation can be estimated by (Hinds, 1999)

$$T_d = T_\infty + \frac{(6.65 + 0.345T_\infty + 0.0031T_\infty^2)(S_R - 1)}{1 + (0.082 + 0.00782T_\infty)S_R} \tag{5–5}$$

where T_∞ is in °C. The quantity p_d is evaluated at T_d by Eq. 5–1.

The last factor in Eq. 5–4 corrects for complications in the calculation of mass transfer by diffusion within one mean free path of the particle surface. This correction is known as the *Fuchs correction*. The Fuchs correction factor ϕ is given by Davies (1978) as

$$\phi = \frac{2\lambda + d_p}{d_p + 5.35(\lambda^2/d_p) + 3.42\lambda} \tag{5–6}$$

This factor can be omitted with little error for growing or evaporating droplets larger than about 2 μm.

Equations 5–3 to 5–5 apply only to pure materials, that is, single-component liquids without any dissolved salts or impurities. The growth rate for droplets less than the mean free path is independent of droplet size, but it is inversely proportional to droplet size for droplets larger than the mean free path.

EXAMPLE 5–3

What is the rate of growth by condensation for a 5 μm water droplet at a saturation ratio of 1.04 and a temperature of 293 K [20°C]?

Answer: Because 5 μm is greater than the mean free path (0.066 μm), we can use Eq. 5–4. We can neglect ϕ because $d_p > 2\,\mu m$.

$$\frac{d(d_p)}{dt} = \frac{4D_v M}{\rho_p R d_p}\left(\frac{P_\infty}{T_\infty} - \frac{P_d}{T_d}\right)$$

where $D_v = 2.4 \times 10^{-5}\,m^2/s$ [0.24 cm^2/s]. Because $S_R < 1.05$, $T_d \approx T_\infty = 293\,K$ and $p_d \approx p_s$ at 293 K [20°C]. Saturation vapor pressure p_∞ is given by Eq. 5–1 for $T = 273 + 20 = 293\,K$:

$$p_s = \exp\left(16.7 - \frac{4060}{293 - 37}\right) = 2.318\,kPa = 2318\,Pa$$

$$p_\infty = 1.04 \times p_s = 1.04 \times 2.318 = 2.411\,kPa = 2411\,Pa$$

Substituting in gives

$$\frac{d(d_p)}{dt} = \frac{4(2.4 \times 10^{-5})0.018}{1000(8.31)5 \times 10^{-6}}\left(\frac{2410}{293} - \frac{2318}{293}\right)$$

$$= 4.159 \times 10^{-5}(0.317) = 1.32 \times 10^{-5}\,m/s = 13.2\,\mu m/s$$

Time Required for Growth

The time required for a droplet to grow from d_1 to d_2 can be obtained by integrating Eq. 5–4 over the size limits.

$$t = \frac{\rho_p R(d_2^2 - d_1^2)}{8D_v M\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right)} \quad \text{for } d_1 >> \lambda \tag{5–7}$$

NUCLEATION

Homogeneous

The preceding section describes the growth process for pure materials once the droplets have been formed. The initial formation of the droplet from vapor is a more complicated process. Droplets can be formed in the absence of condensation nuclei, but this process, called *homogenous nucleation* or *self-nucleation*, requires large saturation ratios, usually in the range of 2 to 10, which normally occur only in special laboratory or chemical process situations. Pure water vapor at 293 K [20°C] and at a saturation ratio of 3.5 or greater spontaneously forms droplets by homogeneous nucleation. This corresponds to a Kelvin diameter of 0.0017 μm and suggests that molecular clusters of about 90 molecules are necessary for this process. A detailed description of homogenous nucleation is given by Seinfeld and Pandis (1998).

Heterogeneous

The more common formation mechanism is nucleated condensation or heterogenous nucleation. This process relies on existing submicrometer particles, called *condensation nuclei*, to serve as sites for condensation. Our natural atmosphere contains thousands of these nuclei in each cubic centimeter of air. To a first approximation, insoluble nuclei serve as passive sites on which condensation occurs for supersaturated conditions. Under supersaturated conditions, a solid nucleus with a wettable surface will have on its surface an adsorbed layer of vapor molecules. If the nucleus has a diameter greater than the Kelvin diameter for a particular condition of supersaturation, the nucleus "looks like" a droplet to surrounding vapor molecules and vapor will condense on its surface. Once condensation starts, droplet growth continues as described by Eqs. 5–3 and 5–4.

The situation with soluble nuclei is more complex and more important. Our normal atmosphere contains large numbers of soluble nuclei, formed as the solid residue left behind after the water has evaporated from a droplet containing dissolved material. Many are sodium chloride nuclei formed from droplets of sea water created by the action of waves and bubbles in the oceans. Because these soluble nuclei have a strong affinity for water, they facilitate the initial formation of droplets and enable their growth to occur at lower saturation ratios than would be the case for insoluble nuclei.

Because of the complex effect the presence of dissolved salt has on the rate of growth of a droplet, Eqs. 5–3 and 5–4 cannot be used to determine growth rates for such droplets. The stabilization time for droplets containing salt is described by Ferron and Soderholm (1990). In general dissolved salts increase the rate of growth and decrease the rate of evaporation compared with that for pure liquids. As a droplet grows by the addition of water vapor, the concentration of salt becomes more and more dilute. Consequently, it is convenient to characterize the amount of salt in a droplet not by its concentration but by the mass of salt in the droplet, a quantity that remains constant during condensation and evaporation processes. The mass of salt is also equal to the mass of the original nucleus upon which the droplet formed.

When a dissolved salt is present in a droplet there are two competing effects at work as the droplet evaporates or grows. As a droplet evaporates the concentration of salt increases, because only the water leaves. This enhances the affinity of the dissolved salt to hold water in the droplet. The other effect is the Kelvin effect that results in an increase

in the equilibrium vapor pressure required for a droplet as its size decreases. The relationship between saturation ratio and particles size for droplets containing dissolved salts is illustrated in Figure 5–1 by the three lines, called *Kohler curves*, labeled with their mass of dissolved salt.

Equilibrium Conditions

As with pure materials, the region above a given curve in Figure 5–1 represents a growth region and below the curve represents an evaporation region. Thus, if the saturation ratio is greater than 1.002, any droplet (or nuclei) with more than 10^{-15} g of sodium chloride will grow to a large droplet, although its growth rate will slow as it gets larger, as predicted by Eq. 5–4. When environmental conditions and particle size give a location on Figure 5–1 that is *below and to the left* of the peak for a given curve, a droplet will either grow or evaporate until it reaches the curve. This portion of the line represents a true equilibrium region, and the droplet will remain at that size as long as environmental conditions stay constant. This is true even if the saturation ratio is less than 1.0. Thus, there are a large number of particles in the atmosphere that will experience an increase in their size with an increase in relative humidity and a decrease with a decrease in relative humidity. The line for pure water does not have this type of equilibrium region. It represents only a demarcation between the growth (above) and evaporation (below) regions. As droplets continue to grow the concentration of dissolved salts decreases, eventually reaching the point where the droplets behave the same as pure water, and their curves in Figure 5–1 merge with that for pure water.

EVAPORATION

Rate of Evaporation

The process of evaporation of a pure liquid droplet (no dissolved salts) is similar to the process of growth except that it proceeds in the opposite direction. Evaporation will occur when the ambient partial pressure of vapor is less than the saturated vapor pressure ($p < p_s$). The rate of particle shrinkage due to evaporation can be predicted by Eq. 5–4. During evaporation, the term in parentheses will be negative, giving a negative growth rate, which represents shrinkage due to evaporation.

For volatile particles such as water or alcohol, the quantity p_d must be evaluated at the cooler conditions prevailing at the droplet surface, T_d, which is given by Eq. 5–5.

For particles larger than about 50 μm an additional correction must be included to account for the disruption in the diffusion of vapor away from the droplet surface caused by the settling of the droplet. This effect increases the rate of evaporation of 50 and 100 μm droplets by 10% and 31%, respectively. More detailed information on this effect is given by Davies (1978) and Fuchs (1959).

Drying Time

Figure 5–2 gives droplet lifetimes or drying times, that is, the time for evaporation from an initial diameter to zero for pure water droplets at three conditions of relative humidity. The graph was obtained by numerical integration of Eq. 5–4 from the initial size to zero. For particles initially larger than about 2 μm at standard conditions, ϕ in Eq. 5–4 can be neglected and the equation integrated to give droplet lifetimes.

$$t = \frac{R\rho_p d^2}{8 D_v M \left(\frac{p_d}{T_d} - \frac{p_\infty}{T_\infty} \right)} \quad \text{for initial } d_p > 2\mu\text{m} \tag{5–8}$$

EXAMPLE 5–4

Water droplets 60 μm in diameter are sprayed into 50% relative humidity air at 293 K [20°C]. How long before they evaporate completely?

Answer: Use Eq. 5–8:

$$t = \frac{R\rho_p d^2}{8D_v M\left(\frac{p_d}{T_d} - \frac{p_\infty}{T_\infty}\right)}$$

where

R = 8.31 J/K·mole
ρ_p = 1000 kg/m^3
d = 6×10^{-5} m
D_v = 2.4×10^{-5} m^2/s
T_∞ = 293 K
p_∞ = 0.5×2.34 kPa = 1.17 kPa = 1170 Pa
T_d is given by Eq. 5–5
p_d is given by Eq. 5–1 at 286.4 K.
Substituting into the original equation gives

$$t = \frac{8.31 \times 1000 \times (6 \times 10^{-5})^2}{8 \times (2.4 \times 10^{-5}) \times 0.018\left(\frac{1523}{286.4} - \frac{1170}{293}\right)} = 6.5\text{s}$$

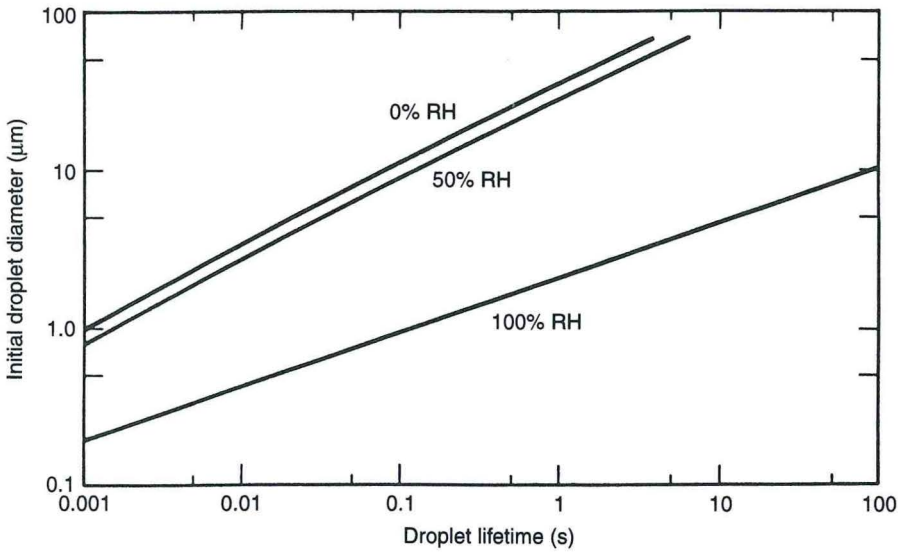

Fig. 5–2. Drying times for pure water droplets at 293 K [20°C]. RH, relative humidity. (From Hinds, 1999, reprinted with permission of John Wiley & Sons, Inc.)

TABLE 5–1. Droplet Lifetimes for Selected Materials[a]

Initial Droplet Diameter (μm)	Droplet lifetimes (s)			
	Ethyl Alcohol	Water	Mercury	Dioctyl Phthalate
0.01	4×10^{-7}	2×10^{-6}	0.005	1.8
0.1	9×10^{-6}	3×10^{-5}	0.3	740
1	3×10^{-4}	0.001	1.4	3×10^{4}
10	0.03	0.08	1200	2×10^{6}
40	0.4	1.3	2×10^{4}	4×10^{7}

[a] Calculated by Eq. 5–4 for vapor-free air at 293 K [20°C].

Source: Adapted from Hinds (1999).

Table 5–1 gives droplet lifetimes for four materials at standard conditions. It illustrates the wide range of droplet lifetimes for different materials. The effect of material properties on droplet lifetime is, to a first approximation, proportional to $\rho_p/D_v M$.

COAGULATION

Coagulation is an aerosol growth process that results from the collision of aerosol particles with each other. If the collisions are the result of Brownian motion, the process is called *thermal coagulation*; if they are the result of motion caused by external forces, the process is termed *kinematic coagulation*. Thermal coagulation is in some ways analogous to growth by condensation except that it is other particles diffusing to a particle's surface rather than molecules that causes the growth. It differs from condensation in that a supersaturation is not required, and it is a one-way process of growth with no equivalent process corresponding to evaporation. The result of many collisions between particles is an increase in particle size and a decrease in aerosol number concentration. In the absence of any loss or removal mechanisms there is no change in mass concentration as a result of coagulation.

To understand the process we look first at a simplified description of coagulation called *simple monodisperse coagulation* or *Smoluchowski coagulation*. The latter is named after the person who developed the theory in 1917. This approach illustrates the process well, is useful for analyzing many situations, and is the basis for further refinements.

Simple Monodisperse Coagulation

For simple monodisperse coagulation we make the simplifying assumptions that the particles are monodisperse, they will stick if they contact one another, and they grow slowly. The latter two are valid assumptions for most aerosol particles and situations. Aerosol particles exhibit Brownian motion and diffuse like gas molecules, but their diffusion occurs at a much slower pace; consequently, the diffusion coefficients for aerosol particles can be a million times smaller than those for gas molecules.

The derivation developed by Smoluchowski is based on the diffusion of other particles to the surface of each particle (see Hinds, 1999). It gives the rate of change (decrease) in aerosol number concentration as

$$\frac{dN}{dt} = -KN^2 \tag{5–9}$$

where N is particle number concentration and K is the coagulation coefficient. For particles larger than the gas mean free path, K is given by

TABLE 5–2. Coagulation Coefficients for Selected Particle Sizes at 293 K [20°C][a]

Particle Diameter (μm)	Coagulation Coefficient (m^3/s)
0.05	9.9×10^{-16}
0.1	7.2×10^{-16}
0.5	5.8×10^{-16}
1	3.4×10^{-16}
5	3.0×10^{-16}

[a] For coagulation coefficients in cm^3/s, multiply table values by 10^6.

Source: Adapted from Hinds (1999). Includes additional correction factors; see Hinds (1999).

$$K = 4\pi d_p D = \frac{2kTC_c}{3\eta} \quad \text{for } d_p > \lambda \tag{5–10}$$

where D is the particle diffusion coefficient m^2/s [cm^2/s], η is the gas viscosity in Pa·s [g/cm·s], and k is the Boltzmann constant, 1.38×10^{-23} J/K [1.38×10^{-16} dyn·cm/K]. The coagulation coefficient has units of m^3/s [cm^3/s] for number concentration expressed in particles/m^3 [particles/cm^3]. The coagulation coefficient is only slightly dependent on particle size being proportional to slip correction factor C_c. Table 5–2 gives coagulation coefficients for different size particles at standard conditions. In the usual situation, the extent of particle size increase is sufficiently limited that the coagulation coefficient can be considered a constant, and the rate of coagulation is proportional only to number concentration squared. Thus, coagulation is a rapid process at high number concentration and a slow one at low concentrations.

As a practical matter, the net effect of coagulation over some period of time is a more useful quantity than the rate of coagulation. The change in number concentration over a period of time t is obtained by integrating Eq. 5–9 to get

$$N(t) = \frac{N_0}{1 + N_0 K t} \tag{5–11}$$

where $N(t)$ is the number concentration at time t and N_0 is the initial number concentration. Number concentration must be expressed in particles/m^3 for K in m^3/s [particles/cm^3 for K in cm^3/s].

As number concentration decreases particle size increases, but, for a contained system with no losses, particle mass will remain constant. If number concentration decreases to one half of its original value, then the same mass (and volume) will be contained in half as many particles, so each particle will have twice its original mass (and volume). For liquid particles, particle size is proportional to the cube root of particle volume, and consequently it is also proportional to the inverse cube root of number concentration.

$$d(t) = d_0 \left(\frac{N_0}{N(t)} \right)^{1/3} \tag{5–12}$$

Thus an eightfold reduction in particle number concentration results in a doubling of particle size. Equations 5–11 and 5–12 can be combined to give a more direct expression for the change in particle size due to coagulation over a period of time t:

$$d(t) = d_0 (1 + N_0 K t)^{1/3} \tag{5–13}$$

Equations 5–12 and 5–13 are correct for liquid droplets and approximately correct for solid particles that form compact clusters. Table 5–3 gives the time required for various

TABLE 5–3. Time Required for Selected Coagulation Processes[a]

Initial Number Concentration (m^{-3})	Time for Number Concentration to Halve (s)	Time for Particle Size to Double (s)
10^{18}	0.002	0.014
10^{16}	0.2	1.4
10^{14}	20	140
10^{12}	2000 (33 min)	14,000 (4 h)
10^{10}	200,000 (55 h)	1,400,000 (16 d)

[a]Assumes simple monodisperse coagulation with $K = 5 \times 10^{-16}$ m^3/s [5×10^{-10} cm^3/s].

Source: Adapted from Hinds 1999.

initial concentrations to reach one half their number concentration and the time for particle size to double. It is apparent from Table 5–3 that whether or not coagulation can be neglected depends on the concentration and time scale under consideration. Thus, over a period of a few minutes coagulation is only important if particle number concentration exceeds 10^{12}/m^3.

Polydisperse Coagulation

The previous description of coagulation is accurate enough for a wide variety of situations, but it requires the assumption of a monodisperse aerosol. In the real case we usually have a polydisperse aerosol, and the situation is more complicated. Because the coagulation process is governed by the rate of diffusion of particles to the surface of each particle, the process is enhanced when small particles with their high diffusion coefficients diffuse to a large particle with its large surface. A 10-fold difference in particle size produces a 3-fold increase in coagulation rate, and a 100-fold difference results in more than a 25-fold increase in coagulation rate. To use Eqs. 5–11 or 5–13 for polydisperse aerosols requires the use of numerical methods because the coagulation for every combination of particle sizes has a different value of K and has to be calculated separately (Zebel, 1966). For the case of coagulation of an aerosol with a lognormal size distribution having a count median diameter (CMD) and a geometric standard deviation σ_g, an equation derived by Lee and Chen (1984) can be used to calculate the average coagulation coefficient $\overline{K}$:

$$\overline{K} = \frac{2kT}{3\eta}\left\{1 + \exp(\ln^2 \sigma_g) + \left(\frac{2.49\lambda}{CMD}\right)\left[\exp(0.5 \ln^2 \sigma_g) + \exp(2.5 \ln^2 \sigma_g)\right]\right\} \qquad (5\text{–}14)$$

This value of $\overline{K}$ can be used in place of K in Eq. 5–11 to predict the change in number concentration over a period of time t for which there is only a modest change in CMD. Equation 5–13 can be used with $\overline{K}$ to predict the increase in CMD over a time period for which $\overline{K}$ is approximately constant. For this type of calculation it is reasonable to assume that σ_g remains constant for modest changes in particle size. For large changes in particle size calculation can be done as a series of steps, each with a constant but different value of $\overline{K}$. Figure 5–3 shows the effect of polydisperse coagulation on number concentration and median size for the indicated initial condition.

Kinematic Coagulation

Kinematic coagulation is a coagulation process whereby the relative motion between particles is created by external forces rather than by Brownian motion. Brief descriptions of several such mechanisms are given below. In all cases the greater the particle number con-

EXAMPLE 5–5

A. An iron oxide fume has an initial number concentration of $10^{13}/m^3$. Assuming the aerosol is monodisperse with a diameter of 0.2 μm, what will be the number concentration and particle size after 2 minutes? Assume standard conditions.
B. Repeat the above example for a polydisperse aerosol having a CMD of 0.2 μm and σ_g of 2.0. Assume σ_g remains constant.

Answer: A. Use Eq. 5–11:

$$N(t) = \frac{N_0}{1 + N_0 K t}$$

where:

$$N_0 = 10^{13}/\text{m}^3$$

$$K = \frac{4kTC_c}{3\eta} = \frac{4(1.38 \times 10^{-23})293 \times 1.88}{3(1.81 \times 10^{-5})} = 5.6 \times 10^{-16}\,\text{m}^3/\text{s}$$

$$t = 120\text{s}$$

substituting in

$$N(t) = \frac{10^{13}}{1 + 10^{13}(5.6 \times 10^{-16})120} = 5.98 \times 10^{12}/\text{m}^3$$

Use Eq. 5–12 or 5–13 to determine the change in diamete:

$$d(t) = d_0\left(\frac{N_0}{N(t)}\right)^{1/3} = 0.2\left(\frac{10^{13}}{5.98 \times 10^{12}}\right)^{1/3} = 0.24\,\mu\text{m}$$

B. Use Eq. 5–14 to get $\overline{K}$

$$\overline{K} = \frac{2kT}{3\eta}\left[1 + \exp(\ln^2\sigma_g) + \left(\frac{2.49\lambda}{CMD}\right)[\exp(0.5\ln^2\sigma_g) + \exp(2.5\ln^2\sigma_g)]\right]$$

$$\overline{K} = \frac{2(1.38 \times 10^{-23}) \times 293}{3(1.81 \times 10^{-5})} \times \left[1 + \exp[\ln^2(2.0)] + \left(\frac{2.49 \times 0.066}{0.2}\right)(\exp[0.5\ln^2(2.0)]\right.$$

$$\left. + \exp[2.5\ln^2(2.0)])\right] = 1.489 \times 10^{-16}[6.986] = 1.04 \times 10^{-15}\,\text{m}^3/\text{s}$$

Substituting into Eq. 5–11 using $\overline{K}$ instead of K gives

$$N(t) = \frac{N_0}{1 + N_0\overline{K}t} = \frac{10^{13}}{1 + 10^{13}(1.04 \times 10^{-15})120} = 4.45 \times 10^{12}/\text{m}^3$$

$$CMD_2 = 0.2\left(\frac{10^{13}}{4.45 \times 10^{12}}\right)^{1/3} = 0.26\,\mu\text{m}$$

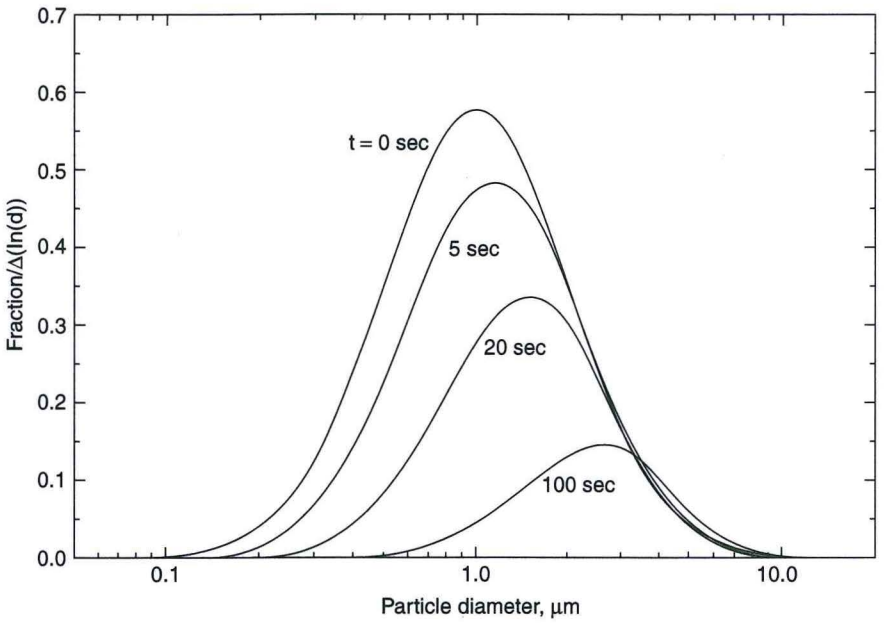

Fig. 5–3. Effect of coagulation on particle size distribution. $N_0 = 10^{14}/m^3$ [$10^8/cm^3$], initial count median diameter = 1.0 μm, and initial geometric standard deviation = 2.0. (From Hinds, 1999, reprinted with the permission of John Wiley & Sons, Inc.)

centration, the greater the rate of coagulation. In general there are no simple equations that describe these process in a complete way. More detailed information is given by Fuchs (1964) and Hinds (1999).

Because particles of different sizes settle at different rates there is a relative motion between settling particles of different sizes. The aerodynamics of the collision process is complicated, and the collision efficiency is low except for the case of very large particles, such as raindrops, settling through micrometer-sized or larger aerosol particles.

A similar process occurs when particles are projected through an aerosol at high velocity. This is an important mechanism for the capture of particles by spray droplets in certain kinds of wet scrubbers used for gas cleaning.

Gradient or shear coagulation occurs for particles moving in a flow velocity gradient. Particles on slightly different streamlines in a velocity gradient travel at different velocities and faster particles eventually overtake the slower ones. If the particles are big enough, particle contact occurs by interception.

In turbulent flow, particles follow a complex path having strong velocity gradients. Relative motion between particles arises from these gradients and from inertial projection of the particles. The resulting coagulation is called *turbulent coagulation*. This mechanism is most effective when the turbulent eddy size is the same order of magnitude as the particle stopping distance. This mechanism is only important for particles larger than about 1 μm. Generally, the more intense the turbulence, the more coagulation that results from this mechanism.

Finally, there is acoustic coagulation where intense sound waves are used to create relative motion between particles. Depending on their size, particles respond to high intensity sound waves differently; large particle may be unaffected, whereas small particles oscillate with the sound waves. The relative motion that results leads to collisions, and the process is called *acoustic coagulation*. Generally sound pressure levels exceeding 120 dB are required to produce significant coagulation.

REACTIONS

Compared with bulk materials, aerosol particles have very high ratios of surface area to mass. For example, 1 g of standard density material (1000 kg/m^3) when divided into 0.1 μm particles has a surface area of 60 m^2. Because of their large specific surface, surface area per gram, aerosols participate actively in many kinds of interaction between gas molecules and liquid or solid particles. Particles can undergo three kinds of reactions: reactions between compounds within a particle, reactions between particles of different chemical composition, and reactions between the particle and one or more chemical species in the surrounding gas phase. In the first case reactions are governed by the usual chemical kinetics. The second case is most likely controlled by the rate of arrival of other particles, which is described by the coagulation process given above. Once dissimilar particles contact each other, reactions proceed by chemical kinetics. The third case may be controlled by the rate of arrival of the appropriate gas molecules at the particle surface. The rate of arrival of gas molecules is described by the condensation growth equations given in this chapter. Absorption and adsorption are related processes that also have as one of their necessary steps the arrival of gas molecules at the particle surface.

These processes can be thought of as having three mass transfer steps in series, any one of which may be the rate-controlling step. First there is diffusion of specific gas molecules to the surface of the particle. Next is the transfer across the interface or reaction at the interface, and finally there is diffusion into the solid or liquid particle.

Reaction

In the case of a chemical reaction between the suspending gas and a particle, any of the three steps given above may control the rate of reaction. For solid particles diffusion into the interior will be relatively slow even though the distances involved are small. Diffusion into the interior of liquid particles will be more rapid and may be augmented by internal circulation. If the reaction is controlled by the rate of arrival of gas molecules at the particle surface, then the maximum rate of reaction is given by

$$R_R = \frac{2\pi d_p D_v p}{kT} \quad \text{for } d_p > \lambda \tag{5–15}$$

where R_R is the rate of reaction in molecules/s. This is equivalent to a condensation process (Hinds, 1999) under uniform temperature conditions. This situation is called a *diffusion-controlled reaction*. The process can continue until all molecules of the particle have reacted.

Absorption

The process whereby gas molecules dissolve in a liquid droplet is called *absorption*. In this process the transfer at the interface is usually not controlling, but diffusion in either the gas phase or liquid phase may be. The process can continue until the limit of solubility of the gas in the liquid is reached. This limit may change with temperature or the presence of other dissolved components.

Adsorption

Adsorption is the transfer of gas molecules from the surrounding gas to a solid surface. There are two types of adsorption that can occur on the surface of a solid particle: physical adsorption, or physisorption; and chemical adsorption, or chemisorption. Physisorption is a physical process where gas molecules are held to a particle's surface by van der Waals forces. It

occurs for all gases when the ambient temperature is below their critical temperature. It is a rapid and readily reversible process. Because the adsorption process is rapid, the diffusion of gas molecules to the particle surface is usually the rate-limiting step. The relationship between the amount of adsorbed gas and the partial pressure of the gas or vapor at a given temperature is called the *adsorption isotherm*. Physisorption is usually not significant if the saturation ratio is below 0.05, but can lead to an adsorbed layer several molecules thick when the saturation ratio is 0.8 or greater. For a particle in adsorption equilibrium, a reduction in the partial pressure of the vapor will lead to a transfer of adsorbed vapor molecules from the particle's surface to the gas.

The process of adsorption is similar to the process of condensation. Highly porous materials, like activated carbon, have enormous surface areas and contain numerous small pores and capillaries that facilitate condensation on their surface and inhibit evaporation. The isotherms for highly porous materials will differ significantly from those for smooth solids.

Chemisorption is similar except that chemical bonds are formed to hold the gas molecules on the particle's surface. It can occur above or below the critical temperature of the gas. In chemisorption only a monolayer can form, and, unlike physisorption, the process is not easily reversible because the chemical bonds are much stronger than van der Waals forces. Either the rate of gas phase diffusion or the rate of reaction can control the rate of this process. The rate of transfer slows as a complete monolayer is approached. In some cases molecules are first held to the surface by physisorption and then slowly react to attach by chemisorption. In other cases a physisorption layer may form on top of a chemisorption layer.

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