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Dynamics of Aerosol Coagulation and Condensation

The dynamic behavior of aerosol size distributions under the influence of coagulation and growth by heterogeneous condensation of gaseous species is studied. Analytical solutions are obtained to the integro-differential equation governing the aerosol size distribution density function. Two modes of coagulation (constant and linear coagulation constants) and two modes of condensation (growth independent of particle volume and linearly dependent on particle volume) are considered. The interaction of the two growth mechanisms on aerosol size distributions is elucidated.

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SCOPE

The growth of aerosols results from a variety of physical and chemical phenomena. For atmospheric aerosols, the most important phenomena are coagulation and heterogeneous condensation. Because of the strong dependence of aerosol properties, such as light scattering, on particle size, it is desirable to understand in as much detail as possible how a size distribution evolves under the influence of these two processes. The size distribution of an aerosol is described by its size distribution density function, which is governed in general by a partial integro-differential equation. For simulations of atmospheric aerosol dynamics including turbulent transport and dispersion, numerical solution of the equation will ultimately be necessary. However, analytical solutions for certain limiting cases of a spatially homogeneous aerosol can be valuable in understanding the qualitative structure of the behavior in more complex situations. The object of this work, therefore, is to obtain analytical solutions to the general equation governing the size distribution density function of an aerosol undergoing simultaneous coagulation and condensation. Beyond their utility in understanding atmospheric aerosol dynamics, the solutions should be helpful in describing the dynamic behavior of any particulate system in which coagulation and condensation are taking place.

CONCLUSIONS AND SIGNIFICANCE

Analytical solutions are obtained to the general dynamic equation governing the size distribution density function of an aerosol undergoing simultaneous growth by coagulation and heterogeneous condensation. The solutions elucidate the influences of simultaneous coagulation and condensation on the evolving size distribution of an aerosol. Because of the complexity of actual coagulation and condensation kinetics, it is necessary to assume simple functional forms for these processes to enable analytical investigation of the dynamics. Consequently, coagulation constants, independent of particle volume and dependent on the sum of the particle volumes, and condensation rates, independent of particle volume and linearly dependent on particle volume, are considered. A

dimensionless group Λ representing the ratio of the characteristic time for condensation to that for coagulation is introduced. When $\Lambda << 1$, for example, coagulation occurs much more rapidly than condensation, and size distributions tend to exhibit the broadening characteristic of coagulation. A linear coagulation rate introduces a marked broadening in size distributions relative to a constant coagulation rate at the same value of Λ. On the other hand, for a constant coagulation rate, the upper end of the size spectrum fills out more rapidly with a linear condensation rate than with a constant condensation rate. Size spectra for actual condensation growth processes can be envisioned to lie between those of the two extremes considered here. Based on an estimated value of Λ, information on the nature of the physical processes taking place can be ascertained for an aerosol for which an evolving size distribution is available.

The dynamic behavior of a population of small particles is a subject of interest in fields as wide ranging as atmospheric physics, crystallization, and colloid chemistry. In all such systems, particles grow through collisions and coalescence with other particles (coagulation) and through accretion of material in the medium containing the particles. In the case of particles in a gas, growth of particles by accretion of vapor molecules is termed heterogeneous condensation. The evolution of the size distribution of an aerosol will depend on the relative importance of the various growth mechanisms present.

The description of the dynamics of the size distribution of an aerosol resulting from coagulation and condensation involves a partial integro-differential population balance equation which generally can only be solved numerically. Because of the extreme computational difficulties inherent in attempting to solve this equation, virtually no solutions were reported until recently (Middleton and Brock, 1976). Analytical solutions of the aerosol population balance equation are available for certain special cases of pure coagulation (Scott, 1968) and pure condensation (Brock, 1972). No solutions have been obtained for the case in which coagulation and condensation occur simultaneously; yet this is often a situation of importance.

The object of this work is to obtain analytical solutions to the general equation governing the size distribution of an aerosol undergoing simultaneous coagulation and condensation. Although the equation considered is of a general nature, the results will be most applicable to atmospheric aerosols. Through the solutions it is hoped to elucidate the interplay between the two growth processes. In the next section we develop carefully the basic equation for simultaneous coagulation and condensation of a homogeneous aerosol.

FUNDAMENTAL EQUATION GOVERNING AEROSOL SIZE DISTRIBUTIONS

A spatially homogeneous aerosol of uniform chemical composition can be fully characterized by the number densities of particles of various sizes as a function of time. Define $n_k(t)$ as the number density (cm^{-3}) of particles containing k monomers, where a monomer can be considered as a single molecule of the species comprising the particle. The basic processes that influence $n_k(t)$ are coagulation and evaporation (the loss of single molecules from a k-mer). We specifically neglect processes in which a k-mer spontaneously dissociates into two particles, of sizes $\tilde{k}$ and $k - \tilde{k}$, if $\tilde{k} > 1$. (Homogeneous nucleation, the process by which original stable particles are formed, is included within the definition of coagulation.)

The dynamic equation governing $n_k(t)$, $k \geqq 2$, can be written as

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{j=1}^{k-1} \beta_{j,k-j} n_j n_{k-j} - \sum_{j=1}^{\infty} \beta_{k,j} n_k n_j - q_k n_k + q_{k+1} n_{k+1} \quad (1)$$

The first two terms on the right-hand side of (1) express the rate of change of n_k as a result of collisional (coagulation) processes, and the last two terms describe the contribution of monomer evaporation.

Equation (1) is a rigorous representation of the kinetics of a system of particles undergoing simultaneous coalescense and evaporation. It proves to be convenient, however, to represent the process of accretion of monomers by other particles in a manner analogous to that of evaporation. Thus, we define $p_k n_k$ as the rate of gain of $(k + 1)$-mers due to collision of a k-mer with a monomer, where p_k (s^{-1}) is the frequency with which a monomer collides with a k-mer. This is the process we commonly refer to as heterogeneous condensation. With this modification, (1) becomes

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{j=2}^{k-2} \beta_{j,k-j} n_j n_{k-j} - \sum_{j=2}^{\infty} \beta_{k,j} n_k n_j + p_{k-1} n_{k-1} - (p_k + q_k) n_k + q_{k+1} n_{k+1} \quad (2)$$

where $p_k = \beta_{1,k} n_1$.

In this formulation, it is assumed that the smallest particle is of size $k = 2$. No distinction has yet been made among the processes of coagulation, homogeneous nucleation, and heterogeneous condensation. In reality, there is a minimum number of monomers in a stable nucleus, call it k_o, and generally $k_o >> 2$. In the presence of a supersaturated vapor, stable clusters at size k_o will form continuously at a rate given by the classical theory of homogeneous nucleation. Let us denote the rate of formation of stable clusters containing k_o monomers from homogeneous nucleation as $r_o(t)$. Then, coagulation and heterogeneous condensation of vapor on particles of size $k \geqq k_o$ become distinct processes in (2). By changing the smallest size stable particle from 2 to k_o, (2) becomes

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{j=k_o}^{k-k_o} \beta_{j,k-j} n_j n_{k-j} - \sum_{j=k_o}^{\infty} \beta_{k,j} n_k n_j + p_{k-1} n_{k-1} - (p_k + q_k) n_k + q_{k+1} n_{k+1} + r_o(t) \delta_{k_o} \quad (3)$$

$$k = k_o, \quad k_o + 1, \quad \ldots$$

Although (3) is still a rigorous representation of the system, it is impractical to deal with discrete equations because of the enormous range of k. Thus, it is customary to replace the discrete number density $n_k(t)$ (cm^{-3}) by the continuous size distribution density function $n(v, t)$ (μm^{-3} cm^{-3}), where $v = k\Delta v$, Δv being the volume associated with a monomer. Thus, $n(v, t)dv$ is defined as the number of particles per cubic centimeter having volumes in the range v to $v + dv$. If we let $v_o = k_o\Delta v$, then (3) becomes in the limit of a continuous distribution of sizes

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_{v_o}^{v-v_o} \beta(v-\tilde{v},\tilde{v})n(v-\tilde{v},t)n(\tilde{v},t)d\tilde{v}$$

$$-\int_{v_o}^{\infty} \beta(\tilde{v},v)n(v,t)n(\tilde{v},t)d\tilde{v} - \frac{\partial}{\partial v}[\alpha_o(v)n(v,t)]$$

$$+\frac{\partial^2}{\partial v^2}[\alpha_1(v)n(v,t)] + r_o(t)\delta(v-v_o) \quad (4)$$

where

$$\alpha_o(v) = \Delta v(p_k - q_k) \quad (5)$$

$$\alpha_1(v) = \frac{\Delta v^2}{2}(p_k + q_k) \quad (6)$$

Since $p_k - q_k$ is the frequency with which a k-mer experiences a net gain of one monomer, $\alpha_o(v)$ is the rate of change of the volume of a particle of size $v = k\Delta v$. The sum $p_k + q_k$ is the total frequency with which monomers enter and leave a k-mer. $\alpha_1(v)$ assumes the role of a diffusion coefficient for the size spectrum. α_o and α_1 can be computed from kinetic theory. Brock (1972), however, has obtained relations for α_o and α_1 based on a continuous size distribution which provide additional insight into their nature. When we consider only condensational growth, if we let $m(\tilde{v}, t)$ represent the size distribution density of the small condensing nuclei, then the evolution of $n(v, t)$ is described by

$$\frac{\partial n(v,t)}{\partial t} = \int_{o}^{\tilde{v}_m} \beta(v-\tilde{v},\tilde{v})n(v-\tilde{v},t)m(\tilde{v},t)d\tilde{v}$$

$$-\int_{o}^{\tilde{v}_m} \beta(v,\tilde{v})n(v,t)m(\tilde{v},t)d\tilde{v} \quad (7)$$

where the condensing species are assumed to have volumes such that $\tilde{v} << v$, and where $\tilde{v}_m$ is the largest volume of the condensing species. By taking advantage of the fact that $\tilde{v}/v << 1$, the first integrand can be expanded in a Taylor series to yield

$$\frac{\partial n(v,t)}{\partial t} = -\frac{\partial}{\partial v}[\alpha_o(v,t)n(v,t)]$$

$$+\frac{\partial^2}{\partial v^2}[\alpha_1(v,t)n(v,t)] \quad (8)$$

where

$$\alpha_o(v,t) = \int_{o}^{\tilde{v}_m} \beta(v,\tilde{v})\tilde{v}m(\tilde{v},t)d\tilde{v} \quad (9)$$

$$\alpha_1(v,t) = \frac{1}{2}\int_{o}^{\tilde{v}_m} \beta(v,\tilde{v})\tilde{v}^2m(\tilde{v},t)d\tilde{v} \quad (10)$$

For $v >> \tilde{v}$, it is reasonable to assume that $\beta(v, \tilde{v}) = \beta(v)$, namely, that the collision rate depends only on the volume of the particle. If, in addition, we assume that all condensing nuclei are of a uniform size $\tilde{v}_1 \leqq \tilde{v}_m$, then $m(\tilde{v}, t) = M\delta(\tilde{v} - \tilde{v}_1)$, and

$$\alpha_o(v) = \beta(v)\tilde{v}_1M \quad (11)$$

$$\alpha_1(v) = \frac{1}{2}\beta(v)\tilde{v}_1^2M \quad (12)$$

where M is assumed to be constant.

Brock (1972) has suggested that the term in (8) involving α_1 can ordinarily be neglected. A quantitative criterion for judging the importance of that term can be readily developed. To do so we introduce the following variables $\eta = v/v_o$, $\epsilon = \tilde{v}_1/v_o$, and $\alpha_o^* = \alpha_o/v_o$. A common functional form for α_o (see later) is $\alpha_o^* = \alpha\eta^\gamma$, where $0 \leqq \gamma \leqq 1$. By using this form for α_o^*, together with the relation $\alpha_1 = 1/2\ \tilde{v}_1\alpha_o$ from (11) and (12), (8) becomes

$$\frac{1}{\alpha}\frac{\partial n}{\partial t} = \eta^{\gamma-1}(\eta+\epsilon\gamma)\frac{\partial n}{\partial \eta} + \gamma\eta^{\gamma-2}\left[\eta + \frac{1}{2}\epsilon(\gamma-1)\right]n$$

$$+\frac{1}{2}\epsilon\eta^\gamma\frac{\partial^2 n}{\partial \eta^2} \quad (13)$$

It is evident that $\eta >> \epsilon\gamma$, and so (13) reduces to

$$\frac{1}{\alpha}\frac{\partial n}{\partial t} = \eta^\gamma\frac{\partial n}{\partial \eta} + \gamma\eta^{\gamma-1}n + \frac{1}{2}\epsilon\eta^\gamma\frac{\partial^2 n}{\partial \eta^2} \quad (14)$$

In order for the last term on the right-hand side of (14) to be of comparable importance to the first term on the right-hand side, it is necessary that

$$\frac{\partial^2 n}{\partial \eta^2}\Big/\frac{\partial n}{\partial \eta} \geqq 0(\epsilon^{-1}) \quad (15)$$

For most actual distributions, this condition is not satisfied, and it is therefore justified to neglect the term involving α_1 in the general dynamic equation for n.

In (4), a stable particle has been assumed to have a lower limit of volume of v_o. From the standpoint of the solution of (4), it is advantageous to replace the lower limits v_o of the coagulation integrals by zero. Ordinarily this does not cause any difficulty, since the initial distribution $n(v, 0) = n_o(v)$ may be specified as zero for $v < v_o$, and no particles of volume $v < v_o$ can be produced for $t > 0$. Homogeneous nucleation provides a steady source of particles of size v_o, according to the rate defined by $r_o(t)$. Subsequently, we shall neglect homogeneous nucleation, as its inclusion is not central to our purpose here. Thus, the equation with which we shall deal is

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_{o}^{v} \beta(v-\tilde{v},\tilde{v})n(v-\tilde{v},t)n(\tilde{v},t)d\tilde{v}$$

$$-\int_{o}^{\infty} \beta(v,\tilde{v})n(v,t)n(\tilde{v},t)d\tilde{v} - \frac{\partial}{\partial v}[\alpha_o(v)n(v,t)]$$

$$(16)$$

The initial and boundary conditions are

$$n(v,0) = n_o(v) \quad (17)$$

$$n(0,t) = 0 \quad (18)$$

DESCRIPTION OF COAGULATION AND CONDENSATION PROCESSES

In order to define completely the physical problem, it is necessary to specify functional forms for the coagulation constant $\beta(v, \tilde{v})$ and the rate of growth by heterogeneous condensation $\alpha_0(v)$. General expressions for $\beta(v, \tilde{v})$ and $\alpha_0(v)$ for cases of actual interest are highly nonlinear functions of v (and $\tilde{v}$) (Hidy and Brock, 1970), necessitating numerical solution of (16). Numerical solutions of (16) are, in fact, so difficult to carry out that none were reported until recently (Middleton and Brock, 1976). Clearly, the addition of spatial variation to n along with the associated turbulent transport terms in (16) makes the evaluation of n virtually intractable. Therefore, as a prelude to such detailed numerical studies, it is valuable to examine certain special cases of coagulation and condensation which, while mathematically tractable, still retain important elements of realism with respect to the rigorously established forms of β and α_0. Analytical solutions for these special cases will enable us to examine how coagulation and condensation interact to influence an evolving size distribution. In this section, therefore, we propose functional forms of β and α_0 for subsequent use in (16).

Coagulation

Coagulation of particles in a suspension may occur through a variety of mechanisms, such as Brownian motion, turbulent diffusion, laminar shear, etc. (Hidy and Brock, 1970). For atmospheric particles, two mechanisms of interest are Brownian motion and turbulent diffusion.

The form of β for Brownian coagulation depends on the sizes of the two particles. When one particle is in the continuum regime, the coagulation frequency factor is given by the Smoluchowski equation

$$\beta(v, \tilde{v}) = \frac{2k\theta}{3\mu}\,(v^{1/3} + \tilde{v}^{1/3})\left(\frac{1}{v^{1/3}} + \frac{1}{\tilde{v}^{1/3}}\right) \tag{19}$$

In the early stages of coagulation of a monodisperse aerosol, β given by (19) is essentially a constant β_0. Fuchs (1964) has suggested that β_0 is a good approximation to β if the Knudsen numbers ($Kn = 2\lambda/d_p$) of both particles are less than 0.1 even for a polydisperse aerosol. Thus, the case of $\beta = \beta_0$ is both physically interesting and mathematically attractive.

When coagulation results from turbulent diffusion, a reasonable approximation for β is (Golovin, 1963)

$$\beta = \beta_1(v + \tilde{v}) \tag{20}$$

From a purely mathematical standpoint, the coagulation constants $\beta = \beta_0$ and $\beta = \beta_1(v + \tilde{v})$ are apparently the only two physically realistic kernels for which analytical solutions of the coagulation equation have been obtained (Scott, 1968).* Subsequently, we shall confine our attention to coagulation processes for which $\beta = \beta_0$ and $\beta = \beta_1(v + \tilde{v})$.

Condensation

The coefficient $\alpha_0(v)$ represents the rate of change of the volume of a particle of volume v by condensation of material on the particle. When the Knudsen number is less than 0.1, the rate of condensation is predicted by classical continuum diffusion theory (Hidy and Brock, 1970). In the regime

$$\alpha_0(v) = \sigma v^{1/3} \tag{21}$$

where σ involves numerical and physical constants and the difference in vapor pressures of the diffusing species in the bulk gas and at the particle surface. (For sufficiently large particles, the effect of surface curvature on the vapor pressure at the surface, the Kelvin effect, can be neglected.) If the rate determining step for condensation is a chemical reaction occurring throughout the volume of the particle, then

$$\alpha_0(v) = \sigma' v \tag{22}$$

In general, therefore, in the continuum regime condensation growth laws can be expressed in the general form

$$\alpha_0(v) = \sigma v^{\gamma} \tag{23}$$

where $0 \leq \gamma \leq 1$. For the purpose of examining limiting situations of condensation growth, we will henceforth confine our attention to the two cases $\gamma = 0$ and $\gamma = 1$ representing the two extremes of condensation, growth independent of particle size, and growth linearly proportional to particle volume.

DYNAMIC BEHAVIOR OF THE SIZE DISTRIBUTION DENSITY

The object of this section is to obtain solutions to (16) for the coagulation and condensation processes outlined in the previous section. We have selected two initial conditions and three coagulation/condensation combinations for study. Specifically, we consider the following cases:*

(1) $\beta = \beta_0$, $\alpha_0 = \sigma_1 v$ (constant coagulation rate, linear condensation rate)

(2) $\beta = \beta_1\,(v + \tilde{v})$, $\alpha_0 = \sigma_1 v$ (linear coagulation rate, linear condensation rate)

(3) $\beta = \beta_0$, $\alpha_0 = \sigma_0$ (constant coagulation rate, constant condensation rate).

Two initial distributions are employed: an exponential and a first-order gamma distribution. We define N_0 as the initial total number of particles and ν_0 as the mean volume of the initial size distribution. Then the two initial distributions are

$$n_0(v) = \frac{N_0}{\nu_0}\exp\left(-\frac{v}{\nu_0}\right) \tag{24}$$

$$n_0(v) = \frac{N_0 v}{\nu_0^2}\exp\left(-\frac{v}{\nu_0}\right) \tag{25}$$

The fact that $n_0(0)$ is nonzero for (24) does not cause difficulties, although it is not physically realistic at $v = 0$.

We begin by considering the behavior of the first two moments of the size distribution in each of the three cases. We then describe briefly the solutions in each of the three cases. Examination of the solutions and a detailed discussion are contained in the next section.

Moments of the Distributions

The first two moments of $n(v, t)$ are $M_0(t)$, the total number of particles present, and $M_1(t)$, the total volume of particles present, defined by

$$M_0(t) = \int_0^\infty n(v, t)\,dv \tag{26}$$

$$M_1(t) = \int_0^\infty v\,n(v, t)\,dv \tag{27}$$

---

* Solutions of the coagulation equation may also be obtained for $\beta = \beta_2 v\tilde{v}$; however, this kernel leads to the prediction that the total number of particles equals zero after a time $2/\beta_2 N_0 \nu_0^2$.

* The obvious fourth case, namely $\beta = \beta_1(v + \tilde{v})$, $\alpha_0 = \sigma_0$, while amenable in principle to analytical solution poses significant difficulties, and a solution cannot be obtained.

TABLE 1. MOMENTS OF THE DISTRIBUTIONS M_o AND M_1

Case	Differential equations for M_o and M_1	M_o and M_1	M_o and M_1 (dimensionless)
(1) $\beta = \beta_o$	$\frac{dM_o}{dt} = -\frac{\beta_o}{2} M_o^2$	$M_o = \frac{2N_o}{2 + \beta_o N_o t}$	$\frac{M_o}{N_o} = \frac{2}{2 + \tau/\Lambda}$
$\alpha_o = \sigma_1 v$	$\frac{dM_1}{dt} = \sigma_1 M_1$	$M_1 = N_o \nu_o \exp(\sigma_1 t)$	$\frac{M_1}{N_o \nu_o} = e^{\tau}$
(2) $\beta = \beta_1 (v + \tilde{v})$	$\frac{dM_o}{dt} = -\beta_1 M_o M_1$	$M_o = N_o \exp\left[\frac{\beta_1 N_o \nu_o}{\sigma_1}(1 - \exp \sigma_1 t)\right]$	$\frac{M_o}{N_o} = \exp\left[\frac{(1 - \exp \tau)}{\Lambda}\right]$
$\alpha_o = \sigma_1 v$	$\frac{dM_1}{dt} = \sigma_1 M_1$	$M_1 = N_o \nu_o \exp(\sigma_1 t)$	$\frac{M_1}{N_o \nu_o} = e^{\tau}$
(3) $\beta = \beta_o$	$\frac{dM_o}{dt} = -\frac{\beta_o}{2} M_o^2$	$M_o = \frac{2N_o}{2 + \beta_o N_o t}$	$\frac{M_o}{N_o} = \frac{2}{2 + \tau/\Lambda}$
$\alpha_o = \sigma_o$	$\frac{dM_1}{dt} = \sigma_o M_o$	$M_1 = N_o \nu_o \left[1 - \frac{2\sigma_o}{\beta_o N_o \nu_o} \ln\left(\frac{2}{2 + \beta_o N_o t}\right)\right]$	$\frac{M_1}{N_o \nu_o} = 1 - 2\Lambda \ln\left(\frac{2}{2 + \tau/\Lambda}\right)$

$$M_o(0) = N_o; \quad M_1(0) = N_o \nu_o$$

Equations governing $M_o(t)$ and $M_1(t)$ for all three cases are easily obtained by integrating (16) over v from 0 to ∞ and by multiplying (16) by v and then integrating, respectively. Table 1 presents the differential equations governing M_o and M_1 and their solutions for each of the three cases.

In case (1) it is clear that the total number of particles is influenced only by coagulation, and the total volume of particles is influenced only by condensation. Since the coagulation rate is independent of particle size, the growth from condensation does not affect the total number of particles. In case (2), however, the total number of particles is influenced by both coagulation and condensation because in this case the coagulation rate is volume dependent. The total particle volume is still unaffected by coagulation because the condensation growth rate is a linear function of particle volume. In case (3), as in case (1), the total number of particles is affected only by coagulation because the coagulation rate is volume independent. However, because each particle grows at the same rate independent of its volume, the total particle volume depends only on the number of particles present.

The moment relations in Table 1 will prove to be very useful when we proceed to obtaining solutions for $n(v, t)$ in the three cases.

Dimensionless Groups and Evolution of M_0 and M_1

Since there are two processes taking place, there are two fundamental characteristic times, one for coagulation and one for condensation. The ratio of these two times is the basic dimensionless group of the problem. Let us define Λ as the ratio of the characteristic time for condensation to that for coagulation. The definitions of Λ in the three cases are:

(1) $$\Lambda = \frac{\sigma_1}{\beta_o N_o}$$

(2) $$\Lambda = \frac{\sigma_1}{\beta_1 N_o \nu_o}$$

(3) $$\Lambda = \frac{\sigma_o}{\beta_o N_o \nu_o}$$

If we define dimensionless times on the basis of the characteristics times for condensation as (1) $\tau = \sigma_1 t$, (2) $\tau = \sigma_1 t$, (3) $\tau = \sigma_o t/\nu_o$, then the moments M_o and M_1 can be expressed in dimensionless form as shown in the last column of Table 1.

Figures 1 to 3 show the time evolution of M_o and M_1 in the respective dimensionless forms, M_o/N_o and $M_1/N_o\nu_o$, for each of the three cases in Table 1. The dimensionless time τ is, as noted above, based on the characteristic time for condensation. Thus, the value of Λ governs the relative rates of coagulation and condensation. For example, for $\Lambda = 10$, the rate of condensation is ten times faster than the rate of coagulation. Figures 1 to 3 show, therefore, the effect of widely varying condensation and coagulation rates ($\Lambda = 0.1$, 1, 10) on the number of particles and the total volume of particles.

When the volume dependence of the condensation rate is linear, that is, $\alpha_o = \sigma_1 v$, variation of Λ has no effect on the evolution of the total particle volume of the system. This occurs because each particle grows at a rate dependent on its volume. Thus, in Figures 1 and 2, there is only a single curve for $M_1/N_o\nu_o$. The total number of particles decreases more rapidly when $\beta = \beta_1(v + \tilde{v})$ than when $\beta = \beta_o$ because coagulation becomes more efficient as particles grow when β is volume dependent. It is evident that in condensation dominated systems ($\Lambda \geqq 10$), the total number of particles is relatively insensitive to the particular coagulation mechanism. In the coagulation dominated regime ($\Lambda \leqq 0.1$), the linear coagulation mechanism is clearly more efficient in removing particles than is the constant coagulation mechanism.

In case (3) ($\alpha_o = \sigma_o$ and $\beta = \beta_o$) M_1 is influenced by the coagulation rate. Since condensation is size independent, the overall rate of growth is dependent only on the number of particles present. The more efficient the coagulation mechanism, the faster the number of particles is depleted and the slower the rate of growth by condensation. This effect is evident by the decrease in the total volume curves for decreasing Λ. The time evolution of M_o is identical to that shown in Figure 1.

Pure Coagulation and Pure Condensation

Solutions of the coagulation equation

$$\frac{\partial n}{\partial t} = \frac{1}{2}\int_0^v \beta(v - \tilde{v}, \tilde{v})\, n(v - \tilde{v}, t)\, n(\tilde{v}, t)\, d\tilde{v} - \int_0^\infty \beta(v, \tilde{v})\, n(v, t)\, n(\tilde{v}, t)\, d\tilde{v} \quad (28)$$

for the cases of $\beta = \beta_o$ and $\beta = \beta_1(v + \tilde{v})$ are given

TABLE 2. SIZE DISTRIBUTION DENSITY FUNCTIONS $n(v, t)$ FOR PURE COAGULATION
INITIAL SIZE DISTRIBUTION $n_o(v)$

Coagulation constant β	$\frac{N_o}{v_o}\exp\left(-\frac{v}{v_o}\right)$	$\frac{N_o v}{v_o^2}\exp\left(-\frac{v}{v_o}\right)$
β_o	$\frac{(1-T)^2}{v_o} N_o \exp\left[-(1-T)\frac{v}{v_o}\right]$	$\frac{(1-T)^2}{\sqrt{T}}\frac{N_o}{v_o}\exp\left(-\frac{v}{v_o}\right)\sinh\left(\frac{v\sqrt{T}}{v_o}\right)$
$\beta_1(v+\tilde{v})$	$\frac{1-T}{\sqrt{T}}\frac{N_o}{v}\exp\left(-(1+T)\frac{v}{v_o}\right) I_1\left(2\sqrt{T}\frac{v}{v_o}\right)$ $T \equiv 1 - \frac{M_o}{N_o}$	$(1-T)\frac{N_o}{v_o}\exp\left(-\frac{(2+T)v}{2v_o}\right)\sum_{k=0}^{\infty}\frac{T^k\left(\frac{v}{v_o}\right)^{3k+1}}{2^k(k+1)!\,(2k+1)!}$

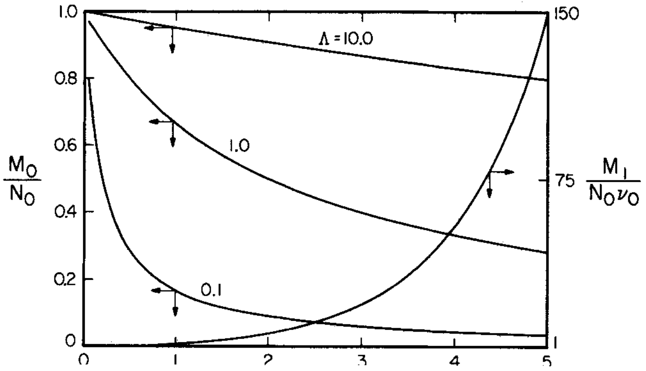

Fig. 1. Time evolution of number and volume fraction for linear condensation and constant coagulation: $\tau = \sigma_1 t$, $\Lambda = \sigma_1/\beta_0 N_0$.

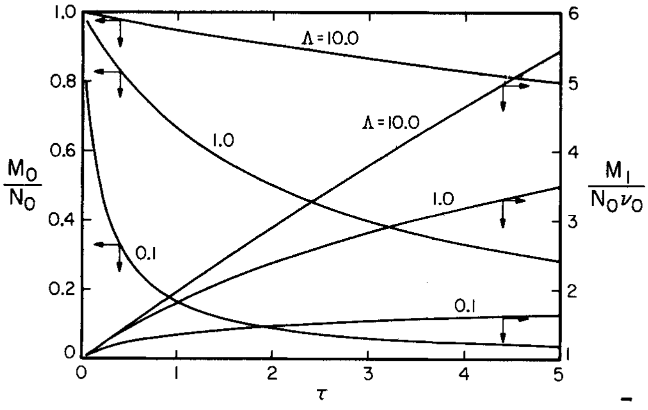

Fig. 3. Time evolution of number and volume fraction for constant condensation and constant coagulation: $\tau = \sigma_0 t/\nu_0$, $\Lambda = \sigma_0/\beta_0 N_0\nu_0$.

in Table 2. Solutions are presented for both coagulation constants for initial condition (24) and for $\beta = \beta_o$ for initial condition (25). The size distribution density in the two cases of pure condensation $\alpha_o = \sigma_o$ and $\alpha_o = \sigma_1 v$ are, respectively

$$n(v,t) = \begin{cases} n_o(v-\sigma_o t) & v - \sigma_o t > 0 \\ 0 & v - \sigma_o t < 0 \end{cases} \tag{29}$$

$$n(v,t) = n_o[\exp(-\sigma_1 t)]\exp(-\sigma_1 t) \tag{30}$$

Figure 4 shows the size distribution density at various times for the cases of constant ($\alpha_o = \sigma_o$) and linear ($\alpha_o = \sigma_1 v$) condensation rates. Figure 5 presents the same comparison for pure coagulation. In all subsequent plots, the dimensionless ordinate and abscissa of Figures 4 and 5 will be used. The abscissa is the logarithm of the ratio v/ν_o, whereas the ordinate is the dimensionless

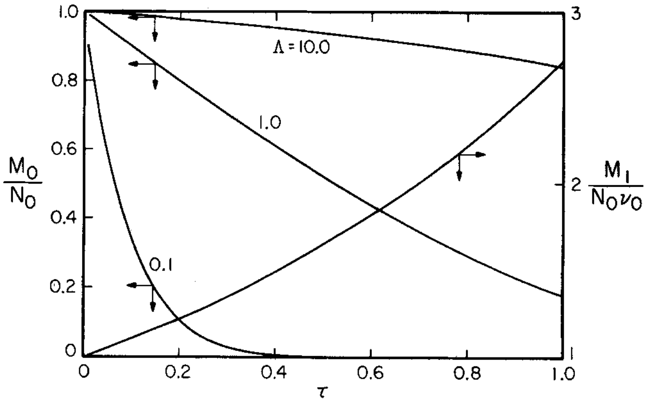

Fig. 2. Time evolution of number and volume fraction for linear condensation and linear coagulation: $\tau = \sigma_1 t$, $\Lambda = \sigma_1/\beta_1 N_0\nu_0$.

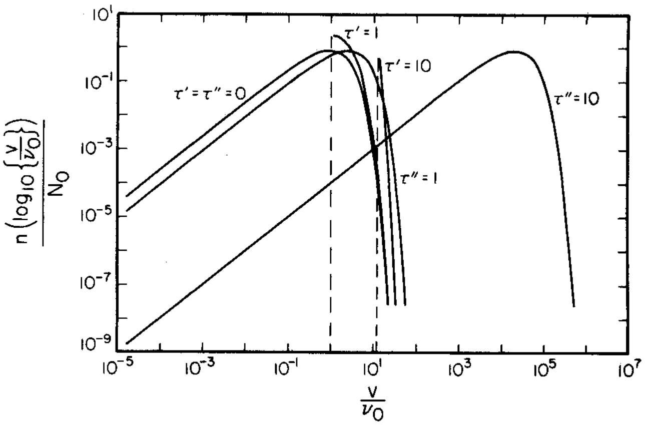

Fig. 4. Pure condensation particle size spectra for constant condensation ($\tau' = \sigma_0 t/\nu_0$) and linear condensation ($\tau'' = \sigma_1 t$).

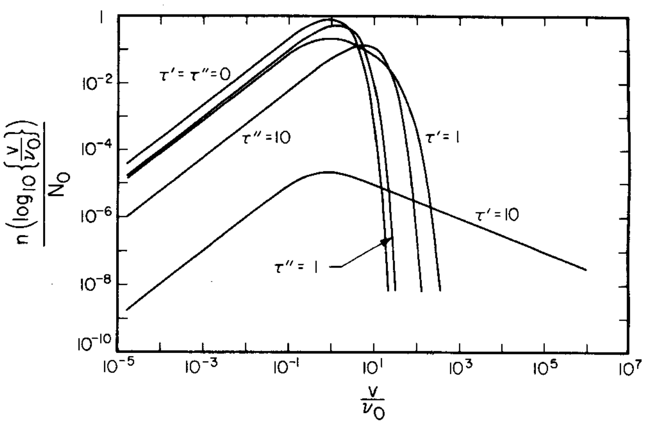

Fig. 5. Pure coagulation particle size spectra for constant coagulation ($\tau'' = \beta_0 N_0 t$) and linear coagulation ($\tau' = \beta_1 N_0\nu_0 t$).

number density corresponding to the abscissa. We note that the ordinate of Figures 4 and 5 is related to $n(v, t)$ by

$$n\left[\log\left(\frac{v}{\nu_o}\right), t\right] = 2.303v\, n(v, t) \qquad (31)$$

In Figure 4 the dimensionless times τ' and τ'' are defined for the two condensation processes. The discontinuous nature of the size distribution is evident with a constant condensation rate. Since all particles grow at the same rate, there remain at any given time, no particles of volume less than $\sigma_o t$. Also, because of the constant growth rate, the relative volume increase becomes smaller for larger particles. The size distribution becomes more and more narrow for long times approximately centered about $v = \sigma_o t$.

The linear condensation growth rate ($\alpha_o = \sigma_1 v$) is characterized by a steady accumulation of particles in the larger sizes. However, unlike the situation of a constant condensation rate, the smaller particles are never fully depleted because of the vanishingly small growth rate for small volumes.

In Figure 5 the normalized size distributions for constant and linear coagulation rates are compared at various times. Note that the characteristic times are now based on the coagulation process. As expected, a linear coagulation rate results in a pronounced shift of the size distribution to larger sizes and a general spreading of the upper end of the size spectrum relative to that for a constant coagulation rate.

Size Distribution Density Function: Case (1)

In case (1), (16) becomes

$$\frac{\partial n(v, t)}{\partial t} + \sigma_1 \frac{\partial}{\partial v}(vn) = \frac{\beta_o}{2}\int_o^v n(v - \tilde{v}, t)n(\tilde{v}, t)d\tilde{v} - \beta_o n(v, t)M_o(t) \qquad (32)$$

The solution of (32) proceeds through Laplace transformation with respect to v to give an equation for $\bar{n}(s, t) = L[n(v, t)]$. If we define $\bar{p}(s, T) = 2\bar{n}(s, t)/(1 - T)^2$, where $T = 1 - M_o/N_o$, the resulting equation for $\bar{p}(s, T)$ is

$$\frac{\partial \bar{p}}{\partial T} - 2\Lambda \frac{s}{(1 - T)^2}\frac{\partial \bar{p}}{\partial s} = \frac{\bar{p}^2}{2N_o} \qquad (33)$$

$$n(v, t) = \frac{N_o}{\nu_o}(1 - T)^2 \exp\left(-\frac{2\Lambda T}{1 - T}\right) \exp\left[-\frac{v}{\nu_o}(1 - T)\exp\left(-\frac{2\Lambda T}{1 - T}\right)\right] \qquad (36)$$

and

$$n(v, t) = \frac{N_o(1 - T)^2}{\nu_o\sqrt{T}}\exp\left(-\frac{2\Lambda T}{1 - T}\right) \exp\left[-\frac{v}{\nu_o}\exp\left(-\frac{2\Lambda T}{1 - T}\right)\right] \sinh\left[\frac{v}{\nu_o}\sqrt{T}\exp\left(-\frac{2\Lambda T}{1 - T}\right)\right] \qquad (37)$$

Size Distribution Density Function: Case (2)

The basic equation for $n(v, t)$ in case (2) is

$$\frac{\partial n}{\partial t} + \sigma_1 \frac{\partial}{\partial v}(vn) = \frac{\beta_1}{2}\int_o^v vn(v - \tilde{v}, t)n(\tilde{v}, t)d\tilde{v} - \beta_1 n(v, t)[vM_o(t) + M_1(t)] \qquad (38)$$

The dimensionless time which is most convenient for this case is

$$T = 1 - \frac{N_o\nu_o}{M_1(t)} = 1 - \exp \tau \qquad (39)$$

Again, the solution is carried out through a Laplace transform with respect to v. If we let

$$\bar{p}(s, T) = \exp\left[\frac{1}{\Lambda(1 - T)}\right]\bar{n}(s, \tau) \qquad (40)$$

then $\bar{p}(s, T)$ is governed by

$$(1 - T)\frac{\partial \bar{p}}{\partial T} - \left\{s + \frac{1}{\Lambda\nu_o}\exp\left[-\frac{1}{\Lambda(1 - T)}\right] \left[\exp\left(\frac{1}{\Lambda}\right) - \frac{\bar{p}}{N_o}\right]\right\}\frac{\partial \bar{p}}{\partial_s} = 0 \qquad (41)$$

Equation (41) is solved by the method of characteristics. In this case we consider only initial condition (24), the exponential distribution since initial condition (25) leads to an analytically intractable situation:*

$$\bar{p}(s, T) = \frac{2(1 - T)(N_o/\nu_o)\exp(1/\Lambda)}{s + \dfrac{(1 - T)(2 - \omega)}{\nu_o} \pm \sqrt{\left(s + \dfrac{(1 - T)(2 - \omega)}{\nu_o}\right)^2 - \left[\dfrac{2(1 - T)}{\nu_o}\sqrt{(1 - \omega)}\right]^2}} \qquad (42)$$

Equation (33) can be solved by the method of characteristics for each of the initial conditions (24) and (25) to give, respectively

$$\bar{p}(s, T) = \frac{2\dfrac{N_o}{\nu_o}\exp\left(-\dfrac{2\Lambda T}{1 - T}\right)}{s + \dfrac{(1 - T)}{\nu_o}\exp\left(-\dfrac{2\Lambda T}{1 - T}\right)} \qquad (34)$$

and

$$\bar{p}(s, T) = \frac{2N_o/\nu_o^2}{\left[s\exp\left(\dfrac{2\Lambda T}{1 - T}\right) + \dfrac{1}{\nu_o}\right]^2 - \dfrac{T}{\nu_o^2}} \qquad (35)$$

Upon inverting (34) and (35), we obtain, respectively (Roberts and Kaufman, 1966)

where

$$\omega = \exp\left[-\frac{T}{\Lambda(1 - T)}\right] \qquad (43)$$

The positive root in the denominator of (42) is found to lead to the physically realistic solution. Upon inverting (42) we obtain (Roberts and Kaufman, 1966)

$$n(v, t) = \frac{N_o\omega}{v\sqrt{1 - \omega}}\exp\left[-(1 - T)(2 - \omega)\frac{v}{\nu_o}\right] I_1\left[2(1 - T)\sqrt{1 - \omega}\frac{v}{v_o}\right] \qquad (44)$$

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* The resultant equation for s_o is cubic, the solution of which (in terms of s) leads to an analytically intractable inversion.

where $I_1(\cdot)$ is the modified Bessel function of the first kind of order one.

Size Distribution Density Function: Case (3)

The basic differential equation for $n(v, t)$ in case (3) is

$$\frac{\partial n}{\partial t} + \sigma_o \frac{\partial n}{\partial v} = \frac{\beta_o}{2} \int_o^v n(v - \tilde{v}, t) n(\tilde{v}, t) d\tilde{v} - \beta_o n(v, t) M_o(t) \quad (45)$$

The dimensionless time appropriate for this case is $T = N_o/M_o - 1$. Taking Laplace transform of (45), and introducing T, we obtain

$$\frac{\partial \overline{n}(s, T)}{\partial T} + 2\left(\Lambda \nu_o s + \frac{1}{1 + T}\right) \overline{n} = \frac{\overline{n}^2}{N_o} \quad (46)$$

where it has been assumed that $n(0, t) = 0$. We now let $\chi = 1 + T$ and define $\overline{p}(s, \chi) = \chi^2 \exp(2\Lambda\nu_o s\chi)$ $\overline{n}(s, T)$, obtaining

$$\frac{\partial \overline{p}}{\partial \chi} = \frac{\exp(-2\Lambda\nu_o s\chi)}{N_o\chi^2} \overline{p}^2 \quad (47)$$

Integrating (47), we obtain

$$\frac{1}{\overline{p}(s, \chi)} = \frac{1}{\overline{p}(s, 1)} - \frac{1}{N_o} \int_1^{\chi} \frac{\exp(-2\Lambda\nu_o s\eta)}{\eta^2} d\eta \quad (48)$$

which can be expressed as (Abramowitz and Stegun, 1965)

$$\frac{1}{\overline{p}(s, \chi)} = \frac{1}{\overline{p}(s, 1)} - \frac{2\Lambda\nu_o s}{N_o} [\Gamma(-1, 2\Lambda\nu_o s) - \Gamma(-1, 2\Lambda\nu_o s\chi)] \quad (49)$$

where $\Gamma(a, b)$ is the incomplete gamma function.

If we note that (Abramowitz and Stegun, 1965)

$$E_n(z) = z^{n-1}\Gamma(1 - n, z) \quad (50)$$

where $E_n(z)$ is the exponential integral of the n^{th} kind, (49) can be written as

$$\frac{1}{\overline{p}(s,\chi)} = \frac{1}{\overline{p}(s, 1)} - \frac{2\Lambda\nu_o s}{N_o}\left[\frac{E_2(2\Lambda\nu_o s)}{2\Lambda\nu_o s} - \frac{E_2(2\Lambda\nu_o s\chi)}{2\Lambda\nu_o s\chi} \right] \quad (51)$$

We note that

$$\overline{p}(s, 1) = \exp(2\Lambda\nu_o s)\overline{n}_o(s) \quad (52)$$

For $n_o(v)$ given by (24) and (25)

$$\overline{p}(s, 1) = \frac{N_o \exp(2\Lambda\nu_o s)}{1 + s\nu_o} \quad (53)$$

and

$$\overline{p}(s, 1) = \frac{N_o \exp(2\Lambda\nu_o s)}{(1 + s\nu_o)^2} \quad (54)$$

respectively.

Substituting (53) or (54) into (51), and returning to $\overline{n}(s, \chi)$, we obtain

$$\overline{n}(s, \chi) = \frac{N_o \exp[-2\Lambda\nu_o s(\chi - 1)]/\chi^2}{1 + \nu_o s - 2\Lambda\nu_o s \exp(2\Lambda\nu_o s) \left[\frac{E_2(2\Lambda\nu_o s)}{2\Lambda\nu_o s} - \frac{E_2(2\Lambda\nu_o s\chi)}{2\Lambda\nu_o s\chi} \right]} \quad (55)$$

and

$$\overline{n}(s, \chi) = \frac{N_o \exp[-2\Lambda\nu_o s(\chi - 1)]/\chi^2}{(1 + \nu_o s)^2 - 2\Lambda\nu_o s \exp(2\Lambda\nu_o s) \left[\frac{E_2(2\Lambda\nu_o s)}{2\Lambda\nu_o s} - \frac{E_2(2\Lambda\nu_o s\chi)}{2\Lambda\nu_o s\chi} \right]} \quad (56)$$

respectively

Equations (55) and (56) cannot be readily inverted. Thus, we investigate the solution for the limiting cases $\Lambda\nu_o s << 1$ and $\Lambda\nu_o s\chi << 1$.

Physically, $\nu_o s << 1$ implies a solution valid in the upper end of the size spectrum, and $\Lambda << 1$ implies a coagulation dominated regime. So long as χ remains of order 1, $\Lambda\nu_o s << 1$ implies $\Lambda\nu_o s\chi << 1$, and no apparent restriction on time [other than $\chi = 0(1)$] is necessary. Hence, we would expect that, for $\chi = 0(1)$, the solution in the regime of approximately equal condensation/coagulation rates ($\Lambda \approx 1$) will be valid only for very large particles, whereas a slightly wider spectrum will be valid under coagulation dominated regimes ($\Lambda < 1$). Also, as condensation begins to dominate coagulation, we would expect that the solution would break down.

By employing the relationships that (Abramowitz and Stegun, 1965)

$$E_2(z) = \exp(-z) - zE_1(z) \quad (57)$$

$$E_1(z) \cong -\gamma_1 - \ln z + z + 0(z^2) \quad (58)$$

where γ_1 is Euler's constant, (55) and (56) can be simplified under the constraints on $\Lambda\nu_o s$ outlined above. Equations (55) and (56) become

$$\overline{n}(s, \chi) = \frac{N_o \exp[-2\Lambda\nu_o s(\chi - 1)]/\chi^2}{\left[1 - 2\Lambda\left(\frac{\chi - 1}{\chi} - \ln\chi\right)\right] s\nu_o + \frac{1}{\chi}} \quad (59)$$

and

$$\overline{n}(s, \chi) = \frac{N_o \exp[-2\Lambda\nu_o s(\chi - 1)]/\chi^2}{\left\{ 1 - (2\Lambda)^2\left[\chi - 1 - \ln\chi - \frac{(\chi - 1)^2}{\chi}\right]\right\} (\nu_o s)^2 + \left\{1 - \Lambda\left[\frac{(\chi - 1)}{\chi} - \ln\chi\right]\right\} 2\nu_o s + \frac{1}{\chi}} \quad (60)$$

Equations (59) and (60) were obtained in a slightly different manner. Equation (59) was obtained by linearization of all terms involving $\Lambda\nu_o s$ and $\Lambda\nu_o s\chi$, such as the exponential and exponential integral functions found in the denominator. Equation (60), on the other hand, was obtained by quadratically approximating the same functions in the denominator. The quadratic approximation is necessary in the case of initial condition (25) in order to retain the ability to regenerate exactly the initial distribution at time $t = 0$. The linearization of (59) is acceptable because the inversion of initial condition (24) involves only first-order terms in s. Indeed, (55) could be (and has been) solved with quadratic approximations

TABLE 3. SUMMARY OF THE SIZE DISTRIBUTION DENSITY FUNCTIONS

INITIAL CONDITION $n_o(v)$

Case	$\frac{N_o}{\nu_o}\exp\left(-\frac{v}{\nu_o}\right)$	$\frac{N_o v}{\nu_o^2}\exp\left(-\frac{v}{\nu_o}\right)$
(1) $\alpha_o = \sigma_1 v$ $\beta = \beta_o$	$\frac{M_o^2}{M_1}\exp\left(-\frac{M_o}{M_1}v\right)$	$\frac{M_o^2}{M_1}\frac{1}{\sqrt{1-M_o/N_o}}\exp\left(-\frac{N_o v}{M_1}\right)\sinh\left(\sqrt{1-\frac{M_o}{N_o}}\frac{N_o v}{M_1}\right)$
(2) $\alpha_o = \sigma_1 v$ $\beta = \beta_1(v+\tilde{v})$	$\dfrac{\frac{M_o^2}{M_1}\exp\left[-\frac{M_o}{M_1}\left(\frac{2N_o}{M_o}-1\right)v\right]I_1\left(2\sqrt{1-\frac{M_o}{N_o}}\frac{N_o v}{M_1}\right)}{\frac{M_o v}{M_1}\sqrt{1-\frac{M_o}{N_o}}}$	
(3) $\alpha_o = \sigma_o$ $\beta = \beta_o$	$\frac{M_o^2/M_1}{1-2\Lambda\nu_o\left(\frac{N_o-M_o}{M_1}\right)}\exp\left[-\frac{\frac{M_o}{M_1}\left(v-2\Lambda\nu_o\left(\frac{N_o}{M_o}-1\right)\right)}{1-2\Lambda\nu_o\left(\frac{N_o-M_o}{M_1}\right)}\right]$	$\frac{M_o/\nu_o^2}{R[g_1-g_2]}\left\{\exp\left[g_1\left(v-2\Lambda\nu_o\left(\frac{N_o}{M_o}-1\right)\right)\right] - \exp\left[g_2\left(v-2\Lambda\nu_o\left(\frac{N_o}{M_o}-1\right)\right)\right]\right\}$

Note: g_1, g_2, Q, and $\mathcal{R}$ are defined in (63) to (66).

throughout, yielding a cumbersome but slightly more accurate solution. However, the difference between the solutions obtained by the linear and quadratic approximations is marginal. Also, as will become evident, the initial condition is obtained readily from the inversion of (59), whereas reduction to the initial condition for the solution obtained by quadratic approximation to (55) can only be shown by successive application of L' Hopital's rule.

It should also be noted that there is no need to approximate the exponential found in the numerator of both Equations (55) and (56). In the Laplace inversion, such a term simply shifts the solution by the value of the argument of the function.

Inversion of Equations (59) and (60) yields [for $v \geqq \Lambda\nu_o(\chi - 1)$] (Roberts and Kaufman, 1966)

$$n(v,\chi) = \frac{(N_o/\nu_o)\exp\left(-\dfrac{\frac{v}{\nu_o} - 2\Lambda(\chi-1)}{\chi - 2\Lambda(\chi - 1 - \chi\ln\chi)}\right)}{\chi[\chi - 2\Lambda(\chi - 1 - \chi\ln\chi)]} \tag{61}$$

and

$$n(v,\chi) = \frac{N_o}{\nu_o^2}\frac{1}{\chi R(\chi)}\frac{1}{g_1-g_2}[\exp\{g_1[v - 2\Lambda\nu_o(\chi-1)]\} - \exp\{g_2[v - 2\Lambda\nu_o(\chi-1)]\}] \tag{62}$$

where

$$g_1 = -\frac{Q+\sqrt{Q^2-R}}{R\nu_o} \tag{63}$$

$$g_2 = -\frac{Q-\sqrt{Q^2-R}}{R\nu_o} \tag{64}$$

$$Q(\chi) = \chi - \Lambda(\chi - 1 - \chi\ln\chi) \tag{65}$$

$$R(\chi) = \chi - (2\Lambda)^2[\chi(\chi - 1 - \ln\chi) - (\chi-1)^2] \tag{66}$$

To show that (61) reduces to the initial condition (24) at $t = 0$, ($\chi = 1$) is straightforward. That (62) to (66) reduce to (25) can be shown by one application of L' Hopital's rule.

Summary of the Solutions

In Table 3 we summarize the solutions for $n(v, t)$ in the three cases studied for the two initial conditions considered. [As noted, an analytical solution for case (2) and initial condition (25) cannot be obtained.] It is important to note that the solutions in case (3) are valid only for large volumes and for $\chi = 0(1)$, that is, $N_o/M_o \lesssim 10$. In the next section we discuss the properties of these solutions. In that section only results for initial condition (24) are exhibited. Results for initial condition (25) are qualitatively similar.

DISCUSSION OF THE SOLUTIONS

Figures 6 to 8 show the normalized size distribution density function for case (1), that is, $\alpha_o = \sigma_1 v$, $\beta = \beta_o$, for $\tau = 0.1$, 1, and 10, and $\Lambda = 0.1$, 1, 10. Figures 9 to 11 and 12 to 14 present cases (2) and (3), respectively, similarly, with the exception that the maximum value of τ in case (2) is 2 rather than 10. We note that in each case τ is defined on the basis of the characteristic time for condensation. When $\Lambda = 1$, the condensation and coagulation time scales are equivalent. However, when

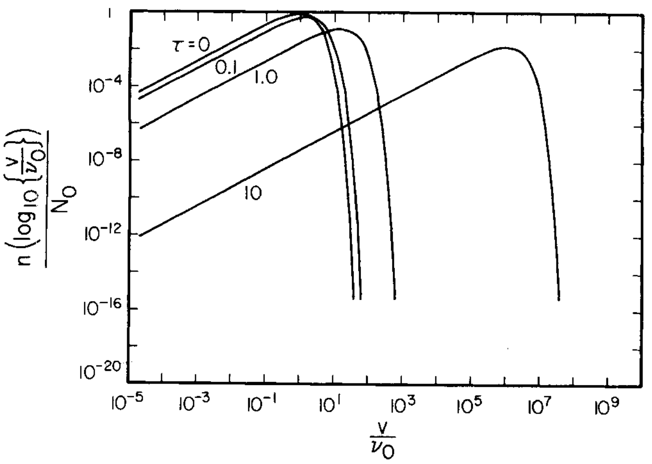

Fig. 6. Particle size spectra for linear condensation and constant coagulation, $\Lambda = 0.1$.

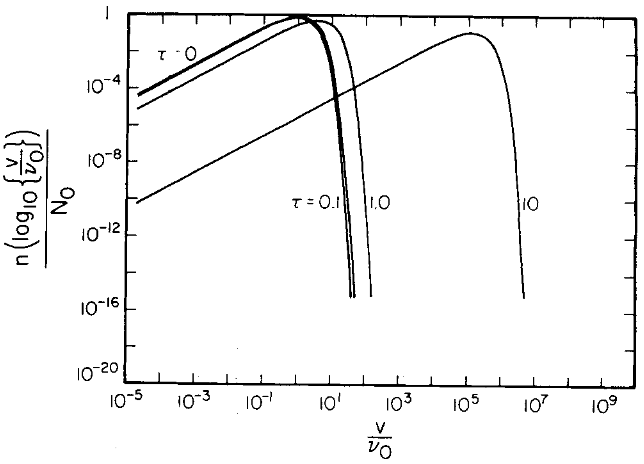

Fig. 7. Particle size spectra for linear condensation and constant coagulation, $\Lambda = 1.0$.

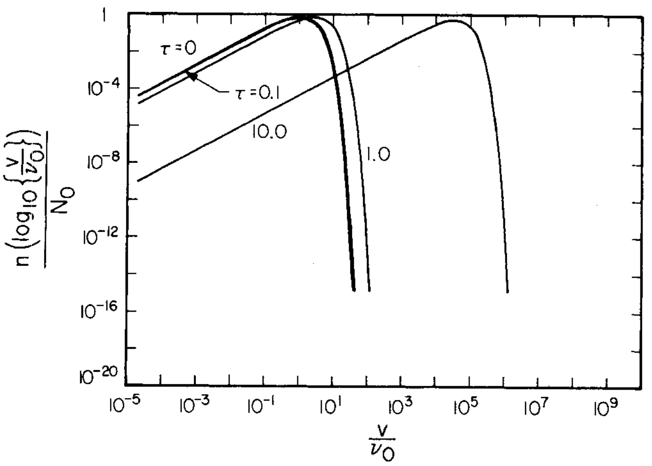

Fig. 8. Particle size spectra for linear condensation and constant coagulation, $\Lambda = 10.0$.

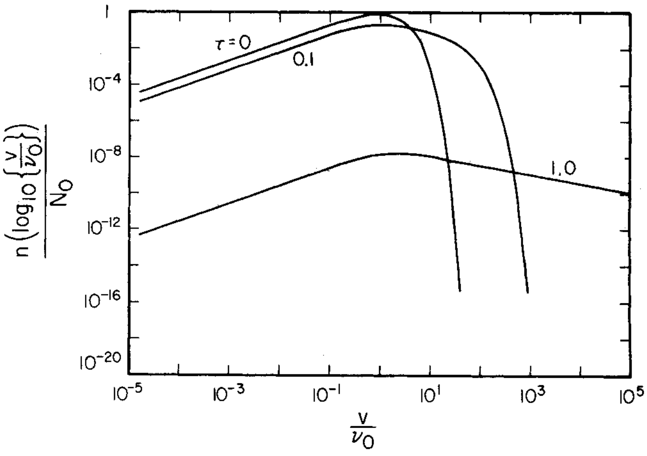

Fig. 9. Particle size spectra for linear condensation and linear coagulation, $\Lambda = 0.1$.

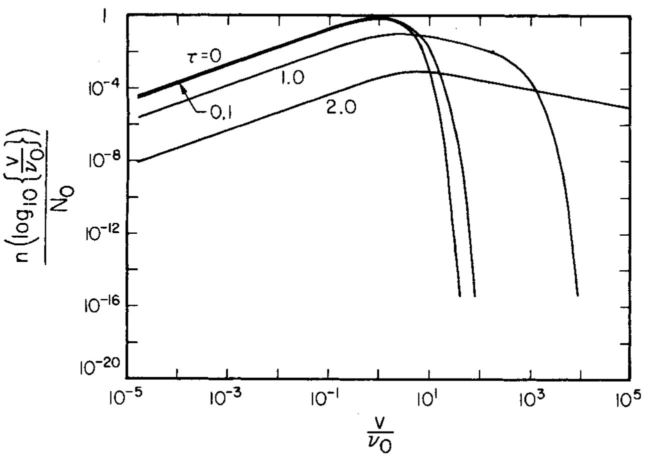

Fig. 10. Particle size spectra for linear condensation and linear coagulation, $\Lambda = 1.0$.

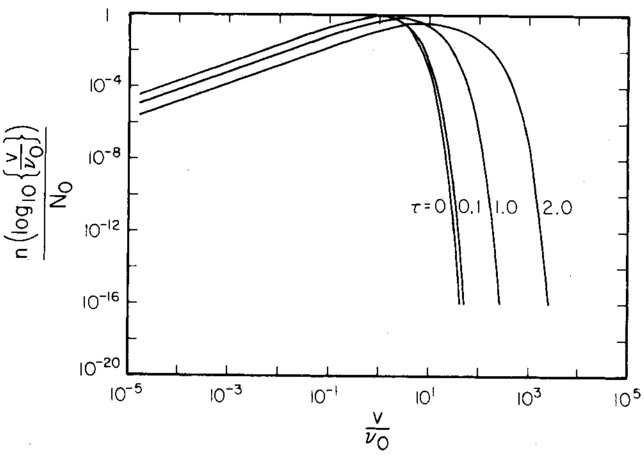

Fig. 11. Particle size spectra for linear condensation and linear coagulation, $\Lambda = 10.0$.

$\Lambda = 0.1$, coagulation is ten times faster than condensation. Thus, when $\Lambda = 0.1$ and $\tau = 10$, coagulation has proceeded for 100 characteristic times, while condensation has proceeded for 10. On the other hand, when $\Lambda = 10$ and $\tau = 10$, condensation has taken place for ten characteristic times and coagulation has taken place for only one. Clearly, all combinations of τ and Λ can be viewed in terms of the time scales of the two phenomena taking place.

As Λ varies in case (1) (Figures 6 to 8) from 0.1 to 10, the size distributions tend to narrow. At $\Lambda = 0.1$, coagulation is occurring rapidly, tending to spread the upper end of the size spectrum. When $\Lambda = 10$, growth occurs mainly by condensation, and the size distribution does not exhibit the broadening characteristic of coagulation growth. In case (2) (Figures 9 to 11), the size distributions are significantly influenced by the value of Λ. A linear coagulation rate introduces a marked broadening in the distributions relative to a constant coagulation rate. As Λ varies from 0.1 (coagulation dominated) to 10 (condensation dominated) in case (2), the size distribution at $\tau = 1$ becomes markedly sharper. For

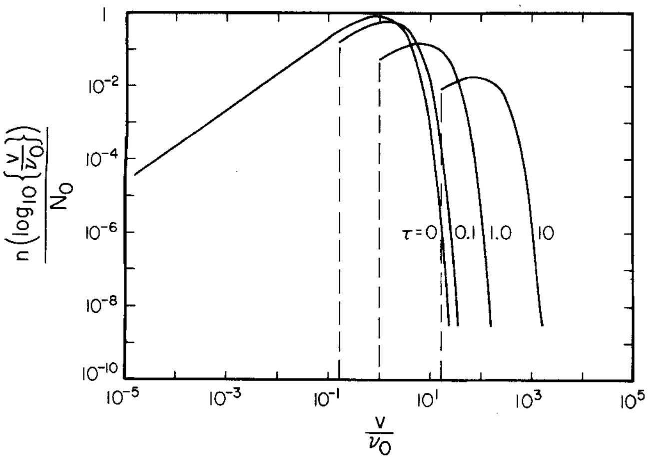

Fig. 12. Particle size spectra for constant condensation and constant coagulation, $\Lambda = 0.1$.

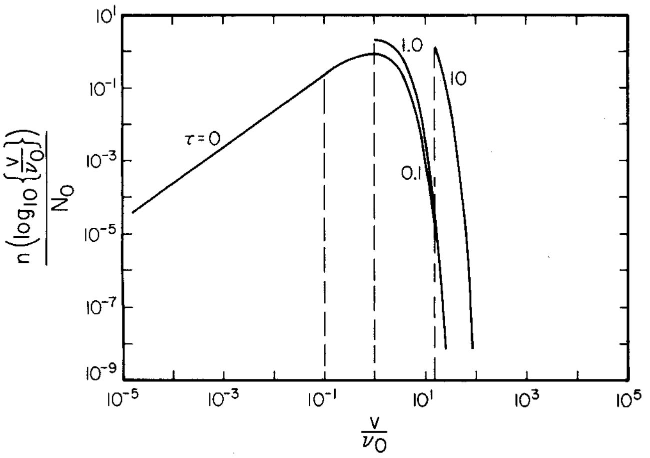

Fig. 14. Particle size spectra for constant condensation and constant coagulation, $\Lambda = 10.0$.

$\Lambda = 0.1$, a comparison of cases (1) and (2) (Figures 6 and 9) reveals the strong influence of the volume dependence of the coagulation rate on the aerosol size distribution. The reason is, of course, that when the coagulation rate is volume dependent, particles tend to coagulate more rapidly as they grow. (We exclude the situation in which the coagulation rate may depend inversely on volume.)

For a constant coagulation rate, the upper end of the size spectrum fills out more rapidly with a linear condensation rate (Figures 6 to 8) than with a constant condensation rate (Figures 12 to 14). The reason is that larger particles tend to grow faster when the condensation rate is volume dependent. In addition, a constant condensation rate establishes a sharp cutoff in the lower end of the size spectrum, as already observed in Figure 4. The cutoff volume is insensitive to Λ at any given time, since the establishment of a cutoff volume is a condensation controlled phenomenon. It is not independent of Λ, however. Large coagulation rates could serve to shift the cutoff volume to a point larger than expected from condensational effects alone. Finally, the limiting solutions for case (3) in Figures 12 to 14 appear to be valid over a wider range than first expected because of the correct prediction of the cutoff volume.

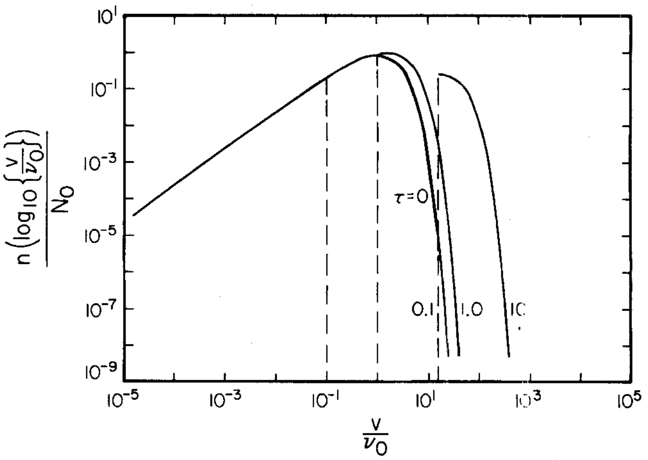

Fig. 13. Particle size spectra for constant condensation and constant coagulation, $\Lambda = 1.0$.

We noted in the beginning that the choice of the simple functional forms for coagulation and condensation rates, while theoretically interesting in certain instances, was largely a result of their mathematical tractability. An important question, therefore, is to what extent the solutions presented here provide insight into the behavior of size spectra under more complex conditions. In studying the solutions in Table 3, similarities are evident between cases (1) and (2) and between cases (1) and (3). Of most interest is the variation in the size spectrum when the condensation rate, given generally by a function of the form $\alpha_0 = \sigma v^{\gamma}$, varies over the range $\gamma = 1$ to $\gamma = 0$, for a fixed coagulation mechanism. Only when γ is strictly zero will a sharp cutoff volume exist. As γ increases from zero, the distribution will tend to broaden, reaching a maximum in dispersion for $\gamma = 1$. Thus, size spectra for condensation growth processes in the range $0 < \gamma < 1$ can be envisioned to lie between those given in Figures 6 to 8 and those in Figures 12 to 14. The key aspect of analyzing actual size spectra is an estimation of Λ for the system.

SUMMARY

The dynamic behavior of an aerosol undergoing simultaneous coagulation and growth by heterogeneous condensation of vapor species has been considered. First, a criterion based on the characteristics of the size distribution was established in order that the population balance equation, as it is commonly written, can be utilized. Second, certain special cases of coagulation and condensation mechanisms, which allow analytic solution of the dynamic equation for the size distribution density function, were selected. The mechanisms, while chosen because of their attractive mathematical nature, nonetheless encompass realistic collision and growth mechanisms for certain physical situations, such as Brownian and turbulent coagulation and volume reaction controlled growth. The solutions obtained suggest more broadly the behavior of general aerosol populations undergoing coagulation and condensation. Thus, whereas the analytical solutions are exact for the cases considered, the qualitative features of the solutions, such as the rate of broadening of the size spectrum, should provide insight into the dynamic behavior of systems with different growth mechanisms. It is anticipated that these results will be useful in the study of particulate formation and growth in hot combustion gases and in aerosol growth in atmospheric plumes.

ACKNOWLEDGMENT

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NOTATION

d_p = particle diameter, μm
E_n = exponential integral function of the n^{th} kind

g_1 = function defined by (63)
g_2 = function defined by (64)
k = Boltzmann constant
k_o = minimum number of monomers in a stable nucleus
Kn = Knudsen number
$\tilde{m}(v, t)$ = size distribution density of the small condensing nuclei, μm^{-3} cm^{-3}
M = constant monomer number density, cm^{-3}
$M_o(t)$ = total number of particles at any time, cm^{-3}
$M_1(t)$ = total volume of particles at any time, μm^3 cm^{-3}
$n(v, t)$ = aerosol size distribution density, μm^{-3} cm^{-3}
n_k = number density of particles containing k monomers, cm^{-3}
$\bar{n}$ = Laplace Transform of $n(v, t)$ with respect to v
$n_o(v)$ = aerosol size distribution density at $t = 0$, μm^{-3} cm^{-3}
N_o = total number of particles at $t = 0$, cm^{-3}
p_k = frequency of collision of k-mer with a monomer, s^{-1}
q_k = frequency of escape of monomer from a k-mer, s^{-1}
Q = function defined by (65)
R = function defined by (66)
$r_o(t)$ = rate of formation of stable clusters containing k_o monomers from homogeneous nucleation, cm^{-3} s^{-1}
s = Laplace transform variable, μm^{-3}
s_o = starting value of the s characteristic, μm^{-3}
t = time, s
T = reduced time
v = particle volume, μm^3
v_m = largest volume of the condensing species, μm^3

Greek Letters

$\alpha_o(v)$ = rate of change of the volume of a particle of size v, μm^3 s^{-1}
$\alpha_1(v)$ = diffusion coefficient for the aerosol size spectrum, μm^6 s^{-1}
α_o^* = α_o/v_o
$\beta(v, \tilde{v})$ = coagulation constant, cm^3 s^{-1}
β_o = coagulation constant, cm^3 s^{-1}
β_1 = coefficient in the linear coagulation constant, cm^3 μm^{-3} s^{-1}
β_2 = coefficient in the quadratic coagulation, cm^3 μm^{-6} s^{-1}
$\beta_{i,j}$ = collision rate between particles of sizes i and j, cm^3 s^{-1}
γ = exponent in the condensation growth law, $0 \leq \gamma \leq 1$
γ_1 = Euler's constant
Γ = incomplete Gamma function
δ = Kronecker delta function
ϵ = defined as v_1/v_o
η = dimensionless particle volume v/v_o
θ = absolute temperature, °K
λ = mean free path of air molecules, μm
Λ = dimensionless group: ratio of characteristic times of condensation and coagulation
μ = viscosity of air, g cm^{-1} s^{-1}
ν_o = mean volume of the initial size distribution, μm^3
σ = constant in condensation growth law, $\mu m^{3(1-\gamma)}$ s^{-1}
σ_o = condensation constant for uniform growth, μm^3 s^{-1}
σ_1 = condensation constant for linear growth, s^{-1}
τ = dimensionless characteristic time for condensation
χ = reduced time defined as $(1 + T)$
ω = function defined by (43)

Superscript

$^-$ = Laplace transform variable

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Denitrification Kinetics in Packed Beds

Bench scale packed columns were used to study the kinetic behavior of biological denitrification. After tracer studies were run to determine flow characteristics, steady state nitrate profiles were determined. A first-order rate expression with an Arrhenius temperature dependence is an adequate model of the reaction for nitrate-nitrogen concentrations of < 100 mg/l and temperatures of 5° to 20°C. The rate constants are proportional to the packing surface area.

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SCOPE

Nitrate discharges from municipal and septic tank sewage systems, agricultural runoff, and some food industries are pollution hazards for aquatic environments. Nitrogen is a primary nutrient for microbiological growth; concentrations of only a few milligrams per liter of nitrate-nitrogen (NO_3^--N) may result in the eutrophication of surface waters. Moreover, nitrate is toxic to human infants. A maximum of 10 mg/l of NO_3^--N has been specified for

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