KINETIC THEORY OF AEROSOLS

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* These preprint copies exclude the photographs (Plates I A, B, C).
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C Pattern of deposition of a sulfuric acid droplet as seen by an electron micrograph with magnification of 59,200 ×. Note the appearance of the circle of satellite droplets around the core. (Photo courtesy of E. Frank and J. P. Lodge, Jr.)

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I. INTRODUCTION

The generic term aerosols, apparently introduced by F. G. Donnan early in the century, covers a broad range of microscopic and sub-microscopic particles suspended in gases. These aerial suspensions have certain general physico-chemical properties that allow them to be classified as colloidal systems. In particular, if the particles are sufficiently small, they may remain in a gas for relatively long periods of time. Such aerial suspensions have a crude similarity to stable particulate dispersions in liquids. Thus in rough analogy to hydrosols, Donnan used the descriptive word aerosol for particulate clouds like fumes, smokes, fogs and mists.

The behavior of aerosols has been of considerable practical interest to men since the dawn of civilization. What more unearthly phenomenon than the often mysterious, aerosol linked, zodiacal light confronted ancient inhabitants of the earth. Undoubtedly smoke from fires provided an irritation to the caveman, and we know that the formation of clouds in the earth's atmosphere to produce rain has been a subject of the earliest writings of natural philosophers. Although pollution of air by combustion processes and other human activity has long existed, widespread regard for this problem has only appeared recently as man has begun to realize how important conservation of his environment is to his future.

Extensive technological application of the special properties of aerosols has come about mainly in the last fifty years. Much was learned about the generation of aerial dispersions in connection with
studies for chemical warfare during World Wars I and II. More peaceful applications have developed recently, however, with the invention of household and industrial sprays for dispensing anything from deodorants to paints. A wide range of agricultural usage has also developed in spreading pesticides in the form of sprays or dusts over fields of crops or sources like swamps and marshes. Fuel injection systems for combustion engines involve the generation of clouds of tiny full droplets. The formation of particles in rocket engines, which cause undesirable erosion of nozzles, has given extensive concern to aerospace engineers. In contrast, the formation of particulate matter in rockets also has been investigated for its potential utility in exotic devices for space propulsion.

Closer to the ground, physicians have determined that aerosols have therapeutic effects for the treatment of certain respiratory disorders. However, other dispersoids, including many air pollutants, just as easily can have detrimental influences on biological systems.

With an inevitable increase in awareness of aerosols in relation to weather, environmental control, and military industrial and household applications, the science of these dispersed systems began to develop as an integral part of physical chemistry by the early part of the 20th Century. Like many subjects of classical science, active interest in aerocolloidal systems waned somewhat with the deluge of important discoveries in atomic and molecular physics after World War I. However, the late 40's and 50's have seen a gradual renewal of activity in aerosol research within the investigations of a wide variety of disciplines ranging from geophysics to medicine.
A. SOME PHENOMENOLOGICAL OBSERVATIONS

Over the years much of the effort of investigators has been devoted to designing adequate methods for collecting aerosol particles, and for characterizing their physical and chemical properties. Because the size of suspended material may range from large molecules to bodies several hundred microns in diameter, the development of collection devices and analytical techniques has required much work. Even today the study of many aerosol systems, particularly highly dispersed ones, is seriously hampered by inadequate experimental methods.

Methods for collection and analysis of aerosols may be divided into indirect and direct techniques. Most indirect means make use of the response of a cloud of particles, or a single isolated particle to incident radiation, usually in the visual range. Direct means first involve trapping particles on a surface of some form, and subsequently carrying out different kinds of more or less standard physical and chemical measurements on the deposited material. Perhaps the keystone of this type of analysis is the ordinary light microscope, or the electron microscope. Observations with these tools reveal the variety in shape and size of captured particles (e.g., Plates IA and IB). Application of electron microscopy has also yielded fruitful information recently about the chemical composition of small particles. One new result has been reported by Lodge and Frank (1), who found that aerosol particles containing sulfuric acid may be identified uniquely by a shaded pattern of spattered material such as the one shown in Plate IC. Invariably with this acid, a pattern of satellite material is observed around a larger nucleus.
The variety of microphysical and microchemical analyses of aerosols seems only limited by the ingenuity of workers in this field. Even a brief discussion of these analytical techniques is well beyond the scope of this short review. Therefore, for further discussion of collection methods and analyses, readers are referred to the well-known book by Green and Lane (2), and the review by Lodge (3). A good discussion of practical techniques of particulate analysis is also presented by Cadle (4).

From experimental observations, much of the phenomenological behavior of aerial suspensions has been documented. Some of the more important observations may be grouped into the following categories: (1) optical effects, (2) ability to take up electrical charges, (3) ability to nucleate a vapor just above the saturation point, (4) chemical reactivity, (5) many physico-chemical properties dependent on particle size, (6) exhibition of thermal agitation (Brownian motion), (7) at constant temperature, patterns of motion, and growth by vapor diffusion vary systematically with particle size and gas pressure, (8) exhibition of substantial induced motion in external fields of force, as well as in nonuniform gases, and (9) growth of particles combined with changes in number distribution of particles by condensation and coagulation.

1. **Optical Effects.** Rather colorful optical effects have long been known to result from scattering of light and from diffraction or refraction of light from liquid aerosols. Perhaps best known are the rainbows and cloud bows in the atmosphere and the higher order
Tyndall spectra observed from nearly monodisperse clouds. The theory for light scattering was developed many years ago by Rayleigh (5) and by Mie (6). Extensive later work has used these theories as a framework for interpreting experimental observations.

2. **Electrical Charging.** The capability of small particles for becoming charged is well known. Indeed, charge induction and transfer mechanism are linked closely to thunderstorm electricity. The present theory for electrical effects in aerosols stems largely from classical electrostatics. One valuable discussion of the subject has been written by Loeb (7). Unfortunately many aspects of charging and electrical interaction in clouds have not yet been explained. Because of many uncertainties in the details of this interaction, electrostatic influences have often been invoked arbitrarily to explain the deviations in aerosol behavior from expected observations. It may well be true that the electrical effects contribute to these deviations, but considerably more careful research usually is needed to verify such conclusions.

3. **Physicochemical Phenomena.** Some of the most fascinating work on aerosols has centered on the ability of these tiny particles to nucleate supersaturated vapor. Although Donnan is credited with naming aerial dispersions, Aitken and C. T. R. Wilson may be considered fathers of modern aerosol science with their research on atmospheric nuclei in the late 19th Century. Older theoretical work suggested that nucleation of water droplets should be only a function of particle size and solubility. However, nearly sixty years of study has failed to
demonstrate conclusively that this is so. The nucleation of ice particles in the atmosphere presents further complications to the physicist and chemist. Because heterogeneous nucleation has proved to be so complicated, much effort has been devoted to investigating homogeneous nucleation of droplets in a vapor. The hope is that this work will produce a relatively simple theoretical framework on which all of the observed nucleation processes can be based. Some of the recent developments in nucleation theory and experiment have been outlined by Hirth and Pound (8). The application of many of these ideas to cloud formation in the earth's atmosphere occupy much of the current texts on cloud physics including Mason (9) and Fletcher (10).

The potential chemical reactivity of particulate suspensions has long been suspected. It is known, for example, that particles themselves may be generated by chemical means. The well known smogs in southern California evidently stem from photochemical reactions of trace gases in the lower atmosphere. Although there exists an amount of speculation about the reactive properties of aerosols, very little information is available at present about this aspect of aerial dispersions. I few reports of experimental investigations of gas-particle reactions have appeared. Some examples include the work of Goetz (11), and the article on the kinetics of atmospheric chemical reactions involving aerosols by Cadle and Robbins (12). The research of Goetz has examined the catalytic influence of introducing polystrene latex spheres into a mixture of photochemically reactive gases, while the work of Cadle and Robbins dealt more extensively with problems of control of reaction rates in gas-particle systems by diffusion in the gas phase, chemical reaction, or by diffusion in the liquid or solid phase.
Another aspect of the physicochemical properties of aerosols involves the nature of the particle surface and its curvature with particle size. Though little experimental information is available on the size dependence of properties of particles, some theoretical studies have been made, especially in relation to curvature in the opposite sense, in capillary tubes. Perhaps best known of the classical results is the thermodynamic relation of Kelvin for the effect of particle curvature on vapor pressure:

\[
\ln \frac{p}{p_\infty} = \frac{2\gamma V}{kT R_1}
\]

where \( p \) is the vapor pressure over the curved surface, \( p_\infty \) is the equilibrium vapor pressure over an infinite flat surface, \( R_1 \) is the droplet radius, \( V \) is the volume of molecules in the condensed phase, \( k \) denotes Boltzmann's constant, \( \gamma \) the surface tension, and \( T \) the absolute temperature. Here we find the vapor pressure depends strongly on \( R_1 \) whenever the particle size falls below \( \sim 1 \mu \).

More recent work has indicated that the surface tension itself depends on the particle size when the particle is sufficiently small.

The dependency on size of properties of a homogeneous particle in a gas, as well as the effect of heterogeneity of the surface, appears to be partly a consequence of the unusual property of aerial disperoids that their surface to volume ratio is exceedingly large compared with most bodies. Perhaps another, better way of specifying this property is in the characteristic ratio of lengths (13):

\[
\Lambda = \frac{\text{(intermolecular distance in the condensed phase)}}{\text{(particle radius)}}
\]
This parameter, $A$, reaches values the order of one-tenth for highly dispersed aerosols, but normally it does not exceed $10^{-5}$ for non-suspended objects commonly found in the laboratory.

4. **Dynamical Properties.** Because the size of aerosol particles is very small, thermal agitation may become a significant part of their motion in a gas. This random motion causes particles to travel in varied paths that may easily be observed in a smoke cloud under a microscope. Perhaps no other dynamical property is so unique to aerosols as thermal agitation, named **Brownian Motion** for its discoverer, Robert Brown.

The theory of Brownian motion in colloidal suspensions was first developed at the turn of the century. Even the well known physicist Albert Einstein has been linked with these developments (14). Because of the fundamental interest of theoreticians in the statistics of Brownian motion, very elegant mathematical treatises have evolved in recent years (see for example, Wax (15)).

Basically, the theoretical model of the diffusion of particles by Brownian motion is a stochastic one, which yields an expression for the distribution of particles in space and time analogous to Fick's law. The diffusivity of the small particles found by Einstein and modified by Whytlaw-Gray and others (16) to conform with experiments, takes a particularly simple form,

$$D_i = B_i kT = \frac{kT(1 + \frac{\lambda}{g R_i})}{(6\pi\eta g R_i)} ,$$

(3)

where $T$ is the absolute temperature, $B_i$ is the particle mobility,
k is Boltzmann's constant, \( \tilde{\mu}_g \) and \( \lambda_g \) are respectively the viscosity and the mean free path of the suspending medium, and \( \hat{A} \) is given by (17)

\[
\hat{A} = 1.257 + 0.400 \exp(-1.10 \frac{R_i}{\lambda_g})
\]  

Thus in a stagnant medium, Brownian diffusion tends to increase in importance with increase in temperature, but with decrease in viscosity and particle radius.

In a moving medium, Brownian motion must be taken into account when the thermal energy exceeds the mean kinetic energy of the particle, or when

\[
\frac{3kT}{m_iq_i^2} > 1,
\]

where \( m_i \) and \( q_i \) respectively are the particle mass and average translational velocity.

A second important feature of aerosol dynamics involves the observation that the transfer of momentum, heat and matter to small particles varies systematically at constant temperature with both particle radius and gas pressure. For example, in connection with his famous oil drop experiments, Millikan (18) found that the particle mobility \( B_i \) could not be predicted by Stokes law alone for very small particles, or for larger spheres in gases at pressures reduced below 1 atmosphere. Account is taken for this experimental conclusion, for example, in the particle mobility when a correction is made in the Stokes mobility, \( (6\pi \tilde{\mu}_g R_i)^{-1} \), for the ratio of the mean free path of the gas to the particle radius, as indicated in Equation [3]. The factor \( \hat{A} \) in [4] is an empirical relation derived from experiments of Millikan and others (17).
The observed dependence on size and Knudsen number, \( \text{Kn} = \frac{\lambda_{\text{g}}}{R_{1}} \) of gaseous transport phenomena to particles reflects the fact the aerosols behave in one extreme of \( \text{Kn} \rightarrow 0 \), as if they are suspended in a continuum, while in the other extreme, \( \text{Kn} \rightarrow \infty \), they appear to be suspended in a near vacuum. Where \( \text{Kn} \rightarrow 0 \), classical aerodynamics applies to the dynamical behavior of the particles. However, where \( \text{Kn} \rightarrow \infty \), the particles may be treated as large molecules, whose behavior may be estimated directly by the kinetic theory of dilute gases. For the transition range of \( 0.01 < \text{Kn} < 10 \), the tools of rarified gas dynamics have to be used to predict the behavior of aerosols.

Particularly in this range, many of the details of gas-condensed phase interactions are only partially understood so that the theory of aerosol dynamics is necessarily incomplete. This theoretical problem and its implications to the behavior of aerosols has been fully appreciated only recently. These questions have occupied a major portion of the recent monograph by Hidy and Brock (13).

Because of the relatively small mass of aerosol particles, they often exhibit significant induced motions in external fields, and are susceptible to accelerations resulting from heterogeneities of the dynamics of gas molecules in non-uniform gases. Small particles are well known to be deposited on surfaces by transverse motions imposed by body forces like gravity or electromagnetic forces. Examples of transverse motions also have been found in gradients of temperature and condensable vapor. In fact, the well known thermal precipitator is a practical application of the induction of movement of small particles in a temperature gradient.
The theoretical treatment of particle motion in the presence of external body forces, or non-uniformities in the suspending gas, are rather complicated especially in view of the dependence on such motions of the gas dynamic regimes given by the Knudsen number. Some details of the theory have been discussed by contributors to Davies' book (17), and by Hidy and Brock (13).

5. Mechanics of Assemblies of Particles. Much of the conceptual modeling of aerosol clouds has implied that the particles suspended in the gas can be treated as if they are points in a continuum, or at least just large gas molecules. With such an assumption the behavior of an assembly of particles may be examined within the structure of continuum theory for multicomponent gases. Application of such a model has been elaborated on by Soo (20).

Aside from irregularities in shape, and surface effects, perhaps the most important distinction that must be drawn between the behavior of molecules and aerosol particles is the fact the aerosol particles may grow or diminish in size by accumulation of condensable vapor, or by collision and sticking (coagulation). These latter two processes complicate the formulation of a complete "continuum" theory for aerosol clouds. For example, in expressing a rate equation for the rate of change in concentration of a particular sized species in the cloud, one has to include some kind of generation term to account for growth by condensation and by coagulation.

There are a number of fundamental questions to be explained before the statistical equations specifying the changes in an aerosol
cloud may be formulated with certainty. In addition to understanding the generation term mentioned above, one must be sure that the application of continuous distribution functions for particles is a meaningful statistical approximation to a physically discrete system like an aerosol, which contains numbers of particles very much less than the surrounding molecules of gas. Some of these points have been discussed by Warshaw (21). However, much more research in this area is necessary before the present theoretical methods can be accepted without criticism.

6. Physical Chemistry of Aerosols and their Kinetic Theory. In a sense, the discussion and description of nine categories of important observational information constitute the major portion of the physical chemistry of aerosols. Optical effects represent an indication of the presence of suspended particles, but may be interpreted rather uniquely in terms of the physical and chemical properties of the particles. Electrification (or the mechanisms of charging), nucleation and chemical reactivity in aerial dispersions represent important factors in the chemistry of aerosols, which may be treated in specialized ways, which have been reviewed in detail in other articles.

Perhaps most fundamental to all of the physical chemistry of aerosols, however, are the gas-dynamical processes experienced by the suspended particles. To investigate nearly every aspect of aerosol behavior it is first necessary to understand the implications of the kinetics of the particles themselves, including their collisions. Since the dynamical aspects of aerosol science are so important, it seems useful to confine this review to discussion of this topic alone.
To generally understand the rate processes affecting aerosols, one really must begin by constructing an idealized mechanical theory for their behavior. As a first step in evolving foundations for comprehensive dynamical treatment of such systems, let us begin with outlining such a kinetic theory patterned after an analogous theory for ideal gases. To introduce some ideas for a second step in constructing the realistic dynamical theory of aerosols, the remainder of the article will be devoted to the description of a few examples of the relations between physicochemical properties of small particles and kinetic behavior of aerial dispersions.

II. AN IDEALIZED DYNAMIC MODEL OF AEROSOLS

In general, particulate material suspended in a gas may consist of a wide variety of shapes and chemical composition. The material may be in a solid or a liquid condensed state, or it may exist in a metastable state involving gas and a condensed phase.

To construct a quantitative theory for the particle dynamics, however, such chemical or thermodynamic considerations necessarily have to be disregarded, at least in the first approximation. Thus the theory assumes at the beginning that the dispersoid is a smooth hard sphere which is chemically inert with respect to the suspending gases, and to other particles. The suspending gas is assumed to be an ideal one described by the kinetic theory of dilute gases, and the collision of particles is assumed to occur with a sticking probability of $e$. All physicochemical properties of the particles enter initially into the formulation only as arbitrarily (or experimentally) specified empirical parameters.
Such an idealization of an aerosol assumes implicitly that one may expect a reasonably accurate theory to evolve without specifying the detailed structures of particles or the suspending gas molecules. An equivalent hypothesis has allowed the development of the kinetic theory of gases whose success, in practice, for predicting properties of real gases, is well known. Of course, one cannot hope for the aerosol model to be equally successful because of the enormously increased complexities of a gas-particle system. Nevertheless, the hard sphere-ideal gas model should provide a reasonable framework for constructing a satisfactory approximate dynamical theory of aerosols. We shall see that this hypothesis appears to be a fairly accurate one based on the pertinent experiments published so far.

A. BASIC PARAMETERS AND CHARACTERISTIC RATIOS

Even with the severe restrictions of the idealized model defined above, a large number of basic parameters are required to describe this model. These basic parameters are tabulated in Table 1. We note that there can be twelve different variables for each particle species, and nine variables for the suspending gas. If the gas phase is a multicomponent mixture, suitable averages for the variables would be taken (e.g., Chapman and Cowling (22)).

Thus, we have scaling parameters that cover particle-gas concentration velocities, lengths, electrostatic changes, temperature, interaction parameters, including collisions or chemical reactions. Typical values of these variables for aerosols involved in the earth's troposphere are indicated in columns 4 and 5 of Table 1.
Table 1

Basic parameters for describing the dynamics of aerosol particles (from Hidy and Brock, 13)

<table>
<thead>
<tr>
<th>Particles</th>
<th>Gas</th>
<th>Atmospheric Aerosols</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number Density (#-cm⁻³)</td>
<td>$n_i$</td>
<td>$n_g$</td>
<td>$10^2-10^5$</td>
</tr>
<tr>
<td>Mean Temperature (°K)</td>
<td>$T_i$</td>
<td>$T_g$</td>
<td>$T_i \approx T_g$</td>
</tr>
<tr>
<td>Mean Velocity (cm-sec⁻¹)</td>
<td>$\bar{v}_i$</td>
<td>$\bar{v}_g$</td>
<td>$10^{-2}-10^3$</td>
</tr>
<tr>
<td>Mean Free Path (cm)</td>
<td>$\lambda_{ij}(\bar{v}_i)$</td>
<td>$\lambda_{ij}(\bar{v}_g)$</td>
<td>&gt;$10^2$</td>
</tr>
<tr>
<td>Particle Radius (cm)</td>
<td>$R_i$</td>
<td>$R_g$</td>
<td>$10^{-6}-10^{-3}$</td>
</tr>
<tr>
<td>Particle Mass (gm)</td>
<td>$m_i$</td>
<td>$m_g$</td>
<td>$10^{-18}-10^{-9}$</td>
</tr>
<tr>
<td>Particle Charge (# electricity)</td>
<td>$\pm e_i$</td>
<td>Weakly ionized</td>
<td>~0-100</td>
</tr>
<tr>
<td>Aerodynamic Length</td>
<td>$L_i$</td>
<td>$L_g$</td>
<td>$L_i \approx R_i$</td>
</tr>
<tr>
<td>Coagulation or Reaction Probability</td>
<td>$C$</td>
<td>0</td>
<td>0 ≤$C$ ≤ 1</td>
</tr>
<tr>
<td><strong>Interaction Parameter</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In mixtures of gases, $m_g$ is the average molecular mass of gas.

** Interaction parameters are accommodation coefficients for particles of type and gas $g$ on a boundary $s$ of the aerosol systems. These may also include such coefficients for interaction between the gas and the particles themselves.
The various characteristic lengths are of some interest. The mean free path \( \lambda_{ij} \) is the average distance traveled by a particle \( i \) before colliding with another particle \( j \). If \( j = g \), the other particle can be a gas molecule. In analogy to averaging procedures used for gaseous systems, similar averages are presumed to apply to particle parameters like \( \lambda_{ij} \) (as well as \( \dot{q}_g \)) (13).

The particle radius serves as a scale for transport phenomena near the sphere. The aerodynamic lengths represent characteristic distances associated with significant changes in number densities of particles or the gas, temperatures, or velocities. Of course, there may be more than one aerodynamic length which may be chosen depending on geometrical considerations or wall effects.

1. **Mechanical Restrictions.** Having chosen an idealized model of an aerosol particle as a rigid sphere, further restrictions are normally made to apply well known results of gas dynamics to such systems. Aerosols are generally confined at the low extreme of size by the criteria,

\[
\frac{R_g}{R_i} < 1, \quad \frac{m_g}{m_i} \ll 1
\]

These limits in themselves do not restrict consideration from the mechanics of large molecules in much lighter molecular media. However, the additional possibility of particle size variation in time by evaporation or condensation, or sticking or collision as provided for, for example, in the parameters \( \varphi \), and \( \epsilon \) give the distinction needed in this case.
In the large extreme of size there has been an arbitrary cutoff of about 30μ. This value is based to some extent on considerations at ordinary temperatures and pressures of low settling velocity of less than a few cm-sec⁻¹, and simplification of dynamical calculations by assuming that the particle Reynolds number, $\frac{\rho q R}{\mu g}$ is less than unity.

The evaluation of a dynamical theory of aerosols has been limited to cases where the suspending gas is dilute and is only weakly ionized. This simplifies the treatment of the gas in that molecule-molecule interaction may be analyzed by well known methods. In addition, the following conditions are presumed to be valid for the gas:

$$\frac{R_g}{\lambda g} \ll 1, \quad \frac{R_g}{L_g} \ll 1$$ (5)

These two restrictions are essential to aerosol theory in that they justify the use of the Boltzmann equation and its solution in analyzing the behavior of aerosols (13). Among other things, these ratios imply that the gas is dilute, and that there exists relatively gradual changes in the average properties of the gas (e.g., temperature and pressure).

Most aerosols of practical importance, including those observed in the earth's atmosphere, fall within the mechanical restrictions discussed above. Thus, particular approximate solutions of the Boltzmann equation provide the framework for the aerodynamic theory of aerial suspensions.

2. **Single Particles in a Gas of Infinite Extent.** Perhaps the simplest aerosol system conceivable is the case of a single particle suspended in
an infinite gas. This "one-particle" cloud is certainly a superficial one but, as we shall see in the next section, it provides the core of virtually all of the mechanical theory of aerosols.

Considering the basic parameters listed in Table 1, we can specify the behavior of a single sphere in the suspending medium with average parameters like the number density $n_k$, the lengths $\lambda_{ij}$, or the interaction parameters $\mathcal{E}$ or $\mathcal{F}_{ig}$. The single particle will have a velocity $v_i$, and temperature $T_i$ ($\approx T_g$) where definitions will depend on the collisional interaction between the gas molecules and the particle surface. Though the length $\lambda_{ij}$ has no meaning in these circumstances, a value of $\lambda_{ig}$ can be assigned by defining such a length in terms of the particle velocity and a characteristic time. Such a length is often used in aerosol calculations (16), and it is tabulated as a function of size with other classical mechanical parameters in Table 2.

The aerodynamic length for a single particle, $L_i$, is arbitrarily assigned the scale of the particle radius. However, the gaseous lengths $L_g$ may vary and may be considered a length of the confining volume or the distance away from another particle. Rigorously $L_g \rightarrow \infty$, but practically it has been found (16) that $L_g \gg 10 R_i$, the assumption of an infinite medium may be applied.

If the aerodynamic length $L_g \rightarrow \infty$, the effect of this parameter may be disregarded, and the dynamics of the single sphere will be ideally dependent upon eight parameters, the mass $m_i$, the mass of gas molecules $m_g$, the radius $R_i$, the radius of gas molecules $R_g$,
Table 2
Some characteristic transport properties of aerosol particles of unit density at 1 atm. pressure, and 20°C (cgs units).

<table>
<thead>
<tr>
<th>Particle Radius</th>
<th>$B_1$</th>
<th>$D_1$</th>
<th>$L$</th>
<th>$\langle v_1 \rangle$</th>
<th>$\lambda_{ig} \ (= \langle v_1 \rangle^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-3}$</td>
<td>$2.94 \times 10^5$</td>
<td>$1.19 \times 10^{-8}$</td>
<td>$8.13 \times 10^2$</td>
<td>$4.96 \times 10^{-3}$</td>
<td>$6.11 \times 10^{-6}$</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>$5.96 \times 10^5$</td>
<td>$2.41 \times 10^{-8}$</td>
<td>$3.24 \times 10^3$</td>
<td>$1.41 \times 10^{-2}$</td>
<td>$4.34 \times 10^{-6}$</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>$3.17 \times 10^6$</td>
<td>$1.28 \times 10^{-7}$</td>
<td>$7.59 \times 10^4$</td>
<td>$0.157$</td>
<td>$2.07 \times 10^{-6}$</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>$6.71 \times 10^6$</td>
<td>$2.71 \times 10^{-7}$</td>
<td>$2.85 \times 10^5$</td>
<td>$0.444$</td>
<td>$1.54 \times 10^{-6}$</td>
</tr>
<tr>
<td>$1 \times 10^{-5}$</td>
<td>$5.38 \times 10^7$</td>
<td>$2.17 \times 10^{-6}$</td>
<td>$4.44 \times 10^6$</td>
<td>$4.97$</td>
<td>$1.12 \times 10^{-6}$</td>
</tr>
<tr>
<td>$5 \times 10^{-6}$</td>
<td>$1.64 \times 10^8$</td>
<td>$6.63 \times 10^{-6}$</td>
<td>$11.7 \times 10^6$</td>
<td>$14.9$</td>
<td>$1.20 \times 10^{-6}$</td>
</tr>
<tr>
<td>$1 \times 10^{-6}$</td>
<td>$3.26 \times 10^9$</td>
<td>$1.32 \times 10^{-4}$</td>
<td>$7.35 \times 10^7$</td>
<td>$157$</td>
<td>$2.14 \times 10^{-6}$</td>
</tr>
<tr>
<td>$5 \times 10^{-7}$</td>
<td>$1.26 \times 10^{10}$</td>
<td>$5.09 \times 10^{-4}$</td>
<td>$1.52 \times 10^8$</td>
<td>$443$</td>
<td>$2.91 \times 10^{-6}$</td>
</tr>
<tr>
<td>$1 \times 10^{-7}$</td>
<td>$3.08 \times 10^{11}$</td>
<td>$1.25 \times 10^{-2}$</td>
<td>$7.79 \times 10^8$</td>
<td>$4970$</td>
<td>$6.39 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
the relative velocity, \( \vec{q}_i - \vec{q}_g = \vec{U} \) the number density of gas molecules \( n_g \), the gas temperature \( T_g \), the free path \( \lambda_g \). From the eight properties, five independent dimensionless groups may be formed, one of which is the ratio \( R_g/\lambda_g \). Fixing the range of the variation of this ratio to very small values, the particle dynamics may be specified by four relevant parameters listed in Table 3. These parameters define various mechanical regimes of the single particle-gas system.

By introducing the thermal velocities,

\[
\langle v_i \rangle = \left( \frac{8kT_i}{m_i} \right)^{\frac{1}{2}}
\]

\[
\langle v_g \rangle = \left( \frac{8kT_g}{m_g} \right)^{\frac{1}{2}}
\]

we see that the definition of the Mach number becomes apparent. The important ratio, \( \langle v_i \rangle / \langle v_g \rangle \), has been named the Brown number, in honor of the discoverer of Brownian motion, the English botanist, Robert Brown.

The first of the dimensionless numbers, the Knudsen number, constitutes a measure of the extent of departure of the behavior of the system from that predicted by continuum mechanics. Only in the limit of \( Kn \to 0 \) does the single particle behave as if it is suspended in a continuum. As \( Kn \) becomes larger and larger, increasingly strong non-continuum behavior should be observed.

When \( Kn > 10 \), the aerosol particle is said to be in the free molecule regime. Under these conditions the mean free path of the gas is large relative to the particle radius, and there are no intermolecular collisions of gas molecules in the neighborhood of the particle. Then it can be assumed that the gas molecules hitting the particle are not
Table 3

Dimensionless ratios of dynamic significance for aerosols in the single particle regime [From Hidy and Brock, 13]

<table>
<thead>
<tr>
<th>Knudsen No.</th>
<th>Kn</th>
<th>$\lambda_g / R_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mach No.</td>
<td>Ma</td>
<td>$</td>
</tr>
<tr>
<td>Schmidt No.</td>
<td>Sc</td>
<td>$R_i^2 n_i \lambda / g g$</td>
</tr>
<tr>
<td>Brown No.</td>
<td>Br</td>
<td>$v_i / v_g$</td>
</tr>
<tr>
<td>Debye No.</td>
<td>De*</td>
<td>$Q_i Q_j \kappa / kT$</td>
</tr>
</tbody>
</table>

$\kappa = \text{Debye length}, \ 4\pi/kT \sum_{i=1}^{s} n_i Q_i$
influenced by the presence of the particle. In the absence of vaporization in free molecule regime, the particle may be regarded as a large molecule making independent, binary collisions with the molecule of surrounding gas.

Within the range $0 < \text{Kn} < 10$, the aerodynamic behavior is considered to be in transition with respect to Knudsen number. It is in this regime that the principal unresolved problems of single particle dynamics exist. Relatively successful approximations to the Boltzmann equations have been found for the behavior of spheres over $0.10 < \text{Kn} < 10$. Below $\text{Kn} \approx 0.10$ only crude, intuitive theory based on extensions of continuum theory have been reported. Such extensions are based on allowance for slippage of gas at the particle surface, a condition untenable in continuum theory.

The second dimensionless parameter, the Mach number, gives the range conditions for the magnitude of the relative translation speed relative to the thermal speed of the particle. Normally gas dynamic usage of this ratio incorporates the speed of sound of the gas for $\langle v_g \rangle$, but the thermal speed appears to have more significance for aerosol dynamics.

Ordinarily, the Mach number is less than unity for aerosol systems so that the gas flow near the particles is considered incompressible and independent explicitly of $\text{Ma}$.

The ratio of the Mach number and the Knudsen number is proportional to the Reynolds number of the particle. That is,

$$\text{Re} = \frac{\text{UR}}{\text{Kn}} \approx \frac{4\text{Ma}}{\text{Kn}}$$

1. We note that continuum theory applies to the limit $\text{Kn} \rightarrow 0$. In this regime $\text{Re}$ becomes very large unless $\text{Ma} \rightarrow 0$. 

where \( v_g \) is the kinematic velocity of the gas. This group gives a relation for the relative importance of inertial forces compared with the viscous forces acting on an element of gas.

The Reynolds number has considerable importance to the theory of particle motion in the classical aerodynamic theory. In fact, when \( \text{Kn} \to 0, \text{Sc} \to \infty \), and \( \text{Br} \to \infty \), the Reynolds number is the sole relevant parameter governing the aerodynamics of the sphere in steady motion. Instead of restricting the size of aerosol particles, the upper limits of aerosol theory often have been limited to the Reynolds number restriction, \( \text{Re} \leq 1 \). Accepting this limitation, we see from Fig. 1 that aerosol mechanics lies only in a small corner segment of the overall regimes of gas dynamics.

Previously we remarked that the random thermal motion of aerosol particles constitutes a significant property of such bodies. The importance of the thermal agitation in the dynamics of single particles is reflected in the Brown ratio and the Schmidt number. The relative magnitudes of directed velocity particles, compared with diffusional spreading, is specified by \( \text{Br} \). The relative importance of diffusion of vorticity (rotational motion in the gas), as contrasted to Brownian diffusion, is given in terms of \( \text{Sc} \). The Brown ratio accounts for the influence of particle mass on diffusion motion. Thus, this parameter is about unity for molecular processes, and much less than one for aerosol systems.

Usually the Schmidt number is defined in terms of viscosity of the medium and the diffusivity \( D_i \), \( \text{Sc}' = \frac{v_g}{D_i} \). The diffusivity of particles is often defined in physical chemistry in terms of the mobility, \( B_i \) (Eq. 3). The ordinary definition of the Schmidt number
Figure 1
has a simpler physical interpretation than the product in Table 3. However, strictly speaking $\text{Sc}'$ has meaning only for aerosols in the free molecule regime. In this limit $\text{Sc}' \sim \text{Sc}$ as readily demonstrated using gas kinetic definitions. For $\text{Kn} < 10$, $\text{Sc}'$ has to incorporate an accommodation coefficient for momentum, $\alpha_m'$. Hence, the use of this ratio in place of $\text{Sc} = R \sum_{i=1}^{s} n_i \lambda_i$ implies that $\alpha_m$ always is unity. This is known to be of limited validity for aerosols (13). Despite this limitation most papers dealing with Brownian diffusion use the customary definition, $\text{Sc}'$.

Frequently it is of interest to know the relative importance of convective diffusion (dispersion by fluid motion) as contrasted to Brownian diffusion. The product of the Reynolds number and the Schmidt number, called the Peclet number, gives such a parameter:

$$\text{Pe} = \text{Re} \cdot \text{Sc}' .$$

(8)

Since $\text{Sc} \approx \text{Sc}'$ is $O(10^6)$, the Peclet number for aerosol systems is always much greater than one. This restriction allows for important assumptions of boundary layer theory to be applied to the convective transport of aerosols (see, for example, 13).

The ratio of a characteristic length of Coulombic interaction, $Q_i Q_j / kT$, to Debye's reciprocal length, $\lambda = 4\pi \sum_{i=1}^{s} n_i Q_i / kT$, is also included in Table 3. The fact that this ratio, which was named earlier (62) the Debye number, $\text{De}$, is always $\ll 1$ for aerosols allows the approximation that charged particles interact electrostatically virtually instantaneously. This approximation constitutes a vital part of the concept of the single particle regime (See also p. 24).
3. **Assemblies of Particles.** With appropriate knowledge of the behavior of single particles in a gas, in principle, it should be possible to extend the mechanical theory to collections of particles. Thus, if we understand the functional dependence of single particle dynamics on the basic parameters in Table 3, quantitative description of assemblages of particles should evolve with additional information about the averaged properties \( n_i, \vec{q}_i, T_i \) and \( \lambda_{ij} \). To speak in any meaningful way in a statistical sense, we must bear in mind that averaging of the parameters must be taken over a volume large enough to contain a large number of particles of species \( i \) or \( j \). Furthermore, care must be taken in considering the velocity \( \vec{q}_i \) and temperature \( T_i \) as unique parameters in an aerial suspension. For example, there may be severe limitations in using a uniform value of \( T_i \) for a particular species if temperature changes occurred in the gas over distances the order of the radius of the particle. Assuming nevertheless, that the averaged properties \( n_i, \vec{q}_i, T_i \) and \( \lambda_{ij} \) uniquely specify the assembly in addition to the single particle parameters, then the range of variation in size and physico-chemical constitution would require an exceedingly large number of variables to specify the state of a cloud at any given time. Such considerations suggest that any truly complete statistical mechanical theory for an idealized gas-particle system is unrealistic, except in the simplest of cases where particles are the same size and the same composition.

---

1. The requirements for averaging of such properties have well known analysis in the statistical mechanics of gases (22).
In view of the apparent hopelessness of approaching an aerosol from a rigorous statistical treatment, evaluation of the dynamical theory has proceeded along highly simplified lines. In effect, a stochastic theory for the behavior of aerosol clouds has been formulated which makes use of the diffusional model based on solutions of the Fokker-Planck equation (23). The application of theory of Brownian motion to spheres in a stagnant, continuous media has been extended arbitrarily to include particle-particle interactions and convective processes by methods similar to those used in studying homogeneous chemical reactions in gases.

Virtually all of the theory of clouds of aerosol particles implies the highly simplifying conditions that:

(a) \( \frac{n_i}{n_g} \ll 1 \) for all \( i \)
(b) \( \frac{\lambda g n_i^{1/3}}{g} \ll 1 \) for all \( i \)
(c) \( \frac{R_{ij} n_i^{1/3}}{g} \ll 1 \) for all \( i \) \( (9) \)
(d) \( \frac{n_i^{-1/3} L_{g}^{-1}}{L_{g}^{-1}} \ll 1 \) for all \( i \)
(e) \( \frac{Q_i Q_j \kappa /kT}{kT} \ll 1 \) for all \( i \)

Under these five restrictions all of the particles in the cloud may be considered independent of one another,\(^1\) and of the enclosing boundaries of the system. Each sphere in the assembly may then be characterized by the groups \( Kn, Ma, Sc \) and \( Br \). Electrical interaction between (two) particles, or a particle and a wall, is assumed

\(^1\) A notable exception is the attempt to incorporate aerodynamic forces in collisions of large spheres (\( \sim 10^4 \) radius) (e.g., Hocking, and Davis, 24).
coulombic in character, and the electrical force acting on one body is treated as an externally imposed field. And phenomena such as collision and coagulation, vaporization or deposition on surfaces are regarded as instantaneous events in the overall history of the aerocolloidal system. This regime of behavior in aerosol clouds has been defined by Brock (13) as the single particle regime.\textsuperscript{1}

Fortunately, examination of the restrictions imposed by the single particle regime apply to almost all cases of aerial suspensions of practical interest, including atmospheric aerosols. Two possible exceptions might be the particulate clouds generated under extreme temperatures in rocket nozzles, or those formed during the initial microseconds after a bomb explosion in the atmosphere.

Having outlined some fundamental restrictions, and the basic variables involved in the mechanical theory of aerosols, let us now consider several examples of important results of such a theory.

B. SINGLE SPHERES IN A CONTINUUM

The oldest and best known foundations of the theory of aerosols stem from results of continuum theory. These results consider the behavior of a single sphere in a fluid of uniform composition and temperature, which is governed by the Navier-Stokes equations. These equations of motion, combined with equivalent relations for conservation of mass and energy (e.g., Bird, Stewart, and Lightfoot, 25), represent

\textsuperscript{1} A detailed comprehensive treatment of aerosol dynamics in the single particle regime is available, for example, in Hidy and Brock's monograph (13).
a first approximate solution to the Boltzmann equation (22).

1. **Steady Motion and Stokes Law.** When \( \text{Kn} \to 0 \), and \( \text{Re} \to 0 \), the equations governing steady gas motion about the sphere are:

   (Conservation of momentum) \( \nabla p = \mu g \nabla \mathbf{U} \)  \( \quad (10) \)

   (Conservation of mass) \( \nabla \cdot \mathbf{U} = 0 \).  \( \quad (11) \)

   If continuum motion, the boundary conditions at the surface of the sphere and in the fluid far from the body are

   \[ \mathbf{U} = 0, \quad \mathbf{r} = \mathbf{R} \]

   \[ \mathbf{U} = \mathbf{U}_\infty, \quad \mathbf{r} \to \infty \]  \( \quad (12) \)

   where \( \mathbf{r} \) is the position vector taken at the center of the sphere.

   G. Stokes (26) first solved the Equations (10) and (11) with (12) in 1851. His result provides the key relation for the drag force on a sphere steadily moving through a fluid:

   \[ \text{(Stokes Drag)} \quad \mathbf{D} = 6 \pi \mu \mathbf{R}_1 \mathbf{U}_\infty \text{ for } \text{Kn} \to 0, \text{Re} \to 0. \]  \( \quad (13) \)

   The mobility of particles is defined in terms of the relation

   \[ \mathbf{U} = \mathbf{B}_i \mathbf{F} \]  \( \quad (14) \)

   Therefore, the mobility of an aerosol particle based on Stokes' law is

   \[ \mathbf{B}_i = (6 \pi \mu \mathbf{R}_1)^{-1} \]  \( \quad (15) \)

   Stokes law for spheres moving in a continuum has been verified by a number of experimenters. Very careful observations have indicated that the theory and experiment agree within less than 5% (16, 27). Such a confirmation gives considerable justification for belief in the soundness of physical laws based on continuum mechanics within the appropriate restrictions of Kn and Re.
Under conditions in which the Reynolds number is finite, or more practically exceeds 0.10, inertial forces action on the fluid become important, and Stokes' analyses have to be modified to account for additional convective terms of $\vec{q}_g \cdot \nabla \vec{q}_g$ on the left side of Equation [10]. Approximations for these terms where $\text{Re} < 1$ were first discussed at the turn of the century by Oseen (28). More recent work of Proudman and Pearson (29) made more rigorous Oseen's early approximations for inertial effects in slow flow. Their results showed that the drag force on spheres in a uniform fluid has the form

$$D = 6 \pi \mu \frac{g}{\rho} \left[ 1 + \frac{3}{8} \text{Re} + 0 \left( \text{Re}^2 \right) \right]. \quad (16)$$

Thus Stokes exact solution for the case, $\text{Re} \to 0$, $\text{Kn} \to 0$, represents only a first approximation to the drag force for finite $\text{Re}$. However, the deviation from Stokes law is only about 4% at $\text{Re} \approx 0.1$.

Experimental observations of the dimensionless drag force, $D/\frac{1}{2} \rho g U_\infty^2$ are shown with predicted values of Equation [16] in Fig. 2. Agreement between theory and observation here is considered very satisfactory (27). Further confirmation of such consistency has been reported recently by Maxworthy (30). Interestingly enough, Oseen's result works as well as any for describing data for the drag on spheres below $\text{Re} = 0.4$.

One classical application of Stokes law is the estimation of the terminal fall velocity $v_s$ of a small particle in a gas. To calculate $v_s$, the medium is assumed stagnant, and the particle motion is steady. Then there must be a balance between the gravitational force and the frictional resistance
Figure 2
\[(\rho_i - \rho_g) g \frac{4}{3} \pi R_i^3 = 6 \pi \mu g R_i U_\infty,\]

where \(\rho_i\) and \(\rho_g\) are respectively the particle and gas densities.

Solving for the particle velocity,
\[U_\infty = v_s = \frac{2}{9} R_i \left(\frac{\rho_i - \rho_g}{\rho_g}\right) g.\] \((17)\)

Similarly the steady particle velocity \(v_c\) in a uniform electric field \(E_0\) may be calculated by balancing the electrostatic force and the frictional resistance. The result is:
\[v_c = Q_i E_0 B = Q_i E_0 \left(\frac{6 \pi \mu R_i}{g}\right)^{-1}\] \((18)\)

where \(Q_i\) denotes the net charge on the particle.

2. Accelerated Motion of Particles. There are many circumstances in which the motion of aerosol particles is not steady. When the sphere is accelerating, analysis of the aerodynamics of its motion is more complicated. The complete balance of forces in a spherical particle moving in a viscous medium was examined many years ago by Basset (31). His equation, for \(Re \to 0, Kn \to 0\), is written as:

\[\frac{4}{3} \pi R_i^3 \rho_i \frac{d \vec{q}_i}{dt} = 6 \pi \mu g R_i (\vec{q}_g - \vec{q}_i) + \frac{4}{3} \pi R_i^3 \rho g \frac{d \vec{q}_g}{dt} + \frac{2}{3} \pi R_i^3 \rho g \left[\frac{d \vec{q}_g}{dt} - \frac{d \vec{q}_i}{dt}\right] + 6 R_i^2 \sqrt{\rho g \mu} \int_{t_0}^{t} dt' \frac{(d \vec{q}_g / dt' - d \vec{q}_i / dt')}{(t - t')^{1/2}} + \vec{F},\] \((19)\)

where \(\vec{F}\) represents external forces acting on the particle, such as gravity or electrical forces. The other terms in Equation \((19)\) have the following meanings: The term on the left is the net force on the sphere. The first term on the right, of course, is the frictional resistance given by Stokes law. The second term on the right denotes
the force resulting from the pressure gradient in the gas immediately surrounding the moving particle. The third term represents the force required to accelerate the apparent mass of the particle relative to the ambient gas. The fourth, the Basset term, accounts for the effect of the deviation in gas flow pattern from steady state. This is generally considered an additional apparent frictional resistance.

It has been shown that in most cases of interest to aerosols, all terms on the right side of [19] but the Stokes resistance and the external forces are small and may be neglected (16). Therefore, the expression for acceleration of a sphere in an infinite pure gas may be considerably simplified to:

\[
\frac{dq_i}{dt} \approx -\vec{A} \vec{U} + a_e \tag{20}
\]

where \( \vec{A} \) is the inverse viscous relaxation time, \( B_i/m_i \) or \( \frac{9\mu}{2R_1^2} \), and \( a_e = \frac{F_e}{m_i} \).

Equation [20] has been used extensively for analyzing the inertial deposition of particles on surfaces and for other dynamical studies (e.g., Fuchs, 16, or Hidy and Brock, 13).

From various experimental observations discussed in reviews in Davies' book (17), it would seem that it should be necessary to add one additional force in the balance of Equation [19] if the gas is non-uniform. This force \( F_{NU} \) would account for forces acting on a sphere which are associated with non-uniformities in the gas; i.e., the thermal force or the diffusiophoretic force. We shall see later that \( F_{Nu} \rightarrow 0 \) for the thermal force. Under these circumstances, momentum transfer is disassociated from heat transport to the sphere\(^1\) (See also Sect. 2C.2).

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1. Formally, coupling can be allowed for in continuum theory through Onsager's reciprocal rules in irreversible thermodynamics (e.g., Prigogine, 32).
3. Heat and Mass Transfer to Spheres. In addition to momentum transfer to small spheres, the dynamics of particles covers the rate processes of heat and mass transfer. These latter phenomena are linked together in the especially important problem of evaporation and condensation of small droplets.

Calculation of the heat flux or the vapor flux to the surface of a sphere is carried out using the equations of convective transport in a continuum. For aerosols it is assumed that viscous dissipation is negligible, and temperature and vapor concentration between the gas and particle are small. If the vapor diffusivity $D_\alpha$ and thermal conductivity $k_g$ are approximately constant in the gas, the transport equations equivalent to the Navier-Stokes equation are written as

\begin{align}
\text{(vapor)} & \quad \frac{\partial \rho_\alpha}{\partial t} + \mathbf{U} \cdot \nabla \rho_\alpha = D_\alpha \nabla^2 \rho_\alpha \\
\text{(heat)} & \quad \frac{\partial T}{\partial t} + \mathbf{U} \cdot \nabla T = \left( \frac{k_g}{\rho_g c_p} \right) \nabla^2 T
\end{align}

Here $k_g / \rho_g c_p$ is the ratio of thermal conductivity to the product of the gas density times its specific heat. To solve these equations for either the distribution of vapor density $\rho_\alpha$, or the temperature in the neighborhood of the particle, $\mathbf{U}$ is taken as the velocity field given by the Stokes-Proudman and Pearson solutions, and the viscous boundary conditions are applied:

\begin{align}
\text{(vapor)} & \quad \rho_\alpha = \rho_\alpha(T_s) \quad \mathbf{r} = \mathbf{R}_i \\
& \quad \rho_\alpha \to \rho_\alpha(\infty) \quad \mathbf{r} \to \infty \\
\text{(heat)} & \quad T_g = T_s \quad \mathbf{r} = R_i \\
& \quad T_g \to T_\infty \quad \mathbf{r} \to \infty
\end{align}
Here $\rho_s$ is the vapor density at saturation for surface temperature $T_s$. The subscript $I$ implies, as in the Stokes' solution for the velocity field, that a uniform condition as $\rho_s$ and $T_s$ exists far from the sphere.

The dimensionless vapor and heat fluxes to the sphere are given by the Nusselt, Nu, and Sherwood numbers, $Sh$:

\[
\text{(mass transfer)} \quad Sh = \frac{2kR}{D} = \frac{1}{2} \int \left( \frac{\partial \rho_s}{\partial r} \right) r_{R_i} dA \tag{23}
\]

\[
\text{(heat transfer)} \quad Nu = \frac{2hR}{k} = \frac{1}{2} \int \left( \frac{\partial T}{\partial r} \right) r_{R_i} dA \tag{24}
\]

In these expressions $k$ and $h$ are the mass and heat transfer coefficients respectively, and $A$ is the surface of the particle.

Under conditions of steady state, in which $(\partial / \partial t) = 0$, Acrivos and Taylor (33) have solved the problem of convective heat or mass transfer to spheres using the flow field of Proudman and Pearson (29). By a perturbation method equivalent to Proudman and Pearson, Acrivos and Taylor found that:

\[
Sh = Nu = 2 \left[ 1 + \frac{Pe}{2} + \frac{Pe^2}{2} \ln 2Pe + (0.0608) Pe^2 + \frac{Pe^3}{4} \ln 2Pe \right] \tag{25}
\]

for $Pe_g \ll 1$.

Here $Pe_g^{(H)} = Pr \cdot Re$, $Pr = (\mu g / \rho_0)$. A form for the Sherwood number would be the same except that $Pe_g^{(M)} = Re \cdot Sc_g$, $Sc_g = \nu g / D\alpha$.

The expansion formulation of Equation [25] represents the analogy for heat and mass transfer of the Reynolds expansion for the drag force shown in Equation [16]. We note that Equation [25] gives the well
known relations for diffusional processes in a stagnant gas. That is, \( \text{Nu} = \text{Sh} = 2, \quad \text{Pe}_g \to 0. \)

The case of diffusional transport at large Peclet number, normally found for Brownian diffusion of aerosols in gas streams, has been studied by Friedlander (34), for example. Within the approximation discussed in D(1), this theory may be used to estimate the efficiency of aerosol removal by falling raindrops, and has application to problems of industrial scrubbing gases as well (see also, Fuchs, 16).

4. **Quasi-stationary Processes of Evaporation.** The application of steady state solutions for diffusional processes to droplet growth or depletion by vaporization is somewhat limited. Strictly speaking, vapor transfer to a small sphere cannot be a steady process in time because the particle radius change causes a change in the transfer rate. However, when the difference between the vapor density far from the body and at the surface of the body is small, one may assume that the rate process is quasi-stationary, and solutions like Equation [25] may be applied. Quasi-stationarity is also assumed implicitly in using the frictional resistance given by Stokes in Equation [16].

The assumptions of quasi-stationarity during droplet evaporation have been examined in detail by Fuchs (35) and more recently by Philip (36). Philip's analysis appears to give a complete and rigorous picture of this class of assumptions in droplet growth or depletion.

In addition to limitations of quasi-stationarity in calculating evaporation rates, one must bear in mind that both condensation and
evaporation are accompanied by latent heat release (or absorption). Thus these problems really are questions of simultaneous heat and mass transfer. Thus, for example, the rates of droplet growth or depletion by vaporization should be given in a form

\[ \frac{dm_i}{dt} = 4\pi R_i D_\alpha (\rho_\infty - \rho_{\alpha g}) \mathcal{J}(Re, Pr_g). \]  

(26)

The convection function \( \mathcal{J} \) has been discussed, for example, by Fletcher (10), and is equivalent essentially to \( \bar{Sh}/2 \) as given in Equation [25]. It has been found, at least for growth of larger droplets, that the heat transfer correction normally is a small effect correcting the growth rate given by mass transfer alone.

We may test the applicability of Acrivos and Taylor's equation to droplet evaporation by comparing this relation and the limited results of Kinzer and Gunn (37). This comparison is shown graphically in Fig. 3. Here we have assumed implicitly that neither the quasi-stationary assumption nor the heat effect will cause large deviations from vaporization rates given by Equation [25]. In the limit \( Pe \to 0 \), theory and experiment agree. However, Kinzer and Gunn's observations depart quite markedly from the theory everywhere else. The scatter in the experiment data, and certain experimental methods used by Kinzer and Gunn, have suggested that their data may not be completely accurate. There are very serious experimental difficulties in measuring vaporization rates of small droplets moving at low velocities. These problems were encountered by Kinzer and Gunn, as their paper notes. Because these experiments appear to be the only ones in the literature bearing on this question, it would be useful for further
Figure 3
experimental work to be undertaken to examine the applicability of Acrivos' and Taylor's theory.

C. SINGLE SPHERES IN NON-CONTINUOUS MEDIA

1. The Free Molecule Regime. In the other extreme of Knudsen number, where \( \text{Kn} \to \infty \), calculation of transport processes to spheres may be carried out directly assuming the applicability of the Maxwellian distribution for molecular velocities. Unlike the distribution implied in the Navier-Stokes approximation, the Maxwellian distribution is an exact solution to the Boltzmann equation when \( \text{Kn} \to \infty \).

The estimation of forces acting on particles in the free molecule regime has been reviewed, for example, by Waldmann (38). To illustrate the principles of these calculations, let us consider the frictional resistance on a sphere suspended in a pure gas. To calculate the force on a surface element it is only necessary to specify the undisturbed distribution function of the gas and the law of reflection on the surface. At steady state the force acting on an element of surface of the sphere in a stagnant gas reads

\[
\frac{dF}{dA} = \left[ \int \frac{m \cdot v \cdot f_\text{g}}{g} \cdot d\vec{v}_\text{g} - \int \frac{m \cdot v \cdot f^+ \cdot d\vec{v}_\text{g}}{g} \right] dA
\]

(27)

where \( \vec{v}_\text{g} \) is the molecular velocity vector, \( v_{gn} \) is the component of molecular velocity normal to the surface, and \( f^- (\vec{v}_\text{g}) \) and \( f^+ (\vec{v}_\text{g}) \) are the distribution functions for incoming and outgoing molecules at \( dA \).

Now the free molecule assumption is made that (a) the aerosol has small influence on the distribution of velocities, of \( f^- = f \),
the distribution function for molecular velocities in the absence of any surface, and (b) the approaching molecules are partly reflected from the surface elastically, (specularly) and partly diffusely. From the latter assumption, it follows that the coefficient for momentum accommodation, $\alpha_m$, is defined by

$$f^+(1 - \alpha_m)f^- + \alpha_m \left( n_g^+ / n_g \right) f^{(0)},$$

where

$$f^{(0)} = f = n_g \left( \beta / \pi \right)^{3/2} \exp\left[ -\beta (\nabla \cdot \mathbf{v}) \right]^2$$

with

$$\beta = m / 2kT.$$ 

Performing the integrations in Equation [27], we find that for small values of $q_1$ (36):

$$\mathbf{D} = \frac{8}{3} R_1 \frac{2}{g} \frac{1}{\pi m \sqrt{kT}} \left( 1 + \frac{\pi}{8} \alpha_m \right) q_1$$

This relation was obtained first in 1924 by Epstein (39). We note that the drag force in this extreme range of Kn differs markedly from Stokes' estimate. In particular the frictional resistance in Equation [30] is proportional to $R_1^2$ instead of $R_1$ as in Equation [13]. We find from Equation [30] that the mobility of particles in the free molecule regime has to be:

$$B_1 = \left[ \frac{8}{3} R_1 \frac{2}{g} \frac{1}{\pi m \sqrt{kT}} \left( 1 + \frac{\pi}{8} \alpha_m \right) \right]^{-1}.$$ 

The main uncertainty in these calculations lies in the value of the accommodation coefficient. This coefficient may vary from 0 to 1 depending on the nature of the surface and the molecules of suspending
gas. Unfortunately, virtually nothing is known about methods for predicting \( \alpha_m \), and only few experimental results are available. It may be seen from \([30]\) and \([31]\), however, that the term containing \( \alpha_m \) is additive, and at worst, the maximum possible error predicted in \( \mathbf{B}_1 \) or \( \mathbf{D}_1 \) can only be \( \pi/8 \).

In cases where the sphere is accelerating relative to the gas, an equation for the net force acting on the particle may be written in analog to Equation \([20]\). For the free molecule regime, however, \( \mathbf{B}_1 \) is given, of course, by \([31]\) and an additional acceleration \( \mathbf{F}_{NU}/m_i \) has to be included.

The forces acting on particles in the free molecule regime are coupled directly to non-uniformities in the suspending gas through modifications of the Maxwellian distribution function \( f \) \((38, 40)\). For example, when a temperature gradient exists in a pure monatomic stagnant gas, a thermally induced force acting on the sphere develops. Since, in this case,

\[
f \approx f(0) \left[ 1 - \frac{2m}{5kT} \left( \frac{m}{2kT} \frac{v^2}{g} - \frac{3}{2} \right) \frac{\partial f}{\partial T} \right]
\]

where \( \mathbf{r} \) is the position vector located at the center of the sphere, the thermal force is \((36)\):

\[
\mathbf{F}_T = - \frac{8}{15} R_i^2 \frac{2m}{kT} \frac{g}{kT} \frac{\partial T}{\partial x}.
\]

Remarkably, the accommodation coefficient does not come into this relation.
If a particle travels with a velocity $\mathbf{q}_i$ through a stagnant gas with an imposed temperature gradient, the thermal force and the frictional resistance balance in steady flow. Therefore,

$$\mathbf{q}_i = \frac{1}{5(1+(\pi/8)\alpha_m)} \frac{k g}{n k T} \frac{\partial T}{\partial x}$$  \hspace{1cm} (33)

in this case.

The thermal forces arise with heat transfer from the gas to the particle. If the particle receives heat from sources other than conduction from the gas, for example, by absorption of incident radiation, a new force may also develop as a result of a temperature gradient within the particle. The development of the photophoretic force has been discussed by Preining (17), and the special case of the Kn $\to \infty$ has been outlined recently by Hidy and Brock (41).

In a manner similar to thermal effects, non-uniformities in composition of a gas mixture may cause a force to act on particles in the free molecule regime. In this case, the distribution function for each component $\alpha$ of the gas mixture is given by

$$f_\alpha \approx f_\alpha^{(0)} \left[ 1 + \frac{m_\alpha}{k T g} \mathbf{q}_\alpha \cdot \mathbf{v}_\alpha \right],$$

when $\mathbf{q}_\alpha$ is the average velocity vector of species $\alpha$, and $f_\alpha^{(0)} = n_\alpha (\beta_\alpha/\pi)^{3/2} \times \exp[-(\beta_\alpha (\mathbf{v}_\alpha - \mathbf{v}_g)^2)].$ Then by the same methods used to derive Equation $[32]$ the force on a sphere in a gas mixture is

$$\mathbf{F}_D = -\frac{32}{3} R_i \sum_\alpha \left\{ \frac{1}{\mathbf{v}_\alpha} \right\} \frac{1}{8} \alpha_\alpha \left[ 1 + \frac{\pi}{8} \alpha_\alpha \right] p_\alpha (\mathbf{q}_1 - \mathbf{q}_\alpha),$$  \hspace{1cm} (34)

where $\langle v_\alpha \rangle = \left[ 8kT/(\pi m_\alpha) \right]^{1/2}$ and $p_\alpha = n_\alpha k T g$ ($n_\alpha =$ number density of component $\alpha$).
The relation between the mass average velocity of the gas mixture and the velocities of each of its components

\[ \dot{q}_g = \frac{1}{\sum \alpha m_{\alpha} n_{\alpha}} \sum \alpha m_{\alpha} n_{\alpha} \dot{q}_\alpha. \]

For a binary gas mixture, a diffusivity \( D_{AB} \) may be introduced such that

\[ \dot{q}_g = \frac{n_A \dot{q}_A + n_B \dot{q}_B}{n_A + n_B} - \frac{m_A - m_B}{m_A + m_B} D_{AB} \left( \frac{\partial \rho_A}{\partial \tau} \right). \]

Then for isothermal conditions in a binary mixture with \( n_A \dot{q}_A = n_B \dot{q}_B \),

\[ \dot{q}_i = \frac{(n_A + n_B) m_A^{\frac{1}{2}} (1 + (\pi/8) \alpha_{mA}) - m_B^{\frac{1}{2}} (1 + (\pi/8) \alpha_{mB})}{m_A^{\frac{1}{2}} n_A (1 + (\pi/8) \alpha_{mA}) + m_B^{\frac{1}{2}} n_B (1 + (\pi/8) \alpha_{mB})} \times D_{AB} \left( \frac{\partial \rho_A}{\partial \tau} \right). \tag{35} \]

If the accommodation coefficients, \( \alpha_{mA} \) and \( \alpha_{mB} \) are equal, Equation [35] further reduced to

\[ \dot{q}_i = \frac{m_A - m_B}{m_A + (m_A m_B)^{\frac{1}{2}}} D_{AB} \left( \frac{\partial \rho_A}{\partial \tau} \right). \tag{35a} \]

This relation indicates that a sphere will drift in the direction of the diffusional flux of the heavier component of the gas in the free molecule regime.

With the use of the distribution functions indicated above, it is also possible to calculate the heat and mass transfer to spheres as \( Kn \to \infty \). Brock (42) has reported such calculations.

Using a distribution function equivalent to those considered for the thermal force and the diffusiophoretic force, Brock gives the rate of evaporation or condensation to a sphere as (42):
Here the superscripts have the meaning outlined in Equation [27], and \( \alpha_{c\alpha} \) is the evaporation coefficient defined as

\[
\alpha_{c\alpha} = \frac{j_{\alpha}^{-}(R_i) - j_{\alpha}^{+}(R_i)}{j_{\alpha}^{-}(R_i) - j_{\alpha}^{+}(R_i)}
\]

\( j_{\alpha}^{\pm} \) and \( j_{\alpha}^{+} \) are, respectively, the fluxes to and from the surface, and \( j_{\alpha}^{+} \) is the outward flux of \( \alpha \) species leaving in equilibrium with the surface. \( \alpha_{c\alpha} = 1 \) means all \( \alpha \) molecules leave at equilibrium from the surface, while \( \alpha_{c\alpha} = 0 \) indicates that no \( \alpha \) molecule is absorbed at the surface but is specularly reflected. The functions \( \xi_{\alpha} \) have been tabulated in the form

\[
\xi_{\alpha} = \int_{0}^{1} d\xi \exp(-Ma^{2}\xi^{2}/\eta)
\]

For a dilute, binary isothermal gas mixture in which the mass average velocity is small relative to the average velocity, \( Ma \to 0 \), Equation [36] reduced to a much simpler form:

\[
J_{M} = 2\pi R_{i}^{2} \sum_{\alpha=A}^{B} \alpha_{c\alpha} \left[ n_{\alpha}^{+} \left( \frac{\nu}{m_{\alpha}} \right)^{\frac{3}{2}} + \left( \frac{2kT_{\nu}}{m_{\alpha}} \right)^{\frac{3}{2}} \right] - n_{\alpha}^{-} \left( \frac{2kT_{\nu}}{m_{\alpha}} \right)^{\frac{3}{2}} \]

\[
+ \sum_{\alpha=A}^{B} \frac{8}{3} \alpha_{c\alpha} \left( \frac{2\nu m_{\alpha} kT_{\nu}}{g g} \right)^{\frac{3}{2}} \rho_{g} \cdot D_{AB} \cdot \nabla \rho_{\alpha} / \rho_{g} \quad , \quad Kn \to \infty , \quad Ma \to 0
\]
Similarly, the heat flux is found to be (42) for a dilute binary mixture:

\[ J_H = 4\pi R_1^2 \sum_{\alpha=A}^B \alpha T_\alpha \left[ n_\gamma^+ kT_g \left( \frac{2kT_g}{m_\gamma} \right)^{\frac{3}{2}} - \frac{n_\alpha^- - n_\alpha^- kT_g \left( \frac{2kT_g}{m_\gamma} \right)^{\frac{1}{2}}} \right] \times \left\{ C_\alpha \left( 1 + 8 \frac{Ma^2}{\pi} \right) + \exp\left\{ - 4 \frac{Ma^2}{\pi} \right\} \right\} \]  

(37)

where \( \alpha T_\alpha \) is the thermal accommodation, defined in an analogous way to \( \alpha c \). For a pure gas in which \( Ma \to 0 \), Equation [37] reduced to (in the absence of radiation):

\[ J_H = 4\pi R_1^2 \alpha T \left[ n_g^+ kT_g \left( \frac{2kT_g}{m_g} \right)^{\frac{3}{2}} - n_g^- kT_g \left( \frac{2kT_g}{m_g} \right)^{\frac{1}{2}} \right] \]  

(37a)

As in the case of momentum transfer, the main uncertainty in calculation dealing with spheres is non-uniform gases when \( Kn \to \infty \) are the accommodation coefficients \( \alpha c \) and \( \alpha T \). Very little is known about these functions even for simple aerosol systems. In fact, neither Equation [36] nor [37] have been studied experimentally in any detail for aerosols.

2. The Zone of Transition in Knudsen Number. From a view of practical applicability of the mechanical theory of aerosols, the transition regime \( 0.01 < Kn < 10 \) is of principal interest. Yet this regime is the most difficult to treat theoretically. Some years ago, the careful experiments of Millikan and others (16) established that the mobility of very small droplets moving steadily in a gas had to be corrected for the effect of Knudsen number. The experimental results were placed in the form of Equation [3] with
the correction given in terms of [4]. Although semiempirical methods have been applied to explain the form of the Factor \( \hat{A} \) (e.g., Fuchs and Stechkina, 43), only recently have there been completely successful theoretical approaches to estimate the frictional resistance in this Kn range.

Early theories relied on intuitive adjustments of continuum theory to account for slippage of gas at the particle surface when Kn \( \neq 0 \). The slip flow condition revises one boundary condition in the pair of [13] to be, at constant temperature,

\[
(t\text{angential component of } \mathbf{U}) \\
U_0 = \frac{c \lambda}{m g} \left[ \frac{r}{\partial r} (U_\infty/r) + 1/r (\partial U_r/\partial \theta) \right], \quad \frac{r}{r} = \frac{r}{R}
\]

\[
(r\text{adial component of } \mathbf{U}) \\
U_r = 0
\]

For these conditions, Basset solved Stokes problem and obtained a relation (30):

\[
D \approx 6 \pi g \left[ \frac{1 + 2c Kn}{1 + 3c Kn} \right] P_i m
\]

(39)

where \( c_m \) is the slip coefficient.

Comparison between this result and the form of Equation [3] for small values of Kn demonstrates that the slip flow approximation is in error, except for Kn \( \rightarrow 0 \) (Jacobsen and Brock, 44). Equation [3] should give a linear relation between Kn and the frictional resistance as Kn \( \rightarrow 0 \), with \( C_m = A \approx 1.0 \). However, Equation [39] departs from the linear rule at Kn > 0.03 for \( C_m \approx 1 \) as noted in the calculations in Table 4.
Recently progress in the general theory of rarified gas dynamics has suggested that iterative expansions of molecular distribution functions in terms of Knudsen number may be useful approximate solutions to the Boltzmann equation. The form

\[ f_{\alpha} \approx f_{\alpha}^{(0)} + \frac{1}{Kn} f_{\alpha}^{(1)} + \ldots \]

has been used by Willis (45) to calculate satisfactorily the frictional resistance of a sphere over the range \(0.5 < Kn < \infty\). Willis' result is:

\[ \delta \approx \delta^* [1 - 0.366 Kn^{-1}] \tag{40} \]

where \(\delta^*\) is given by the free molecule limit, Equation [30].

This expression agrees with Equation [3] in the free molecule limit. And comparison between the correction Factor \((1 + \hat{M} \Delta g / R_i)\) with Davies' coefficients, and those given by Willis' equation substantially agree, as indicated in Table 4.

The regime below \(Kn < 1\) remains unspecified theoretically, but the functional form of \(\hat{A}\) can be taken relatively well established by extrapolating to \(Kn \to 0\).

As indicated by the analysis for free molecule aerosols, thermal forces or diffusiophoretic forces may act on particles suspended in a non-uniform medium. It has been demonstrated by means of a slip flow analysis (38, 46, 47), and by arguments based on the theory of irreversible thermodynamics (48, 49) that these forces can be predicted from the theory of gas dynamics. In cases where \(Kn \to 0\), the thermal force reduces to zero, according to Brock's (44) calculations. Brock's theory based on a "first order" slip flow analysis
Table 4

Comparison between Basset's slip flow theory, Willis' theory (45) and experimental values for the Knudsen number correction of the frictional resistance in air at values of 1 atm. pressure and 20°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>c_m = 1</td>
<td>α_m = 1</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>1.082</td>
<td>-</td>
<td>-</td>
<td>1.13</td>
</tr>
<tr>
<td>0.5</td>
<td>1.25</td>
<td>4.18</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>2.67</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>-</td>
<td>9.13</td>
<td>8.89</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>-</td>
<td>17.5</td>
<td>17.2</td>
<td></td>
</tr>
</tbody>
</table>
yields the following expression for the thermal force:

\[ \mathbf{F}_T = -\frac{12\pi R_i^2 (c_t \text{Kn})(k_g/k_i + c_t \text{Kn}) \nabla T}{(1+3c_t \text{Kn})(1+2k_g/k_i+2c_t \text{Kn})} \]

for \( \text{Kn} < 0.05 \),

where \( c_t \) and \( c_{tm} \) are respectively the temperature jump coefficient and the thermal velocity coefficient. Here \( k_g \) and \( k_i \) are the thermal conductivities of the gas and the particle. From Equation [41], we note that \( \mathbf{F}_T \to 0 \) as \( \text{Kn} \to 0 \).

Derjaguin and Yalamov's theory [48] for the thermal force predicts a relation differing from Equation [41]. The method of analysis used by these authors is a phenomenological one which should be similar to Brock's direct application of continuum equations. Evidently the difference lies in the form of the slip conditions used at the boundary. Brock's result, Equation [41], agrees with the experiments of Schmitt (50) for M-300 silicone aerosols in argon, and Rosenblatt and La Mer (51) for TCP aerosols, but Equation [41] had to be corrected to second order to obtain agreement with data of Jacobsen and Brock (46) for sodium chloride particles in argon. Derjaguin and Yalamov have indicated that their theory agrees best with data taken for oil droplets in helium with a flow method by Derjaguin, Rabinovich and Storzhilova (52). The results of workers (42, 48, 49) were obtained by the Millikan cell technique, which Derjaguin has criticized as being inaccurate.

Drift of large aerosol particles where \( \text{Kn} \to 0 \) in a gas containing concentration gradients may arise in two ways. The first is an effect resulting from Stefan flow compensating a diffusional flow of a gaseous component. In the second case, particle motion results from the slip
of gas at the particle surface which is associated with gradients in concentration of gaseous components. This type of slippage is directly analogous to thermal slip. In the special case of a binary gas at constant pressure and temperature, the diffusion force reduces to zero as \( Kn \to 0 \). However, other situations such as equimolar counter diffusion or diffusion of a species through a stagnant gas can lead to a diffusion force even in the limit of zero Knudsen number (46).

Several aspects of the theory of thermophoresis and diffusiophoresis in the free molecule regime and the slip flow regime where \( Kn \to 0 \) are discussed in more detail by Waldmann and Schmitt (17).

In the regime where \( Kn > 0.2 \), the thermal force can be estimated a priori with much more confidence than in the slip flow regime. In the range of \( 0.2 \leq Kn \leq \infty \) experimental results taken by the Millikan cell method can be correlated by the empirical relation:

\[
\overrightarrow{F_t} = \overrightarrow{F^*} \left\{ \exp \left( -\frac{\lambda R_i}{g} \right) \right\},
\]

(42)

where \( \overrightarrow{F^*} \) is given by the free molecule value for monatomic gases (53) (see also Equation [32]).

Application of an integral iteration method by Brock (53) has indicated that \( \tau \) may be estimated theoretically in terms of the momentum accommodation coefficient \( \alpha_m \) and the thermal accommodation coefficient \( \alpha_T \):

\[
\tau = 0.06 + 0.09 \alpha_m + 0.28 \alpha_m \left[ 1 - \alpha_T \frac{k}{2k_i} \right].
\]

(43)

This relation holds for polyatomic gases; for monatomic gases, \( \alpha_T \) is equal to \( \alpha_m \).

Using a classical relation between the slip coefficient \( C_m \) and the momentum accommodation coefficient \( \alpha_m \),
Table 5

Estimated values of the parameters $c$ and $a_m$ from experimental data for the thermal force (from Brock, 53)

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Gas</th>
<th>Eq. 43</th>
<th>$a_m$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M300</td>
<td>A</td>
<td>0.39 ± 0.01</td>
<td>0.80</td>
<td>48</td>
</tr>
<tr>
<td>M300</td>
<td>N$_2$</td>
<td>0.38 ± 0.01</td>
<td>0.81</td>
<td>48</td>
</tr>
<tr>
<td>M300</td>
<td>CO$_2$</td>
<td>0.36 ± 0.02</td>
<td>0.80</td>
<td>48</td>
</tr>
<tr>
<td>M300</td>
<td>H$_2$</td>
<td>0.22 ± 0.04</td>
<td>0.79</td>
<td>48</td>
</tr>
<tr>
<td>TCP</td>
<td>Air</td>
<td>0.41 ± 0.02</td>
<td>0.88</td>
<td>49</td>
</tr>
<tr>
<td>NaCl (Amorph.)</td>
<td>A</td>
<td>0.47 ± 0.01</td>
<td>0.91</td>
<td>42</td>
</tr>
<tr>
<td>NaCl (Cryst.)</td>
<td>Air</td>
<td>0.46 ± 0.02</td>
<td>(0.91)</td>
<td>52</td>
</tr>
</tbody>
</table>
\[ C_m = 1.00 \frac{(2-\alpha_m)}{(\alpha_m)} \, , \]

Brock (53) has calculated values of \( T \) and \( \alpha_m \) based on experimentally determined numbers for \( C_m \). His estimates are shown in Table 5. Data reported using the flow method, e.g. (51) yield unrealistically low values of \( T \), departing markedly from the other data in Table 5. Results of the flow method that \( T \approx 0 \) would suggest that the reduction in thermal force to zero from the free molecule value must occur in the region \( 0 \leq Kn \leq 0.2 \). Extensive qualitative observations of the behavior of thermal precipitators indicate that this abrupt change is not true; therefore, Brock (53) has concluded that the flow method, as it has been applied so far, has inherently larger experimental errors than the Millikan cell technique.

Similar calculations can be made by the slip flow analysis or the integral iteration technique for the diffusiophoretic forces. Here again there appears to be disagreement between authors (e.g., Brock (47) and Derjaguin and Yalamov (49)) for the slip flow calculations. Unfortunately, very little data is available with which to compare the theory because of experimental difficulties. Some very limited experiments have been discussed by Goldsmith and May (17) and by Waldmann and Schmitt (17).

Some aspects of problems of heat transfer to bodies in an infinite gas in the regimes of \( Kn > 0 \) have been reviewed by Schaaf and Chambre (55), and later for concentric spheres by Brock (56). Mass transfer or evaporation from a sphere in the transition regime of \( Kn \) has been investigated recently by Brock (57). Brock's calculations are restricted to the situations where species A evaporates from a sphere into an
infinite pure gas composed only of species B under conditions of the ratio $\frac{q_g}{\langle v_g \rangle} \ll 1$ (see above for the case, $Kn \rightarrow \infty$).

In these circumstances, as $Kn$ decreases below the free molecule limit, collisions between molecules leaving the particle surface and those hitting the surface begin to appear. Such collisions effectively retard the escape of evaporating molecules from the immediate neighborhood of the sphere. When relative motion between the gas and the particle exists, such motion will increase the evaporation rate by modifying the collisional trajectories (57). Of course, the relative motion here must reach the order of the thermal velocities of the gas molecules to be important in modifying in the collisional trajectories. Thus, when the gas contains an evaporating species in flow past the particle in the regime $0 < Kn < 10$, two distinct effects may contribute to increasing the evaporation rate over that expected in a stagnant medium. These two effects are (57): (a) induced evaporation through asymmetry in incident concentration of the evaporating species, and (b) increased evaporation by modification of trajectories in molecular collision tending to remove outward traveling species from the vicinity of the sphere. Under the restriction $|\vec{q}_g| / \langle v_g \rangle = |\vec{q}_B| / \langle v_B \rangle \ll 1$, or for small relative particle-gas velocities, both of these effects are small and the contribution of $\vec{q}_B$ to the evaporation rate vanishes. Thus, the external relative motion has no effect on the evaporation.

This conclusion is directly analogous to the result of Acrivos and Taylor (Equation [25]), as $Pe_G \rightarrow 0$.

For small values of $R_i/\lambda_B$, Brock (57) finds that the overall evaporation rate of component A from a sphere is:
\[ J_M = \pi R_1^2 \beta A n_A^+ \langle \nu A \rangle (1 - \beta A \varphi R_1 / \lambda_B) \text{Kn}^{-1}, M_a \ll 1, \]

where \( n_A^+ \) is the molecular density of evaporating molecules at the particle surface calculated on the basis of thermodynamic equilibrium at the surface. The parameter \( \varphi \) reads

\[ \varphi = 0.807 (m_A + m_B/m_B)^{3/2} (R_A + R_B/2R_B)^2 I_o, \]

where \( I_o \) is an integral function tabulated by Brock (57). In Table 6 are shown typical values of \( \varphi \) for various values of \( m_A \) and \( m_B \).

We note that for fixed \( R_B, m_B \) and \( n_B, J_M \) is largest for \( m_A/m_A + m_B \rightarrow 0, R_A/R_B \rightarrow 0 \). As these ratios increase, \( J_M \) decreases. Physically this result may be interpreted that the mean free path of component \( A, \lambda_A \), is largest for fixed parameters of component \( B \) when \( m_A/m_A + m_B \rightarrow 0 \) and \( R_A/R_B \rightarrow 0 \). As these ratio increase \( \lambda_A \) decreases. Thus the probability of return to the sphere of evaporating species \( A \) is directly related to \( \lambda_A \), the distance molecules \( A \) traveled before their first collision with other gas molecules. As \( \lambda_A \) gets larger, the probability of return of molecule \( A \) decreases, or the evaporation flux should be maximum with minima in the foregoing ratios.

Several experimental studies reviewed by Fuchs (35), for example, have indicated that the evaporation rate takes the form of

\[ J_M = \pi R_1^2 \beta A n_A^+ \langle \nu_A \rangle / (1 + \hat{B} \text{Kn}). \]

Equation [44] represents a first term in a series expansion of this relation, and in fact the Knudsen iteration carried to higher order would yield such a form. Therefore, it seems likely that \( \hat{B} \) may be identified with the coefficient \( \beta A \varphi \), and
Table 6

Coefficient $\phi$ of inverse Kn for evaporation of molecule A into a gas of species B from a smooth sphere (after Brock, 57).

<table>
<thead>
<tr>
<th>System</th>
<th>$\frac{m_B}{m_A + m_B}$</th>
<th>$\frac{R_A}{R_B}$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A - B</td>
<td>1.000</td>
<td>0.000</td>
<td>0.060</td>
</tr>
<tr>
<td>A - B</td>
<td>0.500</td>
<td>1.000</td>
<td>0.206</td>
</tr>
<tr>
<td>Water (A)-Air (B)</td>
<td>0.616</td>
<td>1.235</td>
<td>0.264</td>
</tr>
<tr>
<td>N-Octane (A)-Air (B)</td>
<td>0.21</td>
<td>2.00</td>
<td>0.46</td>
</tr>
<tr>
<td>Diamyl-sebacate (A)-Air (B)</td>
<td>0.08</td>
<td>2.8</td>
<td>1.18</td>
</tr>
</tbody>
</table>
appears to represent a good approximation for the evaporation in the transition regime of Kn.

Limited data of Monchik and Reiss (58) for diamyl sebacate evaporation provides a rough check on Brock's theory. These authors give \( \beta_A \approx 0.5 \), and from their data, \( \beta_A = \hat{\beta} \approx 0.6 \), yielding a value of \( \Phi \approx 1.2 \). From Table 6, the theoretical value is \( \Phi \approx 1.18 \). Such close agreement must be considered fortuitous, however, because of scatter in Monchik and Reiss' data, and uncertainties in Brock's kinetic model.

The theory for evaporation in the non-continuum regime which has been used most frequently until recently stems from Fuchs (59). Fuchs' earlier analysis is a semi-empirical one which assumes a concentration jump near the particle surface. The jump occurs over a thickness \( \Delta \). In this layer free molecule transport occurs, while outside this layer continuum transport is postulated. Apparently errors in such an analysis should occur mainly at high ratios, Kn. Fuchs' analysis will yield

\[
J_M = \frac{\pi R_1^2 \beta_A n_A^+ \langle v_A \rangle}{(1 + \frac{\beta_A \Phi R_1}{A_B})}
\]

\( 0.2 < Kn < \infty, Ma << 1 \)

at small values of \( Kn^{-1} \). This suggests, in contrast to Equation [45], that no linear correction exists to the evaporation flux. Though the theory should be valid for small Knudsen number in the sense that a slip analysis is valid, this model may seriously underestimate corrections for transitional behavior at high Kn, provided that Brock's theoretical calculations are correct.
Lastly in this section, let us consider briefly the implications of quasi-stationarity in the transition regime of Knudsen number.

In the continuum regime it is possible to show that a characteristic time \( \theta_c(g) \) for achievement of a steady state in diffusional processes of gases near a surface is the order of

\[
\theta_c(g) \approx \frac{R_i^2}{D_{\alpha}},
\]

where \( D_{\alpha} \) may be the diffusivity of gas molecules in a mixture, or the thermal diffusivity, for example.

The equivalent characteristic time to realize steady state in a non-continuum environment is:

\[
\theta_{nc}(g) \approx \frac{R_i}{v_g}.
\]

Evaluation of \( \theta_c(g) \) and \( \theta_{nc}(g) \) at normal temperatures for a 0.1 \( \mu \) particle indicates that these times are the same order, \( \sim 10^{-10} \) sec.

To assume quasi-stationarity in gaseous transport processes to aerosol particles, one must place restriction that

\[
\theta_c(g) \ll \theta_c(p),
\]

where \( \theta_c(p) \) is the characteristic time of transport in the particle; that is, \( \theta_c(p) = \frac{R_i^2 \rho C_p}{k_i} \) for heat transfer. Such a restriction is satisfied in general, for example, with particles with thermal conductivities of ordinary liquids, but not with particles of conductivity equal to many solid metals. For similar problems in the non-continuum regimes, the quasi-stationary assumption has to be justified in terms of particle sizes and speeds of gas molecules, or

\[
\theta_{nc}(g) \ll \frac{R_i}{v_g}.
\]

This condition cannot be fulfilled in general.
Applying these ideas to evaporation, where the particle radius changes continuously, Brock (60) has noted that quasi-stationarity in the transfer rates involved in gaseous evaporating particles requires that

\[ \Theta_{nc}^{(g)} \ll \Theta^{(pR)} \]  \hspace{1cm} (47)

Here the characteristic time for change in radius, \( \Theta^{(pR)} \), is defined for all Knudsen numbers as

\[ \Theta^{(pR)} = \frac{R_i}{dR / dt} \geq 4 \Xi^{(p)} R_i / \Xi^{(g)} < v_g > \]

\( \Xi^{(p)} \) and \( \Xi^{(g)} \) being respectively the gas and particle molar densities. Inequality [47] is satisfied, in general, in systems where the pressure of the suspending gas is not too high.

D. RATE PROCESSES IN PARTICULATE CLOUDS

When dealing with collections of particles, essentially two limiting cases have been considered. When time scales of particle-boundary interaction are much shorter than time scales of particle-particle interaction, the behavior particles commonly are treated in terms of isolated bodies in the single particle regime. Examples of problems in this case include particle capture on surfaces and settling, filtration, etc. Such extreme restrictions may be extended somewhat further to Brownian diffusion of particles. In the other extreme, particle-particle interaction or particle-gas interaction may dominate the behavior of a particulate cloud in such cases where the cloud is effectively unbounded. Some examples of this are spontaneous
condensation and evaporation phenomena, and collision-coagulation phenomena. The notion of a single particle regime also has been applied in this extreme. One simple example is well known (2). Suppose we consider a cloud of condensing droplets. In the single particle regime, we argue that condensation on all droplets will tend to make the droplet size distribution monodispersed. This is readily seen by noting that growth by diffusion of vapor is governed by a rule that $\frac{dR_1}{dt} = \text{const}$ in the absence of depletion of vapor far from the droplets. Thus $R_1^2 = R_0^2 + Ct$, where $R_0$ is the initial radius and $C$ is a constant. The term $Ct$ is much larger than $R_0^2$, and nearly the same for all particles. Therefore, the final radius of all droplets has to be nearly the same regardless of $R_0$. Such crude arguments have been verified for condensing clouds, for example, by Reiss (61), and have been applied successfully to predicting the operation of aerosol generators like the La Mer device.

The classical theory of coagulation of sols by Brownian motion (62) relies on a substantial simplification that particle-particle interaction is instantaneous, and the problem can be treated as an application of the theory of Brownian motion. Continuum models of the collisional interaction have been developed by extending restrictions of the single particle regime to incorporate in a relatively simple way electrical interaction and aerodynamic interaction. These theories effectively add a drift velocity to the diffusional flux in estimating the collision rate. Non-continuum calculations, however, can be made somewhat less restrictive than this (63, 64).
In any case, let us examine some features of the kinetic equations that are commonly applied to collections of particles. We restrict attention to the situation where the particles do not affect strongly the distribution functions of gas molecules, so that only the statistics of the particles themselves are estimated.

1. **Brownian Motion.** If, in addition, we further restrict ourselves to conditions where no particle-particle interaction exists, the statistical behavior of the particulate cloud rigorously can be expressed in terms of a stochastic model yielding the Fokker-Planck equation for the time rate of change of the probability distribution function of the particles. This conclusion is the first one stemming from the classical theory of Brownian motion (23).

Under conditions when displacements of particles are followed after a time interval $t > (m_i B_i)$, the well known diffusion equation results from the theory. For a given class of particle,

$$\frac{\partial n_i}{\partial t} = \nabla \cdot \left[ D_i \nabla n_i - m_i B_i \vec{F} n_i \right]$$

(48)

if $n_i$ the concentration of the $i$th species of particle is identified with the probability distribution function of this species. The particle velocity, $B_i \vec{F}$ denotes the average drift of particles of class $i$ relative to a fixed location.

Equation [48] essentially indicates that the transport of particles by convection and Brownian motion in a gas may be analyzed in terms of equations equivalent to the conservation equations for transfer of gas molecules, provided the restrictions enumerated above are met. The
main problem in doing this, of course, is arriving at a proper
definition for the drift velocity, \( \vec{B}_i \) in a polydisperse cloud.

The classical theory of Brownian motion revealed an important
simple relation between the mean square displacement of a particle \( \langle x^2 \rangle \)
and the diffusivity. Einstein (14) found that

\[
\frac{\langle x^2 \rangle}{2t} = \text{const} = D_i
\]  

(49)

where \( t_r \gg (m_i/B_i) \).

Because the relaxation time \( t_r \) is very small for most aerosol
particles, little attention has been given to cases where the particle
motion remains "correlated," i.e., where \( t_r \leq m_i B_i \). In analogous
problems of the random dispersion of particles in a turbulent gas, it
is necessary to examine such questions because the motion of a particle
can remember where it came from for time scales much longer than the
time \( m_i B_i \) associated with Brownian motion. The general problem of
constructing the statistics of particle displacement in turbulent
media is a difficult one, because of the mathematical complexities of
accounting for eddying motion in the fluid and the inertia of the
particle (67). Here we shall illustrate some simple conclusions by
considering an ideal case where the particle density is identical
to the density of the suspending gas, and the turbulence is isotropic.
For this case Taylor (68) worked out the relations for particle
displacement. We can follow his arguments first by noting that the
displacement

\[
x = \int_{t_0}^{t} v_i \, dt
\]
Squaring this relation, averaging we find that
\[ \langle X^2 \rangle = 2 \langle v_i^2 \rangle \int_{t_0}^{t} dt_1 \int_{-\infty}^{t} dt_2 R_L dt_1, \]
where
\[ R_L = \frac{\langle v_i(x_0, t) v_i(x_0, t_1) \rangle}{\langle v_i^2 \rangle} \]
But after long time intervals, \( \Delta t \to \infty \), \( \int_{t_0}^{t} R_L dt_1 \approx \text{const} \), so that
\[ \Delta t \to \infty , \quad \langle X^2 \rangle \approx 2 \langle v_i^2 \rangle \text{const} \Delta t. \]
This last result is precisely that of Einstein's, given in \([49]\).
Thus Taylor's idealized model of dispersion of particles by turbulence is entirely analogous to the model of displacement by Brownian motion.

For relaxation times \( t_r = \Delta t \) short, so that the particle motion is correlated, the average displacement is linear, whereas at longer times \( t_r \gg \Delta t \), the average displacement \( \langle X^2 \rangle^{\frac{1}{2}} \) should be parabolic in time.

In the absence of any particle drift, Eq. \([48]\) without the second term on the right, has been applied extensively to analyze the diffusion of aerosol in a stagnant medium. An equation of the same form with an "eddy" diffusion coefficient also has been applied to idealized turbulent media without mean motion. When the diffusion of aerosols takes place in a moving gas, Eq. \([48]\) has been applied in practice by assuming that the drift velocity \( \mathbf{B}_D \mathbf{F} \) equals the mass average speed of the gas, \( \mathbf{q}_g \). It is clear from the Basset equation \([19]\) that this assumption is fundamentally unjustified. Nevertheless a wide variety of theory has evolved using this simplification for motion and deposition of aerosols resulting from aerodynamic effects.
and Brownian motion. Despite its limitations, this type of theoretical approach generally has been successful in predicting at least qualitatively the observed behavior of clouds of non-interacting aerosols in flowing gases. Representative recent work of this kind is reported by Friedlander (63), Zebel (64), and Spurny and Pick (17). Many of the theoretical investigations have been reviewed by Fuchs (16) and more recently by Hidy and Brock (13).

2. **Conservation Equations.** The successful application of the diffusion equation to aerosol systems has led some workers to extend such relations arbitrarily to incorporate the generation or destruction of particles via condensation or coagulation by adding a source term to Equation [48]. Such a procedure is justified heuristically by analogy to the continuum equations for gases undergoing homogeneous chemical reaction (e.g., Bird, Stewart and Lightfoot, 25). This type of extension may be dangerous and unjustified on theoretical grounds. However, it is not clear at this time exactly what form the complete rate equations should take for aerosol clouds. In the absence of a better theory, such arbitrary assumptions of the form of the kinetic equation appear to be useful.

Formally, it is possible to construct a generalization of the results of Brownian motion to include collisions of particles. If certain "internal" variables are included, such a phenomenological theory displays distinctive differences from the conservation equations applying to gas mixtures. One attempt to formulate such a generalized approach has been reported by Soo (20); another
has been reported by Berry and Mordy (67). Let us follow briefly some of the discussion of the latter authors, whose formalism includes diffusive action, and the processes of coagulation and vaporization.

To describe a system of interacting particles, let us use the number density which is a function of "external" parameters, particle size, spatial location and internal parameters. An internal parameter is a property of a particle that affects its rate of growth by phase change, or its probability of agglomeration after collision, but this parameter does not change as a result of these processes. The only parameter influenced by vaporization or agglomeration is assumed to be particle size. Examples of such properties include electrical charge, and the activity of a nucleus as a condensation center.

Extensive variables will be assumed to be additive for a particle which results from the collision of two other bodies. This restriction implies that particle velocity may not be used as an independent parameter.

To complete such a formulation, parameters of the mechanics of collision and the environment have to be specified. This is done by restricting consideration, as before, to cases of a quasi-single particle regime, in which instantaneous binary collisions are of interest, and the state of the gas is given by its thermodynamic variables. Specifically the rate of condensation will be determined by the vapor pressure of condensable species near the particle. This

1. For a somewhat different statistical approach, see also Hulburt and Katz (70).
local vapor pressure, of course, is subject to adjustment resulting from the particle distribution in the gas.

Now suppose we define a distribution function $w$ as

$$w(m, I, \vec{r}, t)dm dI d\vec{r} = n(m, I, \vec{r}, t), \quad (51)$$

which is the number of particles in the volume element $dm dI d\vec{r}$ of $w$-space at any time $t$. $I$ denotes the internal parameters associated with a particular species of mass $m$. There may be more than one of these variables, or a surface film on a particle restricting its evaporation.

External conditions affecting the growth rate will appear, at least in the case of condensation, in an auxiliary equation relating $m$ to $m$, $I$, $\vec{r}$, and the suspending gas. In the case of coagulation, the environmental influence enters through a collisional parameter or kernel describing the physical mechanisms of collision.

One can use various integrals to eliminate the specification of internal parameters. For example,

$$w'(m, \vec{r}, t) = \int_0^\infty w \, dI,$$

which is equivalent to the number density of particles of mass $m$ around point $\vec{r}$ in physical space at time $t$.

From the definition of $w$, Equation [51], we note that each particle consists of a single point in $(m I \vec{r})$ or $w$-space. When no agglomeration occurs, each point retains its identity, and the number of points in $w$-space is conserved. Motion of a point along the $\vec{r}$ coordinate denotes particle motion in physical space, while motion along the $m$ coordinate constitutes change in mass by condensation or evaporation. The mass of a particle represented as a point in $w$-space cannot be conserved, but its identity is, in the absence of collisions.
The rate of change in time of \( w \), \( \frac{\partial w}{\partial t} \) may now be calculated in terms of the external and internal variables \( m, I, r \) and \( t \). For convenience let us split the partial derivative into two parts:

\[
\frac{\partial w}{\partial t} = \left( \frac{\partial w}{\partial t} \right)_{\text{drift}} + \left( \frac{\partial w}{\partial t} \right)_{\text{agglom}}
\]

The drift term may be calculated by specifying the flux of particles of one species in and out of a fixed enclosed volume \( \Omega \) in \( w \)-space. If the surface of \( \Omega \) is \( A \), conservation of species requires that the change in number of points in the volume per unit time equals the net number of points drifting across \( A \) into \( \Omega \) per unit time:

\[
\frac{\partial}{\partial t} (w d\Omega) + \oint \mathbf{w} \cdot d\mathbf{A} = 0
\]

where

\[
d\Omega = dmd\mathbf{I} d\mathbf{r}, \quad \text{and} \quad \mathbf{w} = \mathbf{m} \cdot \mathbf{m} + \mathbf{I} \cdot \mathbf{i} + \mathbf{j} \cdot \mathbf{j} + \mathbf{k} \cdot \mathbf{k}
\]

The term \( \mathbf{m}, \mathbf{i}, \mathbf{j}, \mathbf{k} \) and \( \mathbf{I} \) are unit vectors, and \( \mathbf{v} \) is the velocity of a point in \( w \)-space.

Making use of Gauss' theorem we find that an expression for continuity of species of particles in \( w \)-space is derived:

\[
\left( \frac{\partial w}{\partial t} \right)_{\text{drift}} + \nabla \cdot (w \mathbf{v}) = 0, \quad (52)
\]

which is directly analogous to the expression for continuity of species in a gas mixture.

The rate of change in \( w \) by collisional processes is given by the difference between gains in the number of particles of a given size, location and intensive variables by binary collisions and the loss in particles of this class by collisions with all other classes:
The gain of particles into a particular class will depend on collision and sticking of two smaller species to form a given mass \( m \), or on the break up of a larger mass to form smaller particles, one of which is mass \( m \). Assuming that only binary processes are of importance, then two terms may be expressed formally as

\[
\frac{dw}{dt} = \dot{a} = g_{\text{gain}} - g_{\text{loss}}. \tag{53}
\]

The limits of integration in \([53a]\) and \([53b]\) may be taken such that vaporization processes can be included. Thus, the mass \( m \) would represent a single molecule of condensable vapor. If the process of condensation or evaporation is excluded, molecular agglomeration can be excluded by assigning a collision or break up rate of zero for particles of arbitrary size less than some fixed mass, \( m \).
In general, the agglomeration process in aerosols is considered irreversible, and break up is disregarded. The agglomeration parameter $S_{ij}$ is given by

$$S_{ij} = b \left( \frac{m}{m_i}, \frac{I}{I_i}, \left( \frac{\xi}{\xi_i}, \eta \right) \right) w \left( \frac{m}{m_i}, \frac{I}{I_i}, \frac{\xi}{\xi_i}, \eta, \gamma, \tau, t \right)$$

Here collision parameter or kernel $b$ is a function of the colliding particles and their internal parameters. It has the dimensions of volume swept out per unit time of a larger sphere with respect to a smaller sphere, or (particles/unit volume)$^{-1} \times$ (time)$^{-1}$.

Combining Equation [52] with Eq. [53] the expression for the total rate of change of the distribution function $w$ is derived:

$$\frac{dw}{dt} + \nabla \cdot (w \nu) = \mathcal{J}$$

This relation is strikingly similar to the Boltzmann equation.

Examining the properties of Equation [55] and its moments (like mass density $\rho_i = m_i w$) it is possible to deduce the following differences between Equation [55] and the Boltzmann equation: (a) In contrast to the molecular function $f$, the distribution function $w$ is not a function of velocity while it is a function of size and internal parameters, (b) the Liouville theorem does not apply to $w$-space,\(^1\) (c) the collision integrals given by $\mathcal{J}$ cannot be combined because their limits differ,

---

\(^1\) However, the Liouville theorem in a generalized form applies to non-interacting systems governed by the Fokker-Planck equation (23).
and (d) there appear to be no general conservation laws for combined effects of vaporization and agglomeration.

Finally, to complete the set of phenomenological equations for a cloud of aerosols, the rates of change of the particle parameters $m$, $I$, and $\mathbf{r}$ have to be expressed in terms of known quantities. The condensation or evaporation rate $\dot{m}$ may be written in terms of $m$, $I$ and upon the distributions of partial pressure of condensing species and of fluid velocity in the environment. By definition the internal parameters will not change in this model. The particle velocity $\mathbf{r}$ relative to a fixed system of coordinates will vary with the parameters $m$ and $I$, and with the gas velocity nonuniformities in the gas and any external fields of force present. If the environmental parameters can be described as functions of position $\mathbf{r}$ and time $t$ only, we can collect into a known relation $E (\mathbf{r}, t)$. Then our theory is complete, at least formally, when the rates of change in particle parameters are given by the expressions

\[
\dot{m} = \dot{m} \left[ m, I, E (\mathbf{r}, t) \right]
\]

\[
\dot{\mathbf{r}} = \mathbf{r} = \mathbf{r} \left[ m, I, E (\mathbf{r}, t) \right].
\]

So far the calculations that have been reported in the literature, which involve the formulation of the phenomenological theory above, have been confined to simplified limiting cases of growth by condensation or depletion by evaporation (also nucleation) of particles in a stagnant vapor, or growth by the collision and agglomeration of particles in a stagnant medium. Examples of the former are found in
references (8), (61) and (71). These studies all have utilized ideas of the theory of growth by vapor diffusion in a quasi-single particle regime. Experimental evidence, though scanty, appears to verify semi-quantitatively most aspects of this kind of treatment, at least for very dilute systems like rain clouds.

To illustrate the efforts devoted to two limiting cases of collision processes, let us next outline briefly the theoretical studies of homogeneous nucleation and the mechanisms of agglomeration.

3. Homogeneous Nucleation. One extreme case encompassed by the rate equation [53] is the theory of spontaneous nucleation of a super-saturated vapor in the absence of foreign particles (nuclei). The classical theory of Becker and Döring (74, see also Friedlander, 72 and Frenkel, 73) assumes that all terms in [53] are neglected except for four involving single molecular species of condensable vapor. Suppose [53] is integrated over real space and internal parameters are disregarded. If the molecular species is referred to by subscript 1, and embryos are considered clusters of K units of molecules, the discrete form of [53] for this case is:

\[
\mathcal{A}_{BD} = S_{j,k} - S_{j,k+1} + S'_{j,k} - S'_{j,k+1}
\]

This formula holds for the rate of embryo formation. The disregard for collisions of molecular agglomerates is justified by the immense concentration of single molecules in a supersaturated vapor compared with any polymerized species. Similarly the evaporation of single molecules is assumed to be much more probable than splitting off of clusters of vapor molecules. In
other words, the time of condensation in a highly supersaturated vapor is considered much smaller than the time for coagulation to occur.

Equation [56] may be rewritten in terms of molecular fluxes of vapor to a region where a molecular cluster may be identified. Following Friedlander's argument (72):

\[ \mathbf{\dot{N}}_{BD} = \mathbf{j}_{k-1} n_1 A_{k-1} n_{k-1} + \mathbf{j}_{k+1} A_{k+1} n_{k+1} \]
\[ - \mathbf{j}_{k} n_1 A_{k} n_{k} - \mathbf{j}_{k} A_{k} n_{k} . \]  (57)

Here \( j_{k} n_{1} \) is the flux of molecules of condensing species, \( n_1 \) is the concentration of vapor molecules, and \( A_{k} \) is the surface area of a cluster of size \( k \), \( j_{k} \) is the evaporative flux of molecules lost from the \( k \)th class.

The relations for the flux of condensing species have been given in different forms. A simple one used by Brenkel (75) is that given by kinetic theory:

\[ j_{k} n_{1} = \alpha_{e} p_{1} / (2 \pi m_{e} k T) \]

where \( p_{1} \) is the partial pressure of the vapor, and \( \alpha_{e} \) is the evaporation coefficient (taken equal to the condensation coefficient).

An expression for the evaporative flux may be obtained by considering conditions of equilibrium between species of clusters. The process of spontaneous condensation may be visualized as a reaction of ideal gas species \( K-1, e_{K-1}, \) and one, \( e_{1}, \) to give an embryo of class \( e_{K} \). That is,

\[ e_{K-1} + e_{1} \xrightarrow{\text{cond}} e_{K} \]  (58)
The flux $\mathbf{j}_k$ now is estimated from the equilibrium constant of this reaction assuming that the principle of detailed balance holds, or that the rate of forward reaction in [58] is exactly equal to the rate of back reaction. Then, one finds that

$$\mathbf{j}_k' \approx \frac{\alpha_c \rho_s}{(2\pi m kT)^{3/2}} \left( \frac{A_{k-1}}{A_k} \exp \left[ -\frac{(A_k-A_{k-1})\gamma/kT}{A_k} \right] \right)^{1/2},$$

where $\rho_s$ is the partial pressure of saturated vapor at temperature $T$, and $\gamma$ is the surface free energy per unit area of embryo (assumed bracketed portion on the right independent of size). Evidently the $\gamma$ represents a kind of correction factor which is related to the geometry of the embryo.

No general solution to the Becker-Döring equation [57] has been found. However, the steady state case where $\mathbf{j}_k = 0$ has been solved. This case gives the constant rate of formation of embryos of size $K$, which are assumed to be "critical" in the sense that growth beyond size $K$ by condensation will be stable, whereas growth to clusters of size less than $K$ is considered unstable, and these smaller clusters will evaporate. The rate expression for formation of critical sized droplets as determined by the steady state theory takes a form familiar to chemical kinetics:

$$\mathbf{j}_k = K n_s \exp \left[ -\frac{\Delta G_K}{kT} \right], \quad (60)$$

where the pre-exponential factor has been given by Becker and Döring (74)

$$K = \frac{\alpha_c}{V} \left( \frac{kT}{\gamma} \right)^{3/2} \left( \frac{\rho_s^2}{2\pi m kT} \right)^{1/2} \frac{4\pi\rho_s^2}{\alpha_c} \frac{1}{n_s^2} \frac{\rho_s}{\rho_s},$$

and the free energy of formation of critical embryos

$$\Delta G_K = \frac{16\pi\gamma^3 V^2}{3(kT)^3} \frac{1}{n_s^2} \frac{\rho_s}{\rho_s}.$$
Because of uncertainties in the Becker-Döring treatment, and incomplete agreement between theory and experimental observations of homogeneous nucleation, a variety of research has been devoted to this subject in recent years. A review of the state of knowledge on nucleation has been published by Hirth and Pound (8). Of possible interest to specialists in this field is the recent controversy over Lothe and Pound's (75) modification of Eq. [59] to account for degrees of freedom in translation and rotation of embryos. Reiss and Katz (76) have presented arguments which disagree with Lothe and Pound's conclusion, but the controversy apparently has not been resolved as yet.

4. Particle Interaction-Coagulation. One can consider another extreme case of the rate of agglomeration given by Eq. [53]. Suppose the molecular vaporization is excluded by carrying out the integrations in [53] beyond an arbitrary particle mass $m_0$, which is much larger than the molecular mass $m$. Neglecting the terms accounting for break up, making use of Eq. [54], and integrating [53] over $I$ and $\tilde{r}$ yields the well known rate equation for the coagulation of aerosols in a stagnant medium. For particles of unit density, the relation for coagulation rates reads (69):

$$\frac{d \omega' (\tilde{r}, t)}{dt} = \frac{1}{2} \int_{\tilde{c_0}}^{c} \mathcal{C}(I)' b (\tilde{r}, \tilde{r}') w' (\tilde{r}', t) w' (\tilde{r}' - \tilde{r}, t) d \tilde{r}'$$

$$- \int_{\tilde{c_0}}^{c} \mathcal{C}(I) b (\tilde{r}, \tilde{r}') w' (\tilde{r}'', t) w' (\tilde{r}', t) d \tilde{r}'',$$

(60)
where \( \vec{\nu} \) is particle volume, taken here as a continuous variable rather than a discrete value, \( \vec{\nu}_i \).

Generally investigations of agglomeration processes in clouds have assumed that the probability of sticking of particles after collision \( C(I) \) is an empirically determined function. Thus, in the kinetic theory of aerosols, the analysis centers attention only on the calculation of the collision parameter \( b \). Both the extremes of free molecule behavior have been examined for restrictions implied by the set of inequalities in [9]. In the limit of \( Kn \to 0 \), the theory for coagulation by Brownian motion of particles was worked out by Smoluchowski (62) at the turn of the century. Whytlaw-Gray and Patterson (77) modified Smoluchowski's results empirically to account for the increased mobility of particles as \( Kn \) increases. The results of these authors were later shown to be limited in applicability after the investigations of Fuchs (16), Zebel (78) and Hidy and Brock (64).

In the continuum calculations, it has not been possible to construct a generalized collision theory so that specific collisional mechanisms have been treated separately. Some examples include collision by Brownian motion, by shear in the gas, by differences in settling rates, by electrical interaction, etc. However, it has been found (63) that a general treatment can be developed for collision rates of aerosols in the free molecule regime, including Brownian motion, effects of gaseous non-uniformities, and external forces.
Several examples of theoretical relations for $b$ for kinetic mechanisms are listed in Table 7.\textsuperscript{1} These relations display functional dependence on particle size which is quite non-linear, and which may be different depending on the mechanism considered. Perhaps best known are Smolackowski's results for Brownian motion, and the sweep out results for collisions of droplets in rain clouds.

To illustrate how different mechanisms may control collision processes in clouds, consider an aerial dispersion in a weakly turbulent medium that contains particles of uniform density over the size radius range of $0.1 - 10 \mu$. On the basis of continuum calculations (81) of the collision rates based on Brownian motion, sedimentation and turbulent shear suggests that Brownian motion will dominate agglomeration below $\sim 1 \mu$, but sweep out by sedimentation will control interaction between particles of $1 \mu$ radius and particles of $2 \mu$ and larger. This is shown graphically in Fig. 4.

Analysis of collision rates of particles in the transition regime is accompanied by the difficulties of uncertainties in the specification of the mobilities of particles far from each other, especially in the regime

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\textsuperscript{1} To be consistent with the discussion of the single particle regime the collision parameters listed in Table 7 are written in discrete form, designated by $b_{ij}$. The expressions may be transformed into continuous variables $[b(\tilde{v}, \tilde{v}')]$ of particle volume $\tilde{v}$ or radius $\tilde{r}$ by direct substitution into the relations for $b_{ij}$. 

Figure 4
Table 7

Collisional parameters for several kinetic mechanisms in aerosols of unit density particles.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Collision parameter $b_{ij}^*(\text{cm}^3/\text{sec})$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Continuum, $Kn \to 0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Brownian Motion</td>
<td>$4 \pi (D_i + D_j)(R_i + R_j)$</td>
<td>(62)</td>
</tr>
<tr>
<td>B. Brownian Motion with interaction of potential field ($\bar{F}$)</td>
<td>$4 \pi (D_i + D_j)(R_i + R_j) \int_{R_i+R_j}^{\infty} \frac{1}{r^2} \exp \left[ \frac{(Bi + Bj) \bar{F}}{D_i + D_j} \right] dr$ (^{-1})</td>
<td>(16)</td>
</tr>
<tr>
<td>C. Shear</td>
<td>$\frac{4G (R_i + R_j)^3}{3}$, $G =$ shear rate.</td>
<td>(62)</td>
</tr>
<tr>
<td>D. Turbulence</td>
<td>$1.67 (R_i + R_j)^3 (\epsilon / \nu_j)^{1/2}$, $\epsilon =$ dissipation rate</td>
<td>(79)</td>
</tr>
<tr>
<td>E. Sweep out by sedimentation (geometrical)</td>
<td>$\pi (R_i + R_j)^2 (v_{sj} - v_{si})$</td>
<td>(80), (81)</td>
</tr>
<tr>
<td>E. Sweep out by sedimentation (with aerodyn forces)</td>
<td>$\pi (R_i + R_j)^2 (v_{sj} - v_{si}) \epsilon_o$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\epsilon_o(R_i, R_j) =$ collision efficiency (Ref. 24).</td>
<td></td>
</tr>
</tbody>
</table>
Table 7 (continued)

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Collision parameter $b_{ij}$ (cm$^3$/sec)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>II. Free Molecule, Kn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Brownian Motion</td>
<td>$\left[ 6 k T g \left( \frac{R_j}{R_i} \right)^3 \left( \frac{R_i}{R_j} \right)^3 + 1 \right]^{1/2} \left( R_i + R_j \right)^2$</td>
<td>(64)</td>
</tr>
<tr>
<td>B. Generalized</td>
<td>$\left[ 6 k T g \left( \frac{R_j}{R_i} \right)^3 \left( \frac{R_i}{R_j} \right)^3 + 1 \right]^{1/2} \left( R_i + R_j \right)^2 a_{ij}$</td>
<td>(63)</td>
</tr>
<tr>
<td>a_{ij} = a_{ij} [ R_j, R_i, T_g, \bar{u}_j, \bar{u}_i, \bar{T}, ... ]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III. Transition of Kn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Brownian Motion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. $\Delta$ Theory (monodisperse)</td>
<td>$8 \pi D_i R_i \left[ (1 + A) \lambda_g / R_i \right] / \left[ (R_i / R_i + \Delta A) + \pi \lambda_i / 2 \sqrt{2} R_i \right]$</td>
<td>(16)</td>
</tr>
<tr>
<td>2. Extended Free Molecule</td>
<td>$(R_i+R_j)^2 \left[ 6 k T g \left( \frac{R_j}{R_i} \right)^3 \left( \frac{R_i}{R_j} \right)^3 + 1 \right]^{1/2} \left( 1 - \frac{\pi}{2} \right) \left( 1 + \pi \right) e^{- \pi / 2} \left( R_i^3 + R_j^3 \right)^{1/2} x^{1/2} \left( R_i + R_j \right)^2$</td>
<td>(64)</td>
</tr>
<tr>
<td>$\frac{16 \pi g \left( R_i R_j \right)^2}{(R_i + R_j)^2} \left[ \exp \left( - \left( \frac{R_i + R_j}{\lambda_g} \right) \lambda_g \right) + \left( \frac{\lambda_j}{\lambda_j + \lambda_g} \right) \left( R_i + R_j \right)^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\left{ 0.577 + \ln \left( \frac{\lambda_j}{\lambda_g} \right) + \sum_{y=1}^{\lambda_j} \left( -1 \right)^y \left( \frac{\lambda_j}{\lambda_g} \right)^y \right}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda \approx 4/28$.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Fokker-Planck (monodisperse)</td>
<td>$8 \pi D_i R_i \left[ \frac{1 + 0.08 \lambda_i / R_i}{1 + 0.5 \lambda_i / R_i + 0.2 \left( \lambda_i / R_i \right)^2 + 0.015 \left( \lambda_i / R_i \right)^3} \right]$</td>
<td>(82)</td>
</tr>
</tbody>
</table>
Kn $\lesssim 0.5$, combined with the difficulties in estimating the effects of aerodynamic interaction between particles as they near each other. Since the gas dynamics of particle-gas interaction has not been worked out completely, the theories for collisions of particles in the transition regime only can be expected to be semiquantitative. Only the case of collision by Brownian motion in a stagnant gas has been examined in this regime. Three different models have been studied, only one of which attempts to bridge the entire range, $0 \leq Kn \leq \infty$. The first model, reported by Fuchs (16), and later independently studied by Zebel (78), attempted to extend Smoluchowski's diffusion model, taking into account the concentration jump of particles near an absorbing particle surface. This model is essentially an extension of Fuchs' intuitive $\Delta$ theory for evaporation (59). This model is required to give the correct form of $\phi$ in the extremes $Kn \to 0$, and $Kn \to \infty$. However, the use of the $\Delta$ layer may lead to errors, particularly in the regime of larger Kn, as discussed for evaporation theory previously. An alternate approach given by Hidy and Brock (64) gives an expression for collision rates based on an extended free molecule theory. This theory crudely takes into account aerodynamic interactions, but appears to have validity only in the range $Kn \gtrsim 5$. One of Fuchs' colleagues, Astakhov (82) has reported a third alternate approach for monodisperse aerosols. This result stems from an approximate solution to the Fokker-Planck equation, and appears to apply primarily below Kn of unity.

In Table 7 the functional form of the collision parameters for aerosol coagulation in the transition regime of Kn are listed. Though there is some overlap in range of applicability, their forms are quite different. For monodispersed aerosols, the estimates of $b$ from these three theories are tabulated in Table 8. Also included for comparison are values of $b$ based on an extension of Smoluchowski's theory using only the Stokes-Cunningham correction for particle mobility. All the predictions, except for the latter, show a maximum in collision rate at $Kn \approx 5$. Both the relations of Hidy and Brock and Astakhov show departures from Fuchs' "forced" theory in ranges of Kn beyond their applicability. It appears that the earlier intuitive approach of Whytlaw Gray and Patterson is correct even for small Kn.

Little data is available to test the theoretical predictions for coagulation in the transition regime. Some of the older results are reviewed by Hidy and Brock (64). And Fuchs and Sutugin (83) have reported data for the free molecule regime. Their experiments, corrected for interparticle forces, suggest that the theory for $Kn \gtrsim 10$ underestimates the collision rate.
Table 8

Comparison between various theoretical predictions of the collision rate for monodisperse aerosols in Brownian motion over a range of Kn.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>1.13</td>
<td>1.13</td>
<td>1.14</td>
<td>-</td>
</tr>
<tr>
<td>0.5</td>
<td>1.65</td>
<td>1.79</td>
<td>1.76</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>2.39</td>
<td>2.42</td>
<td>2.45</td>
<td>-</td>
</tr>
<tr>
<td>5.0</td>
<td>8.89</td>
<td>4.04</td>
<td>3.95</td>
<td>4.04</td>
</tr>
<tr>
<td>10.0</td>
<td>17.2</td>
<td>3.03</td>
<td>2.14</td>
<td>3.03</td>
</tr>
<tr>
<td>50.0</td>
<td>-</td>
<td>1.51</td>
<td>-</td>
<td>1.51</td>
</tr>
</tbody>
</table>
Since the collisional parameter $b_{ij}$ depends so strongly on the particle size, it has been necessary to seek particular solutions to the integral differential equations of the form of Equation (60). Because of the importance of this equation for predicting the behavior of coagulating aerosols, considerable effort has been devoted to finding such solutions. Complexities introduced by the non-linearities in $b_{ij}$, however, until recently have resulted in limited success in analyzing for solutions to (60).

Perhaps the first solution to Equation (60) of physical interest was found sometime ago by Smoluchowski (62). This result, later given in a different form by Schumann (84), referred to the initial coagulation of aerosols by Brownian motion where $b_{ij} = \text{constant}$. For this case, the solution to (60) is:

$$w = \frac{N^2(t)}{\Phi} \exp \left[ -\frac{N(t) \Phi}{\Phi} \right]$$

(61)

where $N$ is the total number of particles per unit volume, and $\Phi$ is the volume fraction of particles in the gas.

Recent efforts to find other solutions for Equation (60) which are more general than Equation (61) have yielded limited results by application of integral transform techniques (for example, Melzak, 85), and by application of the method of series decomposition (86). The latter technique appears limited because a very large number of terms in a power series are needed to specify a polydisperse cloud. The integral transform method shows more promise, but difficulties have arisen in finding general techniques for transforming these solutions in Fourier space back into real variables.

Numerical integrations of the kinetic equations for coagulation have provided considerable information about the evolution of size spectra for particular initial distributions and particular collisional mechanisms. The case of collisions by Brownian motion has been studied by Zebel (78) and Hidy (87), and the problem of collisions by sweepout has been examined by Berry (88).
An alternate method for finding at least asymptotic solutions to Equation [60] that shows considerable promise is the similarity theory proposed by Friedlander and co-workers (e.g., Friedlander and Wang, (90)). In this analysis the distribution function is assumed to have the form

$$\eta(\tilde{v}, t) = \psi\left(\frac{\tilde{v}}{\tilde{v}^+}\right) g(t)$$  \hspace{1cm} (62)

where $g(t)$ and $\tilde{v}^+$ are functions of time. Substitution of this expression into Equation [60] yields an ordinary integro-differential equation with $\tilde{v}/\tilde{v}^+$ as the independent variable. This demonstrates that Equation [62] is a particular solution to the kinetic equation for coagulation, but perhaps not the only one. The reduced spectrum function $\psi(\tilde{v}/\tilde{v}^+)$ is termed self preserving since it depends only on the reduced volume $\tilde{v}/\tilde{v}^+$, and not explicitly on time. Explicitly, the functional forms of $g(t)$ and $\tilde{v}^+(t)$ can be found from integral constraints. The specific relations commonly used are

$$\omega'(\tilde{v}, t) = \left[\frac{N(t)}{\Phi}\right]^2 \psi\left[\frac{N(t)}{\tilde{v}/\tilde{v}^+}\right]$$  \hspace{1cm} (63)

where $N(t) = \int_0^{\tilde{v}^+} \omega'(\tilde{v}, t) d\tilde{v}$, and $\Phi(t) = \int_{\tilde{v}}^{\tilde{v}^+} \omega' d\tilde{v}$.

Friedlander and Wang (89, 90) have determined on rigorous grounds that self preserving solutions exist for $b = \text{const.}$, and Smoluchowski's form of $b$. This was determined earlier on experimental grounds by Hidy (87). The self preserving size distribution for Smoluchowski's theory (Table 7-1A) is given for illustration in Fig. 5. Hidy's numerical calculations are shown with Friedlander and Wang's approximate analytical results, and agreement between the two is satisfactory. For comparison, Smoluchowski's result for constant $b$ is also drawn in Fig. 5.

Wang and Friedlander (90) have also found other classes of self preserving behavior for combinations of shear and Brownian motion, and for Brownian motion in non-continuum conditions.
Figure 5

$\psi = e^{-\eta (b(\bar{v}, \bar{v}')} = \text{const.}$

SMOLUCHOWSKIS' SOLUTION

HIDYS' NUMERICAL EXPERIMENTS

SOLUTION OF FRIEDLANDER & WANG

$\eta = \frac{\bar{v}N}{\Phi}$
One of the practical applications of interest that motivated the formulation of the theory of self-preserving aerosols was the fact that it has long been known that aerosol distributions in the earth's troposphere have displayed such similarity in behavior. Junge (91) discovered many years ago that such aerosol distributions have similar shapes, which have a form

$$w'(\tilde{R}, t) \sim \tilde{R}^{-4}$$

(64)

in the upper end of the size spectrum. Here $\tilde{R}$ is the continuous variable of the distribution function which equals particle radius. Further experimental measurements put together, for example, by Clark and Whitby (92) have verified this conclusion. Several examples of data on atmospheric aerosols, placed in the self preserving framework are shown in Fig. 6. The $\tilde{R}^{-4}$ rule extends over many decades in the reduced distribution function.

If the distribution is self preserving and the $\tilde{R}^{-4}$ rule holds, then $w' = \text{const} \cdot \tilde{R}^{-4}$. Thus by measuring the volume fraction $\tilde{\phi}$, which is relatively simple to do, one can determine the shape of much of the spectrum for larger particles.

It is interesting to note that the near log-normal distribution found for Brownian coagulation by Friedlander and Wang, and Hidy does not correspond at all to the Junge distribution in Fig. 6. However, it is possible to obtain the $\tilde{R}^{-4}$ behavior for any collisional mechanism by postulating steady state behavior in addition; i.e., $\partial w'/\partial t = 0$. This recently was suggested by Liu (93). Equation [60] does not contain other possible influences of mechanisms shaping the aerosol distribution.
\[ \omega'(R) \Phi^{1/3} / N^{4/3} \]

- Whitby and Clark (Minneapolis)
- Friedlander and Pascier (Baltimore)
- Junge (Frankfurt)
- Junge (Zugspitze)
- Cartwright (Sheffield)
- Cartwright (Buxton)

\[ \eta = \tilde{R} (N / \Phi)^{1/3} \]
in the atmosphere, such as depletion in large sizes by sedimentation, or washout by rainfall. Therefore, Liu's suggestion for explaining Junge's form may not be the only possible one. To attain a steady state in relations like [60], other terms must be added to account for sources or sinks of particles in the volume under consideration. Thus Liu's model is certainly unrealistic physically. However, Mockros et al. (94) have shown by numerical calculation that distributions having the form $R^{-n}$ can be generated by including an arbitrary source of aerosols in Equation [60]. Certainly further studies of this interesting question will be useful in better understanding the evolution of aerosol distributions in the earth's atmosphere.

III. SOME POTENTIALLY SIGNIFICANT FEATURES OF THE PHYSICAL CHEMISTRY OF AEROSOLS

In the introductory section a few phenomenological observations were mentioned which suggest intuitively that certain properties of aerosol particles may be unique, and may be significant attributes of such systems. Although comparatively little information is known directly about the physical chemistry of very tiny particles, there exists a wealth of information about the nature of liquids and solids in the literature which can serve as hints to potentially unique chemical properties of aerosols. It is well beyond the scope of this article to discuss in any detail the state of knowledge in various fields of the theory of liquids, crystals, etc. We can only point to a few illustrative examples of important properties
of the particles themselves as they may affect various aspects of aerosol behavior. Let us consider three different classes of chemically important influences; first, in keeping with the previous section, regarding uncertainties in dynamical processes caused by surface properties of particles; second, concerning the size dependence of thermodynamic properties of particles; and third, regarding the possible influences of heterogeneities which may distinguish properties of a bulk phase from aerosols, partly with reference to the ratio given by Equation [2].

Before taking up these examples, let us provide a possible framework for classifying properties of aerosol particles. It has been suggested by Brock (13) that chemical properties of small particles may be classed as **intrinsic** or **extrinsic**. Intrinsic properties are defined as those which are inherent to any particle because of their small size, or large $\Lambda$ ratio. These properties represent deviations from bulk behavior resulting, for example, from the smallness in size of the particles. This must in turn involve peculiarities in physico-chemical behavior (in a statistical sense) because any one molecule in the condensed phase will be surrounded by an increasingly limited number of neighboring molecules as $\Lambda$ increases. Extrinsic properties, on the other hand, will involve deviations from expected behavior of homogeneous material resulting from microscopic departures from equilibrium in mode of formation, lack of control during formation, etc. Some examples of intrinsic properties include: vapor pressure, heat of vaporization, freezing temperature, surface tension, solubility, azeotropic composition, optical properties, crystal structure, work function, and evaporation coefficient.

1. With impurities in particles some of these properties may also become extrinsic.
Examples of extrinsic properties include: freezing temperature, condensation temperature, physical adsorption, catalytic activity and accommodation coefficients.

Both these classes of properties of aerosols are exceedingly important in practice to interpretation of the behavior of such systems. Indeed it has been all too easy, in past work, to ascribe departures from predicted dynamical behavior, for example, to various "unknown" influences of the intrinsic or extrinsic properties of a particular aerosol.

Within this general framework now let us examine briefly some aspects of the dependence on dynamic behavior of idealized aerosols in terms of surface properties of the spheres.

A. UNCERTAINTIES IN DYNAMICAL BEHAVIOR

In Section II the discussion of the dynamical theories for aerial dispersions revealed that chemical properties of even idealized spheres may produce significant uncertainties in the theoretical results. In particular, such uncertainties may come about in the case of heat, mass and momentum transfer through the various accommodation coefficients; indeterminacies in vaporization processes also may stem from the presence of soluble materials in the bulk phase of a condensation nucleus, and by adsorbed films on droplet surfaces; variations in coagulation rates may derive from ionization in the gas, additional dipolar interactions of adsorbed molecules, and differences in the sticking probability, which depend on adhesive properties.

1. Accommodation and Evaporation Coefficients. From comparison between Equations [31, 34, 36, 37, 43], it seems that the main effect of variations in various accommodation coefficients appear in the cases of heat and mass transfer to spheres in the non-continuum regimes. In considering momentum transfer, the principal uncertainty resulting from variations in these coefficients comes about in the estimation thermal force and, no doubt, in the diffusio-phoretic force where the coefficient \( \tau \), Equation [43], is proportional to \( \overline{J}_m \). As mentioned previously the viscous resistance is relatively insensitive to \( \alpha_m \).
Various accommodation coefficients and the vaporization coefficients have been measured in several ways. All of these parameters, which must be associated with the nature of the surface of particles, are similar in magnitude. Methods of measurement of thermal accommodation coefficients and available data of this property have been reviewed recently by Wachmann (95). A comprehensive review of evaporation coefficients, and their relation to the momentum and thermal coefficients of accommodation has been given by Paul (96).

Several values of the (tangential) accommodation coefficients $\alpha_m$ for momentum are shown in Table 5 and Table 9A. From these data it appears that this parameter is likely to be nearly unity for most gas-surface interactions encountered in practice.

In contrast to momentum accommodation, the accommodation of thermal energy, as expressed by $\alpha_T$ varies from surface to surface considerably more. Some values of the thermal accommodation coefficient, $\alpha_T$, taken from Paul's article (96) are shown in Table 9B. Here the variation for different gas-solid surfaces is much greater than for $\alpha_m$. Since heat transfer in the non-continuum regimes is sensitive to $\alpha_T$, it may be important to be able to correct the theoretical calculations for $\alpha_T \neq 1$.

Selected values of the evaporation coefficient $\alpha_c$, are listed in Table 10. If such measurements of such vapor-condensed phase systems are correct, this parameter may vary over an exceedingly wide range of values. Vaporization rates of particles are directly proportional to the evaporation coefficient, so that one must exercise considerable care in making estimates of these rates on theoretical grounds unless experimental values of $\alpha_c$ for a particular system are available and can be trusted.

1 Though workers like Knacke and Stranski (97) have been careful to make distinctions between the processes of evaporation and condensation from surfaces, it is often assumed in practice, that evaporation coefficients and condensation coefficients are equal in the absence of experimental data.
Table 9

Some typical data for momentum and thermal accommodation coefficients.

A. Momentum Accommodation

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_m$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air on old shellac or machined brass</td>
<td>1.00</td>
<td>(18)</td>
</tr>
<tr>
<td>Air on oil</td>
<td>0.895</td>
<td>(18)</td>
</tr>
<tr>
<td>CO$_2$ on oil</td>
<td>0.92</td>
<td>(18)</td>
</tr>
<tr>
<td>Air on glass</td>
<td>0.89</td>
<td>(18)</td>
</tr>
<tr>
<td>He on oil</td>
<td>0.87</td>
<td>(18)</td>
</tr>
<tr>
<td>Air on Ag$_2$O</td>
<td>0.98</td>
<td>(96)</td>
</tr>
<tr>
<td>He on Ag$_2$O</td>
<td>1.0</td>
<td>(96)</td>
</tr>
</tbody>
</table>

B. Thermal Accommodation

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_T$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air on machined bronze</td>
<td>0.91-0.94</td>
<td>(53)</td>
</tr>
<tr>
<td>Air on polished cast iron</td>
<td>0.87-0.93</td>
<td>(53)</td>
</tr>
<tr>
<td>Air on etched aluminum</td>
<td>0.89-0.97</td>
<td>(53)</td>
</tr>
<tr>
<td>Air on machined aluminum</td>
<td>0.95-0.97</td>
<td>(53)</td>
</tr>
<tr>
<td>O$_2$ on bright Pt</td>
<td>0.808</td>
<td>(96)</td>
</tr>
<tr>
<td>Kr on Pt</td>
<td>0.699</td>
<td>(95)</td>
</tr>
<tr>
<td>N$_2$ on Wo</td>
<td>0.35</td>
<td>(96)</td>
</tr>
<tr>
<td>He on Na</td>
<td>0.090</td>
<td>(95)</td>
</tr>
<tr>
<td>Ne on K</td>
<td>0.199</td>
<td>(95)</td>
</tr>
<tr>
<td>He on Wo</td>
<td>0.017</td>
<td>(95)</td>
</tr>
</tbody>
</table>
Table 10

Typical data for the evaporation coefficient (from Paul, 96).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha_0$</th>
<th>Temperature Range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>≈1</td>
<td>898-1279</td>
</tr>
<tr>
<td>Copper</td>
<td>≈1</td>
<td>913-1193</td>
</tr>
<tr>
<td>Iron</td>
<td>≈1</td>
<td>1044-1600</td>
</tr>
<tr>
<td>Nickel</td>
<td>≈1</td>
<td>1034-1329</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>(3.9-29.0) x 10^{-4}</td>
<td>118-221</td>
</tr>
<tr>
<td>Iodine</td>
<td>0.055-1</td>
<td>-21.4 to 70</td>
</tr>
<tr>
<td>Mercurous Chloride</td>
<td>0.1</td>
<td>97,102</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>0.11-0.23</td>
<td>601-657</td>
</tr>
<tr>
<td>Potassium Chloride</td>
<td>0.63-1.0</td>
<td>-</td>
</tr>
<tr>
<td>Water (liquid)</td>
<td>0.04-0.25</td>
<td>15-100</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.85-0.95</td>
<td>6</td>
</tr>
<tr>
<td>Camphor (synthetic)</td>
<td>0.139-0.190</td>
<td>-14.5-5.5</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>≈1</td>
<td>-</td>
</tr>
<tr>
<td>Diamyl Sebacate</td>
<td>0.50</td>
<td>25, 35</td>
</tr>
<tr>
<td>Di-n-butyl phthalate</td>
<td>1</td>
<td>150-350</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>0.0241-0.0288</td>
<td>12.4-15.9</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Unity, 0.052</td>
<td>18-70</td>
</tr>
<tr>
<td>Napthalene</td>
<td>0.036-0.135</td>
<td>40-70</td>
</tr>
<tr>
<td>Tetradeconal</td>
<td>0.68</td>
<td>20</td>
</tr>
</tbody>
</table>
2. More Influences on Growth Rates by Vaporization. In addition to the importance of the evaporation coefficient, growth or depletion by vaporization will be sensitive to the chemical composition of the bulk phase as well as the surface of the particle.

An example of the importance of the bulk phase to droplet growth is a classical one in cloud physics. In the atmosphere, water droplets form in regions of supersaturation by condensation on nuclei composed of both insoluble and soluble material. The driving force for droplet growth by vapor diffusion, of course, is the difference between the vapor pressure far from the droplet and at the droplet surface. If the nucleus is soluble in water, it can change the surface vapor pressure by a substantial amount. We have already remarked that the equilibrium vapor pressure for very small droplets is sensitive to the radius of curvature, as given by Kelvin's equation, Equation [11]. The solubility effect tends to reduce the increase in vapor pressure at the droplet surface with radius considerably. The importance of this effect to the formation of rain drops was recognized some years ago by Kohler. (See, for example, Kohler and Wright, 90.)

The solubility effect, as given in the framework of the Kelvin equation (60) reads:

\[
\frac{p'}{p_\infty} \approx 1 + \left(\frac{2Y'}{n_L kT}\right) \frac{1}{R_i} - \left(\frac{i m \text{M}_s}{4 \pi \rho \text{M}_w} \right) \frac{1}{R_i^3} + \ldots, \tag{65}
\]

where \(n_L\) is the number of molecules per unit volume of liquid, \(i\) is the so-called vant Hoff factor accounting for dissociation of inorganic salts, \(m_s\) denotes the mass of substance of molecular weight \(M_s\) dissolved in water (molecular weight \(M_w\)), and the primes refer to properties of the solution. The variation of the pressure ratio \(p'/p_\infty\) with particle radius for various values of the ratio \(i m / M\) are shown in Fig. 7. As the amount of soluble material in the droplet increases, the vapor pressure at the surface of the droplet decreases for a given droplet size. Such an effect will tend to increase the growth rate of such water droplets over that expected for pure water.
Figure 7

DROPLET RADIUS ($\mu$)

$\frac{(1-P/P_\infty)}{\text{in \%}}$

Pure Water

T=0°C

$10^{-18}$ $10^{-17}$ $10^{-16}$ $10^{-15}$ $10^{-14}$ $10^{-13}$ $10^{-12}$ $10^{-11}$ $10^{-10}$ $10^{-9}$ $10^{-8}$ $10^{-7}$ $10^{-6}$ $10^{-5}$ $10^{-4}$ $10^{-3}$ $10^{-2}$ $10^{-1}$ $0.01$ $0.1$ $1$ $2$ $4$ $6$ $8$ $10$

Figure 7
It has been known for sometime that the presence of surface films can reduce vapor transfer across a gas-liquid interface significantly. Such an effect has been explored quantitatively for water droplets recently by Derjaguin, et al (97). In this investigation it was found that the adsorption of cetyl alcohol on water droplets, of \( \frac{1}{10} \) radius, slowed down evaporation. These workers also determined that in their technique with monolayer adsorption, one could investigate simultaneously the evaporation rate, the effect of heat absorption, the lifetime of adsorbed molecules on the droplet surface, and the coefficient of diffusion of the adsorbate.

3 Collision and Agglomeration. Like other rate processes involved in aerosol dynamics, the coagulation process has to be at least somewhat sensitive to the chemical properties of the particles. Uncertainties in the coagulation rate can come about through changes in induced forces between the particles by adsorbed species, or by differences in the sticking probability \( C \). It may not be possible to isolate these effects, since they may be lumped empirically into \( C \). However, it may be useful to consider that the probability of sticking is associated only with phenomena contributing to the variability of adhesion of particles. And the connection between adsorbed species and interparticle forces may be incorporated into the collision theory in a manner analogous to electrostatic forces (e.g., Hidy and Brock, 13). The current knowledge of adhesion of particles to surfaces has been reviewed recently by Corn (17) and in articles of Fish's book (100). Therefore, this phenomenon will not be discussed further here.

By the 1930's it was known that certain materials could reduce coagulation rates of aerosols. For example, Radushkevich and Chugunova (101) demonstrated that the rate of agglomeration of ammonium chloride aerosols could be reduced by 23% by the presence of phenol vapor, but vapors of methyl alcohol, ethyl alcohol or oleic acid had no effect. Their explanation attributed the change to capillary condensation of films of phenol which lowered the stability of the aggregate. A few years ago, experimental evidence also appeared which indicated that adsorbed species, like surface active agents on solid aerosol particles, could affect their coagulation. Sussi (102) explained these observations by suggesting that the adsorbed species changed the distribution of electrical charge on the particles.
Later Vold (103) developed a possible theoretical explanation. She found that the adsorption of material on interacting spheres in concentric layers still would produce a net negative (attractive) interaction energy, but the interaction energy could be reduced as much as 5-50 times that for unsolvated particles in liquids. Stabilization of sols by introducing could best be brought about by choosing adsorbates with Van der Waal's constants differing from those of the particle.

In contrast to Vold's work, Martynov and Smilga (104) have reported that the adsorption of dipole molecules on the surface of colloidal particles also may lead to increased attraction between colloidal particles over that expected from Van der Waal's interaction. The dipole-dipole interaction becomes significant only at surface concentrations of $10^{12-10^{13}}$ molecules-cm$^{-2}$, and this induced force field diminishes exponentially with increasing distance between particles.

B. SIZE DEPENDENCE OF THERMODYNAMIC PROPERTIES

The considerations above largely stem from the assumption that the surface curvature of particles may be disregarded. There exists ample evidence now that one can expect deviations in a number of thermodynamic properties of spherical particles when their size is small enough. These departures can be predicted both from macroscopic analysis and atomistic models. Because of the small size of many natural aerosol particles, and artificially generated suspensions, this type of variability may well be considered unique to the systems.

The macroscopic theory of systems in which surface effects are important have been reviewed, for example, by Goodrich (105). Microscopic analyses have been treated in a general way in several texts, including the book of Hill (106).

In applying thermodynamic arguments to curved surfaces, it is convenient to associate definite quantities with a given area of the surface. These quantities, of course, provide the framework for nearly all of the theoretical treatment of equilibrium and rate processes at the surface so that their calculation from measurements is essential to colloidal theory. To recapitulate
how the influence of surface comes about in macroscopic arguments, suppose we examine briefly the surface energy.\(^1\)

The association of thermodynamic quantities to a surface was worked out first by Gibbs (107), who constructed a geometrical dividing surface coinciding approximately with a physical region of discontinuity, but defined such that it "passed through all points which are similarly situated with respect to the condition of adjacent matter." Different choices of the nature of these points leads to a different dividing surface. Useful conventions to complete this definition have been discussed by Herring (101). Assuming that a surface can be defined meaningfully, the surface energy \(E_s\) may then be defined in terms by the total energy

\[
E = E_L + E_g + E_s. \tag{66}
\]

Similarly other extensive quantities like entropy, \(S\), may be divided in this manner.

The surface tension then may be defined by

\[
\gamma = f^{(s)} - \sum \mu_\alpha / \Gamma_\alpha \tag{67}
\]

where \(f^{(s)}\) is the Helmholtz free energy per unit area of surface, \(\mu_\alpha\) is the chemical potential of the bulk phases, and \(\Gamma_\alpha\) is the surface density \(n_\alpha^{(s)}\) of the \(\alpha\) component. The work done on the surface by \(f\) then reads

\[
\text{Surface work} = \Delta \int \gamma dA, \quad (T, \mu_\alpha \text{ const.}) \tag{68}
\]

For no net surface work, one obtains the Gibbs adsorption relation

\[
d\gamma = -S^{(s)} dT - \sum \Gamma_\alpha d\mu_\alpha \tag{69}
\]

where \(S^{(s)}\) is the entropy of the surface per unit area. Further,

\[
df^{(s)} = \sum \mu_\alpha d\Gamma_\alpha - S^{(s)} dT \quad \text{ (surface work = 0)} \tag{70}
\]

Any arbitrary infinitesimal reversible changes can be wrung from changes

\(^1\) Quantum considerations are disregarded here because these effects appear to be important primarily in condensed materials of low atomic or molecular weight (108).
in which conditions of $[68],[69]$ or $[70]$ are fulfilled. Thus a quantitative relation may be derived for this change involving differentials of $\psi$, $A$, $T$, $N$ and any additional variables such as surface strains, on which surface work may depend. With such equations, the equilibrium behavior, at least of chemically active particles, should be predictable.

The size dependence of surface tension and other variables then arises in a way out of the choice of a convention for the location of the dividing surface. For a curved surface, $\psi$ depends to some extent on this location, and different conventions result in slightly different expressions of the variation of $\psi$ with curvature. For fluid-fluid interfaces the convention that appeared most advantageous to Gibbs was that which made explicit dependence of $\psi$ on curvature zero. "Explicit dependence" meant that the change in $\Delta \psi$, with curvature in a hypothetical displacement of the interface at const. $T$ and $N$ as distinguished from a $\Delta \psi$ with curvature when $N$ changes in such a way that the condition of mechanical equilibrium is satisfied. For Gibbs' location of the interface the requirement that surface work vanish for a normal displacement of the interface gives for the fluid-fluid systems,

$$\beta g = \rho L + \frac{2 \psi}{R}$$

(71)

as the relation between the pressures of the two bulk phases and the mean $(1/2)$ of the two principal curvatures of the interface. The dividing surface, located such that $[71]$ is exactly true, is called the surface of tension. Any other location of the dividing surface located a distance $L$ away, Equation $[66]$, is in error by the magnitude $2 \psi \left[ (R-\Delta)^{1} - R^{1} \right]$. The Gibbs criterion for the location of a fluid-fluid interface is one that simplifies formal considerations. Nevertheless, its advantages are somewhat illusory because it is a difficult problem in statistical mechanics to locate this surface of tension in terms of other physical characteristics of the interface ($110$).

Even though the convention of establishing the dividing surface is chosen generally for $[69]$ and $[70]$ to hold, $\psi$ has been found to be dependent on radius for small enough particles. Using the restriction that mechanical
equilibrium exists at a fluid interface, the form of \( Y(R) \) may be estimated from macroscopic arguments which indicates a reduction in \( Y \) with curvature for very small particles. This result, due to Tolman (111), is indicated in Table 11. Tolman's estimate has been confirmed, at least qualitatively, by a microscopic analysis of Kirkwood and Buff (110), and by empirical considerations of Scherbakov (112). Some indirect evidence from nucleation experiments confirms this functional dependence, but other studies, for example, by Schuster (113), possibly indicates an increase in \( Y \) with radius for small droplets of water.

Dealing with solid-fluid interfaces leads to additional complications. As Herring (109) has remarked, there appears to be no advantage to locating a dividing surface by Gibbs' criterion in this case. The stresses near the surface of a solid are generally complicated in nature, and involve both \( Y \) and its derivatives with respect to strain. Moreover, these stresses are usually unimportant and of less interest than other properties which involve \( Y \) more simply. Gibbs himself recognized these difficulties and proposed that the dividing surface be located so that the surface density of the main constituent of the solid vanishes. This is particularly convenient when the solid is a non-volatile component, and when no other component is adsorbed since \( Y \) then coincides with the surface density of free energy. This convention is also useful for fluid interfaces because the corrections in [69] and [70] have particularly simple forms (109).

Like the surface energy, other thermodynamic properties can display dependence on curvature. Analysis of this dependence again has to be self-consistent with definitions of \( Y \) and the dividing surface. Without going into the details of such analyses, it is useful to call attention to the results found by workers for several quantities in addition to \( Y \). These are listed in Table 11. Calculations based on these functional relationships suggest that certain quantities are more sensitive than others to curvature. However, this effect generally appears to introduce small corrections until the particles are very small, \(~ 10^{-6} \) cm. In this size range, such macroscopic quantities are listed in Table 11, and may well lose their meaning in a commonly accepted sense. Indeed in particles of this size range, where particles are really large molecules, only atomistic considerations may provide meaningful relationships for equilibrium behavior of particles.
Table 11

Variation of some properties of aerosol particles with size

Tabulation of thermodynamic variables as a function of

Particle radius (from Hidy and Brock, 13).

<table>
<thead>
<tr>
<th>Ratio of Effective Property to Same Property for Bulk Particle Radius (μ) State (Particle Radius &gt; 10μ)</th>
<th>&gt;10μ</th>
<th>10μ</th>
<th>1μ</th>
<th>0.1</th>
<th>0.01</th>
<th>0.001</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Pressure, of Water, P/P at 5°C</td>
<td>1</td>
<td>1.0001</td>
<td>1.0012</td>
<td>1.012</td>
<td>1.124</td>
<td>3.32</td>
<td>From Eq. [1]</td>
</tr>
<tr>
<td>Heat of Vaporization of Water at 4°C, ΔHv/ΔHv0</td>
<td>1</td>
<td>0.999994</td>
<td>0.99994</td>
<td>0.994</td>
<td>0.94</td>
<td>(114)</td>
<td></td>
</tr>
<tr>
<td>Surface Tension of Water at 4°C γ/γ0</td>
<td>1</td>
<td>0.9996</td>
<td>0.996</td>
<td>0.968</td>
<td>0.755</td>
<td>(114)</td>
<td></td>
</tr>
<tr>
<td>Solubility of Crystalline Substances,</td>
<td>1</td>
<td>~1</td>
<td>~2</td>
<td></td>
<td></td>
<td>(115)</td>
<td></td>
</tr>
</tbody>
</table>
Since one finds that a dependence on curvature affects equilibrium properties, quantities related to transport processes may also reveal variations with particle size. For example, significant alterations may develop in such parameters as the thermal conductivity $k$, the surface diffusivity of adsorbed material, or in the evaporation coefficients, $\alpha_c$. In the latter case, Okuyama and Zung (116) have found, for example, that the evaporation coefficient for liquid droplets will change with curvature. Associating $\chi$ with the free angle ratio; the ratio of the rotational partition functions of an evaporating molecule in the bulk liquid and the bulk gas phase, Okuyama and Zung found that

$$\alpha_c(R_i) \approx \alpha_\infty e^{\chi \frac{3T}{R_i} \frac{R_i}{kT}}$$

(72)

where $\alpha_\infty$ is the flat surface value of the evaporation coefficient. This correction depends somewhat on temperature, $T$ and molecular volume $V$ of a liquid molecule, but in practice it does not significantly affect until $R_i \approx 10^{-7}$ cm.

Similarly, treatments of chemical rate processes on the surface of solids or liquids, such as adsorption or recombination, and for diffusional transfer between surfaces and bulk material have hinted at special problems associated with small bodies. For example, Osherov (117) has argued that the kinetics of surface reactions proceed at velocities higher than equivalent processes in the bulk phase. Increases in such rates are believed to be the result of heating effects and energetic distortations of molecules at the surface. Such a result may well indicate that kinetic processes occurring on very small particles where $A$ is larger will be somewhat faster, and may differ from calculations based on much larger particles.

For physical changes of a solid surface, transport of matter over appreciable distances is often involved. Such transport may take place by plastic flow, evaporation and condensation, volume diffusion, and surface or grain boundary migration. Of these, volume diffusion appears to be most amenable to treatment by macroscopic theory. Herring (109) has noted that macroscopic concepts to diffusional processes for changes of surface configurations may be applied
if (a) chemical potentials may be uniquely defined, (b) the diffusion fluxes are non-divergent, and (c) there exists sufficiently free exchange of lattice defects between the surface and the volume immediately adjoining it.

For a one-component substance Herring has found that equilibrium with respect to free energy changes from the interior to the surface, with an increase in molecular density just beneath the surface, gives

\[
\mu_s = \mu_{s0} \left[ \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{\partial^2 \gamma}{\partial n_x^2} \frac{1}{R_1} + \frac{\partial^2 \gamma}{\partial n_y^2} \frac{1}{R_2} - \beta_{xx} \right] \nabla^2 \phi \tag{73}
\]

Here \( \mu_s \) is the chemical potential of material just under an arbitrary point of a curved surface; \( \mu_{s0} \) is the value of \( \mu_s \) beneath a flat surface. \( R_1 \) and \( R_2 \) are the principal radii of curvature of the surface and the derivatives with respect to \( n_x \) and \( n_y \) measure changes in \( \gamma \) with changes in orientation of the surface normal \( n \) in the direction of the radii of curvature. \( \beta_{xx} \) is the externally applied traction. Here again, we find that diffusion rates in the condensed phase will be quite sensitive to particle size through modifications in the chemical potential. The sensitivity stems not only from the radius of curvature increase, but also from changes of gradients in \( \gamma \) at the particle surface.

C. SURFACE AND STRUCTURAL HETEROGENEITIES

The discussion in the last two sections calls attention to the significance of the nature of the particle surface in relation to the bulk phase, and particle geometry for introducing ambiguities in the equilibrium and kinetic behavior of small particles. Further complications may arise in the behavior of aerosols when consideration is given to the consequences of heterogeneities in surface or bulk structure of particles. This aspect of aerosol chemistry remains virtually unexplored, mainly because of the extreme difficulties in analyzing for such variations in single particles.
The nature of heterogeneities on surfaces not in equilibrium with bulk phases on either side of the dividing surface has been investigated extensively in recent years. Because of its importance to solid state physics, much of the research on this subject has been reported in the crystallographic and metallurgical literature (see for example, Gomer and Smith (118)), and consequently will not be discussed here. Much of such information should be applicable to aerosols in which the particles are about 0.1μ in radius or larger.

It seems doubtful that potentially unique departures in physicochemical behavior of aerosols will be discovered until the ratio of intermolecular distance to particle radius λ exceed about 10⁻² i.e., the particles begin to reduce to sizes of ~ 0.01μ or less. In this regime, both extrinsic and intrinsic contributions to surface and bulk heterogeneities may contribute to behavior of aerosol dispersions which reflect highly non-equilibrium conditions in the condensed phase. In fact, clusters of 100-1000 molecules in this size range may well exhibit only "bulk" properties which will be characteristic of surface layers overlaid on much larger bodies.

One wonders, for example, what the implications are of very small particle interactions with the gas phase in relation to surface forces. Recent studies by Distler and Kobsarena (119) have implied that the influence of active centers for selective adsorption may extend 1-10μ away from a surface. Surface influences of such a long range character may cause rather severe deviations in catalytic effects in reactive gases containing very small particles as contrasted to larger suspended material.

The measurements of Stöber(120) dealing with adsorption of gases like CO₂, NH₃, H₂O and SO₂ on silica particles greater than 0.1μ radius have indicated no unusual influences of particle size on adsorption rates. That is, the rate of adsorption in all cases investigated remained proportional to the surface area of the fine powders. Stöber, however, did notice that silica particles of the 0.1μ size range exhibited a more than 20% decrease in density as compared with the bulk material. The reason for this deviation
was believed to be related to widening of the lattice spacing under a "constrained" equilibrium condition in such particles with very large surface curvature. The changes in lattice structure with curvature, in terms of the lattice constant, were examined some time ago by Lennard-Jones(121). He determined that the equilibrium lattice constant for a small crystal composed of atoms interacting pairwise as a simple potential energy function should be larger the smaller the particle.

The failure to observe deviations in chemical behavior of very small particles may be associated with the fact that most experiments are designed to observe macroscopic variables which tend to statistically smooth out heterogeneities in individual species of a system. Adamson, et al (122) recently have noted this in connection with studies of adsorption on surfaces. They determined that such parameters as entropy were largely insensitive to different theoretical models of rate processes going at the particle surface. Therefore, it was suggested that a more appropriate parameter to explore would be, for example, the distribution of interaction energy between molecules on the heterogeneous surface.

4. SUMMARY

From the very brief discussion of the current state of knowledge in aerosol physics and chemistry, one may transport processes between the suspending gas and a single spherical particle is relatively well established with a few exceptions. This theory has been largely confirmed by experiment. Modifications to account for surface roughness and shapes other than spheres are difficult to incorporate in the dynamical theory, but probably can be taken care of by semi-empirical geometrical factors.

Perhaps the greatest areas of uncertainty in the dynamical processes for spheres lies in the cases where the statistical behavior of assemblies of particles must be estimated. No completely satisfactory theoretical picture has evolved as yet from understanding of the behavior of single particles. So far, there have been few experimental studies which have provided enough information to critically test the existing theory, or to lead the way towards significant improvements in these models.
The nature of the particles themselves provides significant uncertainties in the equilibrium and kinetic properties of aerosols. Care must be taken in applying analytical models even to single particles, especially in the noncontinuum regime, without independent knowledge of certain intrinsic or extrinsic parameters associated with a particular aerosol.

In the last section I have tried to point out, in a very speculative way, that a number of exceedingly important features of the physico chemical properties of highly dispersed aerosols remain to be investigated. The methods to be used for such studies are not at all well established and their development will depend on the inventiveness on the part of workers interested in such phenomena. Despite the extreme difficulties in the task of exploring these features of aerosol behavior, it appears that these problems may well occupy much of the thought of the next generation of aerosol researchers.

Much of this discussion, which outlines the framework of a kinetic theory of aerosols, should provide the basis for investigation of the dynamical processes of particles undergoing chemical reactions. Some examples of cases of practical importance that have not been examined extensively in this light are photochemical smogs and aerial dispersions from combustion processes. The incorporation of the dynamics of suspensions of idealized spheres with theories of chemical rate processes should evolve ultimately into a better understanding of aspects of contamination of the earth's environment.

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