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Transport Phenomena with Single Aerosol Particles

E. James Davis
The Institute of Paper Chemistry, Appleton, WI 54911

This is a review of theory and experiments related to single aerosol particle transport processes. The theories of mass, heat, momentum, and charge transfer are outlined, with emphasis on mass transport in the continuum and noncontinuum regimes. Included in the discussion of mass transfer are single and multicomponent droplet evaporation, a comparison of the results of solutions of the Boltzmann equations for Knudsen aerosol evaporation and growth and experimental methods for the study of single droplet evaporation or growth. Of particular concern here are the experimental apparatus and techniques developed for single particle measurements. These range from the Millikan oil drop experiment through the electrostatic balance (the Millikan condenser with automatic stabilization of the particle) to the electrodynamic balance. The principles and applications of these instruments are reviewed.

INTRODUCTION

The theoretical and experimental tools that lie at the heart of this survey date from 1908–1909. In the former year Mie (1908) solved Maxwell's field equations describing the scattering of a plane electromagnetic wave from an isotropic sphere, and the following year Debye (1909) published his solution of the same problem. That same year Millikan (1909) finished his first measurements of the charge on the electron using his balanced-waterdrop method, and he presented his results to the British Association for the Advancement of Science in August 1909. Millikan quickly improved on his experiment, and by the spring of 1910 he had discarded his balanced-waterdrop technique in favor of the famous oil drop experiment, in which he studied falling and rising charged oil drops in an electric field (Holton, 1978).

Full utilization of these theoretical and experimental tools by aerosol scientists awaited the development of the high speed computer for Mie theory computations, the development of the laser light source, and modifications of the Millikan oil drop experiment to provide automatic stabilization of the charged droplet.

There is little need here to list the applications of Mie theory, for it has become a standard tool of the colloid and aerocolloid scientist for particle size measurement, and Kerker (1969) and van de Hulst (1957) have provided treatises on the subject. It is equally unnecessary to elaborate on the classical Millikan oil drop experiment except to indicate its use in the study of evaporation rates. One additional venerable work should be referenced at the outset of this review, and that is Maxwell's (1877) analysis of the quasi-steady isothermal diffusion-controlled evaporation of a droplet in a stagnant carrier gas. In response to the request of the editors of the Encyclopedia Britannica for a contribution on the wet bulb thermometer, Maxwell obliged with an article that included his treatment of droplet evaporation. Maxwell's result for the flux \( J_c \) of the evaporating species can be written

\[
J_c = \frac{D_{ij}}{a} (C_s - C_\infty),
\]

where \( D_{ij} \) is the binary diffusivity for evaporating species \( i \) in carrier gas \( j \), \( a \) is the droplet radius, \( C_s \) is the vapor concentration in the neighborhood of the droplet surface, and \( C_\infty \) is the vapor concentration far from the surface.

Mie theory, Millikan's oil drop experiment, and Maxwell's equation, Eq. (1), are the starting points for this review, and we shall have more to say about each of these classical works.
TRANSPORT THEORY

Continuum Regime Transport

The evaporation and growth of droplets and the chemical reactions associated with an aerosol particle (liquid or solid) and a reactive species in a surrounding stagnant gas mixture involve mass transfer to or from the particle surface by molecular diffusion. Because there are thermal effects due to the phase change or chemical reaction, the heat and mass transfer processes are coupled. A theoretical analysis of the coupled processes is generally formidable, particularly if the assumptions of quasi-steady-state and quasi-stationary boundaries cannot be considered valid. Droplet combustion problems are particularly complex because of the additional complications of Arrhenius reaction dependence on temperature and radiation effects. Stefan (1881) flow further complicates rigorous analysis when the vapor pressure of the evaporating species is not small, for in this event the convective radial motion of the vapor is significant.

Further difficulties of analysis ensue when the mean free path $\lambda_{ij}$ of the diffusing species $i$ in stagnant gas $j$ is of the same order as the droplet size, that is, when the Knudsen number $Kn = \lambda_{ij}/a$ is of order unity. In this transition regime, or Knudsen aerosol regime, continuum theory is invalid in the vicinity of the particle surface (within a distance of the order of $2\lambda_{ij}$).

In the continuum regime ($Kn < < 1$) the droplet evaporation problem is described by the usual laws of mass conservation, diffusive mass transport, and conduction heat transfer. The unsteady state equations have been analyzed by Kang (1967) and Volkov and Golovin (1970) for droplet evaporation, by Kotake and Okazaki (1969) for evaporation and combustion of a fuel droplet, and by Chang and Davis (1974) for aerosol droplet evaporation. Kang’s solution, which he assumes a uniform temperature field inside the drop, violates the law of conservation of energy and does not satisfy continuity conditions at the drop surface, and the numerical solution of Kotake and Okazaki indicates that the evaporation process does not attain a true quasi-steady state of mass and heat transfer. The results of Chang and Davis indicate that quasi-steady-state transport is reached very quickly for slowly evaporating species such as dibutyl phthalate (DBP) in He, but for water evaporating into air the isothermal quasi-steady-state approximation is questionable because of the much higher heat of evaporation and higher evaporation rate.

Because of the widespread use of the assumption of quasi-steady state, it is desirable to evaluate the conditions for which it is not likely to be valid. For this purpose let us examine the coupled unsteady state equations solved by Chang and Davis, which describe the temperature and gas phase concentration fields for an isolated single component droplet initially at temperature $T_0$ suddenly exposed to a stagnant gas at temperature $T_x$. The mole fraction $x_i$ of the vapor in the gas phase is described by

$$\frac{\partial x_i}{\partial t} = \frac{D_{ij}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial x_i}{\partial r} \right), \quad (2)$$

where Stefan flow has been neglected and the total concentration $C_T$ of the vapor-gas mixture is assumed constant as an approximation (valid for a dilute mixture at uniform temperature).

The inner (inside the drop) and outer temperature fields for droplet and gas are described by

$$\frac{\partial T_k}{\partial t} = \frac{\alpha_k}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_k}{\partial r} \right), \quad k = 1, 2, \quad (3)$$

where $k = 1$ refers to the liquid phase and $k = 2$ to the gas, and $\alpha_k$ is the thermal diffusivity of the appropriate phase.

In addition to transport equations (2) and (3), a mass balance applies,

$$\frac{d}{dt} \left( \frac{1}{M} \frac{4}{3} \pi a^3 \right) = -4\pi a^2 D_{ij} \frac{\partial x_i}{\partial r}(t,a), \quad (4)$$

together with the equilibrium condition

$$x_i(t,a) = x_{ei}(T_a)/P, \quad (5)$$

where $x_i$ and $T_a$ are the interfacial composition and temperature, respectively, $P_{ei}$ is the vapor pressure, and $P$ is the total pressure.
Equation (4) can be simplified to
\[
\frac{da}{dt} = - \frac{D_{ij}M_i}{\rho_l RT_\infty} \frac{\partial p_i}{\partial r}(t,a),
\]
assuming that Dalton’s law applies, the liquid density \(\rho_l\) is constant, and the gas temperature does not vary too greatly from \(T_\infty\).

The remaining conservation equation is an energy balance at the droplet surface,
\[
-(\Delta H)_{\text{vap}} D_{ij}C_1 \frac{\partial T}{\partial r}(t,a) = k_2 \frac{\partial T}{\partial r}(t,a)
\]
\[-k_1 \frac{\partial T}{\partial r}(t,a).
\]

This system of equations, Eqs. (2), (3), and (5)–(7), has been solved, subject to the appropriate boundary and initial conditions, by Chang and Davis using an integral equation formulation. The numerical solutions show that because of the large thermal conductivity of the liquid compared with that of the gas the temperature within the droplet very rapidly approaches the interfacial temperature. In this case the middle term of Eq. (7) can be neglected, and the result indicates that the energy required for the evaporation is supplied almost entirely by the gas phase. Thus, the depression of the interfacial temperature depends strongly on the dimensionless group \((\Delta H)_{\text{vap}} D_{ij}C_1/k_1 T_\infty\) and the vapor pressure.

It was found that for slowly evaporating species and for species with a low heat of vaporization the gas phase temperature gradient is sufficiently small so that isothermal conditions are closely approached. In this limit the energy equation can be neglected and the solution of Eq. (2), using \(x_i = p_i/P\) and Eq. (5), becomes
\[
\frac{da}{dt} = - \frac{D_{ij}M_i}{\rho_1 RT_\infty} \left( p_i^2 - p_i,\infty \right)^{1 + \frac{a}{\sqrt{nD_{ij}}} \right) \}
\]
where \(p_i,\infty\) is the partial pressure of the vapor far from the droplet surface. The quasi-steady-state approximation,
\[
\frac{da}{dt} = - \frac{D_{ij}M_i}{\rho_1 RT_\infty} (p_i^2 - p_i,\infty),
\]
is recovered for times satisfying the inequality \(t > a^2/\pi D_{ij}\). For an \(a = 1\) \(\mu\)m droplet of DBP evaporating into air, \(D_{ij} = 3.7 \times 10^{-6} \text{ m}^2/\text{sec}\), and steady state is reached well within a millisecond (\(t > 8.6 \times 10^{-8} \text{ sec}\)).

When heat and mass transfer processes are coupled, the criterion for quasi-steady state requires the full solution of the problem discussed, but most investigators have assumed quasi-steady state. Fuchs (1959) has reviewed the earlier work based on quasi-steady state, and Wagner’s (1982) recent review emphasized the phenomenological equations based on the quasi-steady state. He also examined the experimental work on aerosol evaporation and growth, particularly growth studies performed with the expansion cloud chamber. The non-rigorous treatments of the coupled heat and mass transport phenomena reviewed by Wagner, such as the study by Fukuta and Walter (1970), require the introduction of numerous correction factors that must be obtained by comparing the approximations with experimental data. Although these approximations are very useful for estimating heat and mass fluxes, they do not reflect a fundamental understanding of the transport processes.

The evaporation of a multicomponent droplet involves additional complexity because of the time-dependent composition of the liquid as it is depleted in the more volatile components. Newbold and Amundson (1973) derived a model for multicomponent droplet evaporation with Stefan flow. They assumed the liquid to have uniform composition (no concentration gradients) and solved the quasi-steady-state transport equations for the gas phase to obtain the heat and mass fluxes, which were then used in volume, mass, and energy balances. The resulting differential equations were solved to obtain the radius, concentration, and temperature histories. It was found that the transport of one component can be augmented by the bulk flow of the others.

Glushkov (1969) studied the evaporation of binary droplets using a torsion balance and cinematography to measure droplet weight and volume for several binary systems involving CCl₄, benzene, ethanol, and chloroform. He reported concentrations and temperatures as
functions of time but did not compare his results with theory. In a theoretical study Glushkov et al. (1970) examined the kinetics of isothermal evaporation of an ideal solution droplet and determined the time required for complete evaporation in terms of an integral. The evaporation rate and droplet size are not obtained explicitly, and they did not take into account the Kelvin effect that should be introduced for small droplets.

Ravindran and Davis (1982) investigated very slow (isothermal) binary droplet evaporation theoretically and experimentally using dioctyl phthalate (DOP) and DBP, which have very low vapor pressures \( p_{DOP} = 3.5 \times 10^{-3} \text{ Pa} \) and \( p_{DBP} = 1.3 \times 10^{-5} \text{ Pa} \) at 295 K. Assuming rapid internal diffusion (no concentration gradients within the aerosol droplet) and quasi-steady state, they modeled the external gas-phase diffusion as though the two dilute vapors diffuse independently. The molar fluxes \( J_i \) and \( J_k \), then, are given by equations of the form of Eq. (1), that is,

\[
J_i = D_i \rho_i^0 x_i / aRT,
\]

where \( x_i \) is the liquid phase mole fraction, Raoult’s law has been applied to obtain the partial pressure of species \( i \) (or \( k \)) at the surface, and the vapor concentration far from the surface is zero.

By means of component balances on the droplet and assuming the molar density of the liquid to be given by \( \rho_m = (x_i V_i + x_k V_k)^{-1} \), where \( V \) refers to the molar volumes of the pure components, the following equations have been obtained describing the droplet size and composition:

\[
\frac{da^2}{dt} = - \frac{2D_{ij}^c}{RT} [x_i \rho_i^0 V_i + \rho_i^0 (1 - x_i) V_i], \tag{11}
\]

and

\[
\frac{dx_i}{dt} = \frac{3}{a^2} \frac{D_{ij}^c}{RT} (\rho_k - \rho_i^0) \times [(V_i - V_i)x_i + V_i](x_i - x_i^2). \tag{12}
\]

Equations (11) and (12) were solved numerically to obtain the radius and composition. Analogous equations can be derived for non-ideal solutions to include the appropriate activity coefficients and mixture densities, but the general outline of the analysis remains the same.

Ravindran and Davis compared the results of this analysis with their experimental results obtained using an electrostatic balance described herein, and Rubel (1982) repeated the experiments in an electrodynamic balance using larger droplets of DOP and DBP. As this paper will show, both techniques involve suspending a charged droplet in an electric field. Figure 1 shows the experimental results of Ravindran and Davis obtained by light scattering measurements, and Figure 2 shows Rubel’s results obtained by photographing the evaporating droplet. Also plotted on the figures are the predicted radii and compositions. The predicted radii are in good agreement with the experimental data.

Rubel (1981) also performed similar measurements for evaporating droplets of diesel oil and “pale oil,” but he did not analyze the multicomponent transport. Instead, he reported “effective vapor pressures” determined as if the droplet were a single component.

**Knudsen Aerosol Transport—Simplified Theories**

Evaporation in the Knudsen regime has been reviewed by Davis and Ray (1978) and Davis et al. (1980), and there has been continuing progress in the theoretical prediction of heat and mass fluxes for this noncontinuum regime. Wagner (1982) discussed and listed some of the semitheoretical and empirical expressions available for the prediction of heat and mass fluxes in the transition regime, but most of the available expressions do not apply to systems of physical significance and interest, as will appear.

The state of our theoretical knowledge of heat and mass transport for Knudsen aerosols parallels that for continuum theory in that only a few attempts have been made to treat the problem fundamentally and rigorously owing to the difficulties associated with solving the governing equations. In this case the migration is described by the nonlinear Boltzmann transport equa-
Transport with Single Aerosol Particles

tions for the mixture of gas and vapor molecules surrounding the droplet. Hidy and Brock (1970) examined Knudsen aerosol dynamics in their monograph, but they did not offer new solutions to the Boltzmann equations.

Early investigations of Knudsen aerosol evaporation and condensation avoided rigorous treatment of the Boltzmann equations by flux matching, that is, by considering the non-continuum effects to be limited to a region $a \leq r \leq \Delta$ beyond the droplet surface and assuming that for $r \geq \Delta - a$ continuum theory applies. The distance $\Delta$, then, is of the order of the mean free path $\lambda_{ij}$ and within this inner region the simple kinetic theory of gases is assumed to apply. Fuchs (1934), by matching the fluxes for the two domains at $r = \Delta$, obtained the flux ratio $J/J_k$ as follows

$$\frac{J}{J_k} = \frac{1 + \Delta/a}{1 + \Delta/a + a\tilde{c}_i/4D_{ij}}.$$  \hspace{1cm} (13)

where $\beta$ is the evaporation coefficient, $\tilde{c}_i$ is the average velocity of the vapor molecules, given

\[ \tilde{c}_i = (8kT/m_i)^{1/2}, \]  \hspace{1cm} (14)

and $J_k$ is the mass flux for free-molecule evaporation. The molecular flux $J_k^* \text{ for this limiting case (Kn} > 1)$ is given by

$$J_k^* = \frac{1}{2} \beta \tilde{c}_i (n_s - n_x).$$  \hspace{1cm} (15)

Here $k$ is Boltzmann’s constant, $m_i$ is the mass of a vapor molecule, $n_s$ is concentration of vapor molecules near the droplet surface, and $n_x = 0$, and if the ideal gas law can be applied, the mass flux $J_k$ becomes

$$J_k = \frac{1}{2} \beta \tilde{c}_i M \rho_i^2 / RT.$$  \hspace{1cm} (16)

Several choices for $\Delta$ have been proposed; the simplest, due to Fuchs, is $\Delta = 0$. Bradley et al. (1946) suggested $\Delta = (1 + z)^{1/2} \lambda_{ij}$, where $z = m_i/m_p$, and Wright (1960) recommended

\[ \Delta = 0.6 \lambda_{ij}, \]
FIGURE 2. The radius and composition history for a binary droplet of DBP and DOP evaporating in air from Rubel (1982; circles). $T = 296$ K; $P = 1$ atm.

$\Delta = 2D_{ij}/\bar{c}_n$ but numerous other possibilities exist.

Equation (13) can be written in an alternative form using results from the kinetic theory of gases to relate $\bar{c}_n$, $D_{ij}$, and $\hat{\lambda}_{ij}$, but on this point the literature is inconsistent because various approximations from kinetic theory have been applied. Let us examine the higher approximations first.

For a binary vapor–gas mixture the mean free paths for the vapor and the carrier gas are given (Jeans, 1954) by

$$\hat{\lambda}_{ij} = \frac{1}{\sqrt{2n_i\pi\sigma_{ij}^2} + \sqrt{1 + zn_i\pi\sigma_{ij}^2}}$$  \hspace{1cm} (17)

and

$$\hat{\lambda}_{i} = \frac{1}{\sqrt{2n_i\pi\sigma_{i}^2} + \sqrt{1 + zn_i\pi\sigma_{i}^2}}$$  \hspace{1cm} (18)

respectively, where $\sigma_{ij}$, $\sigma_{jp}$, and $\sigma_{i}$ are the collision diameters for vapor molecule interactions, gas molecule interactions and vapor-gas molecule interactions, respectively. For a dilute mixture, i.e., for $n_j > n_i$, Eqs. (17) and (18) simplify to

$$\hat{\lambda}_{ij} = \frac{1}{\sqrt{1 + zn_i\pi\sigma_{ij}^2}}$$  \hspace{1cm} (19)

and

$$\hat{\lambda}_{i} = \frac{1}{\sqrt{2n_i\pi\sigma_{i}^2}}$$  \hspace{1cm} (20)

From the Chapman–Enskog theory (Chapman and Cowling, 1970) for the binary diffusion coefficient, we obtain

$$D_{ij} = \frac{3}{8\pi} \frac{\sqrt{\pi k^2 T^3(1 + z) / 2m_i}}{\Omega_{ij}^{(1,1)} \rho \sigma_{ij}^2}$$  \hspace{1cm} (21)

where $\Omega_{ij}^{(1,1)}$ is the collision integral, which has been tabulated by Hirschfelder et al. (1954) as a function of reduced temperature $T^* = kT / \epsilon_{ij}$, and $\epsilon_{ij}$ is the Lennard–Jones molecular interac-
Transport with Single Aerosol Particles

For a dilute mixture the total pressure $P$ is related to the number density of gas molecules $n_j$ by

$$P = n_j kT. \quad (22)$$

For hard spheres $\Omega_{ij}^{(1,1)} = 1$, and in this case Eq. (21) reduces to the Chapman–Enskog first approximation, using Eq. (22):

$$D_{ij}^{(0)} = \frac{3}{8\pi} \frac{\sqrt{\pi kT(1 + z)}}{n_j}. \quad (23)$$

Yet another diffusivity expression has been used by Sitarski and Nowakowski (1979), for they obtained the following expression in their analysis of Knudsen aerosol condensation:

$$D_{ij} = \frac{1}{1 - (1 + z)/10} D_{ij}^{(0)}. \quad (24)$$

Using Eqs. (14), (19), (21), and (22) we obtain a relationship between the mean free path and the diffusivity:

$$\frac{D_{ij}}{\lambda_{ij}\beta_i} = \frac{3\pi (1 + z)}{32 \Omega_{ij}^{(1,1)}}. \quad (25)$$

We note that the molecular mass ratio $z$ appears in Eq. (25). Most investigators of the Knudsen aerosol regime have assumed $z < 1$ either explicitly or implicitly, and this has been the source of some confusion. If we assume $z < 1$ and let $\Omega_{ij}^{(1,1)} = 1$, Eq. (25) becomes

$$\frac{D_{ij}}{\lambda_{ij}\beta_i} = \frac{3\pi /32}{0.2945}. \quad (26)$$

From the zeroth order kinetic theory Fuchs (1934) Fuchs and Sutugin (1970) and others used

$$\frac{D_{ij}}{\lambda_{ij}\beta_i} = \frac{1}{\frac{1}{3}} = 0.3333, \quad (27)$$

and Loyalka (1973) used

$$\frac{D_{ij}}{\lambda_{ij}\beta_i} = \sqrt{\pi /4} = 0.4431. \quad (28)$$

Since relationships (26)–(28) can be and have been used to determine the mean free path in terms of $D_{ij}$ there are several definitions of $\lambda_{ij}$ and $Kn$ in the literature

Now Eq. (13) can be modified using Eq. (27) and introducing $Kn = \frac{\lambda_{ij}}{a}$ to give

$$\frac{J}{J_K} = \frac{1 + Kn\Delta/\lambda_{ij}}{1 + Kn\Delta/\lambda_{ij} + \frac{3}{4}\beta/Kn^{-1}}. \quad (29)$$

An alternative form is obtained using Maxwell’s equation, Eq. (1), with $C_{ij} = 0, C_i = n_i^2 M_i/RT$, and Eqs. (16) and (27) to determine the ratio of the fluxes in the free molecule limit and the continuum limit. Thus,

$$\frac{J}{J_c} = \frac{3\beta}{4D_{ij}} = \frac{3\beta}{4}. \quad (30)$$

Then, multiplying Eq. (29) by $J_K/J_c$ we obtain

$$\frac{J}{J_c} = \frac{3\beta}{4} \frac{1 + Kn\Delta/\lambda_{ij}}{1 + Kn\Delta/\lambda_{ij} + \frac{3}{4}\beta + Kn^{-1} (\Delta/\lambda_{ij})Kn^{-1}}. \quad (31)$$

Numerous equations of the form of Eq. (31) have been proposed as interpolating formulas for the transition regime. Wagner (1982) listed those of Fukuta and Walter (1970) and Smirnov (1971), and Fuchs and Sutugin (1970) fitted Sahni’s (1966) theoretical solution to the Boltzmann equations by means of the expression

$$\frac{J}{J_c} = \frac{1 + Kn}{1 + 1.7104Kn + \frac{2}{3}Kn^2}. \quad (32)$$

For $Kn < 1$, Eqs. (31) and (32) reduce to $J/J_c = 1$, and for $Kn > 1$, Eq. (31) reduces to $J/J_c = 3\beta/4Kn$, while Eq. (32) yields $J/J_c = 3/4Kn$ in this limit. Thus, for $\beta = 1$ the two equations have the same asymptotic limits. It should be pointed out again that Eq. (32) is based on results for $z < 1$, so it is limited to light vapors in a heavier surrounding carrier gas.

We should also point out that heat fluxes in the Knudsen regime can be correlated by expressions analogous to Eqs. (31) and (32), as discussed by Wagner (1982). Again the analysis involves the approximations of a dilute vapor–gas mixture and $z < 1$. In this case, however, the relevant mean free path for energy transport is that of the gas, given by Eq. (20), and the relevant Knudsen number is $Kn_T = 2\eta_j/a$. The thermal conductivity obtained from the Chapman–Enskog theory is

$$K_j = \frac{25}{32\pi} \frac{\sqrt{\pi kTm_j}}{\Omega_{ij}^{(1,1)} C_{ij} \eta_j} \frac{9\eta_j - 5}{10^{10}}. \quad (33)$$
where \( \kappa \) is the ratio of heat capacities, \( C_{p,i}/C_{v,i} \), for the carrier gas, and the collision integral \( \Omega_{ij}^{(2,2)} \) has been tabulated by Hirschfelder et al. (1954), as in the case of \( \Omega_{ij}^{(1,1)} \) for the diffusivity.

In the analogy between heat transfer and mass transfer the diffusivity \( D_{ij} \) is replaced by the thermal diffusivity \( K_{ij}/\rho C_{p,i} \), the mass flux \( J \) is replaced by the heat flux \( Q \), and the concentration \( C \) is replaced by temperature \( T \). For example, Smirnov’s (1971) equation for the heat flux ratio \( Q/Q_c \) for a thermal accommodation coefficient of unity is

\[
Q/Q_c = \frac{1 + \kappa n_T}{1 + 1.7104\kappa n_T + \frac{4}{3}\kappa n_T^{-2}},
\]

which is an exact analogy of Eq. (32).

**Knudsen Aerosol Transport—Boltzmann Equation Solutions**

Considerable progress has been made on solutions of the Boltzmann transport equations for the limiting case of a dilute vapor–gas mixture \((n_v < n_i)\) of a light vapor in a heavier carrier gas \((z < 1)\). In this case collisions between vapor molecules can be neglected, and it is assumed that the concentration and velocity distribution of the gas molecules are only slightly perturbed by the evaporation process. This was Sahni’s (1966) approach. The procedure is to solve the transport equation only for the vapor molecules and to solve the heat conduction equation recognizing that the heat conduction rate is related to the mass transfer rate through the heat of vaporization. As neutron transport theory, this type of theory has been developed extensively, and it is clearly questionable when \( z > 1 \), that is, when the vapor molecule is much more massive than the gas molecule, for then the vapor molecules have a velocity that persists after collision with smaller gas molecules.

Bhatnagar et al. (1954) provided a simpler form of the Boltzmann equation (the BGK approximation) by linearizing the collision term, and Brock (1966, 1967) used the BGK model to obtain a solution for the mass flux valid in the near free molecule regime \((Kn \geq 1)\). Sahni (1966) used the neutron transport approach to solve the problem of condensation on a black sphere for all Knudsen numbers, and Eq. (32) is the Fuchs and Sutugin (1970) correlation of Sahni’s results.

More recently Sahni (1980) extended this neutron transport theory to take into account the accommodation coefficient (nonblack sphere) and the Kelvin effect (the increase in vapor pressure over the curved surface as the radius decreases). His published results for \( J/J_c \) are not in agreement with the Fuchs–Sutugin equation, as will be shown here.

Loyalka (1973) solved the same problem as Sahni by means of a variational solution of the BGK model, and his results are within 3% of the Fuchs–Sutugin equation results for all Kn. Loyalka’s definition of the Knudsen number is related to that of Fuchs, using Eqs. (27) and (28) for \( \lambda_{ij} \), by \( Kn_{\text{Loyalka}} = (4/3\sqrt{\pi})Kn_{\text{Fuchs}} = 1.3293Kn_{\text{Fuchs}} \). Table 1 shows Loyalka’s results compared with the Fuchs–Sutugin equation [Eq. (32) multiplied by \( J_c/J_c = 3/4Kn \)].

Recently Loyalka (1982) extended his earlier analysis to derive new expressions valid for the near continuum regime, and he proposed a generalization of the Fuchs–Sutugin equation based on his new solution of the Boltzmann equations. His generalization is

![Table 1. A Comparison of the Flux Ratio J/J_F Calculated by Loyalka (1973) with the Fuchs–Sutugin Equation](image)

<table>
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<th>( Kn_{\text{Fuchs}} )</th>
<th>Loyalka</th>
<th>Fuchs–Sutugin</th>
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<td>0.0175</td>
<td>0.0176</td>
</tr>
</tbody>
</table>

*Equation (32) multiplied by \( J_c/J_F = 4Kn/3 \).*
Transport with Single Aerosol Particles

\[ \frac{J}{J_c} = \frac{1 + Kn_k}{1 + (1 + f_k \zeta_k)Kn_k + f_k / \pi Kn_k^2}, \quad k = 1, 2, \tag{35} \]

where \( f_k \) and \( \zeta_k \) are constants which depend on various models chosen for the jump coefficient discussed by Loyalka, and \( Kn_1 \) and \( Kn_2 \) refer to the definitions of the Knudsen numbers of Fuchs and Loyalka, respectively.

If \( f_1 = 4/3 \sqrt{\pi} \) and \( \zeta_1 = 0.7104 \), Eq. (35) is identical to Eq. (32). Another expression of the form of Eq. (35) is obtained by means of the model for which \( f_1 = 4/3 \sqrt{\pi} \) and \( \zeta_1 = 1.0161 f_1 \), that is, for the equation

\[ \frac{J}{J_c} = \frac{1 + Kn}{1 + 1.7644 Kn + \frac{3}{4} Kn^2}, \tag{36} \]

Equations (31)—with \( \beta = 1 \) and \( \Delta = 0 \), (32),

\[ \frac{J}{J_c} = \left[ 1 + \frac{3 \beta (1 + z)^2}{4(3 + 5z)} \right] \left( 1 + \frac{15\pi (1 + z)^2}{4 \cdot 9 + 10z} \left[ \frac{\beta (1 + 2z)}{\pi(3 + 5z)} + \frac{1}{2\beta} \left( Kn + \frac{9(1 + z)^2}{8(3 + 5z)} Kn^2 \right) \right] \right) \tag{37} \]

where the diffusivity is given by Eq. (24). Table 2 shows that for \( z = 0 \) Eq. (37) significantly underpredicts \( J/J_c \) in the near free molecule regime, but is in reasonably good agreement with the results of Loyalka (1982), Eq. (36), and the Fuchs–Sutugin equation for \( Kn \leq 1 \).

Figure 3 shows the results calculated using Eq. (37) with \( \beta = 1 \) for various values of \( z \) corresponding to a very light vapor in a heavy carrier gas (\( z = 0 \)), water vapor in air (\( z = 0.621 \)), and DOP evaporating in \( N_2 \) (\( z = 13.9 \)). The DOP–\( N_2 \) system corresponds to one of the experimental systems studied by Davis et al. (1978), and we shall examine the comparison between theory and experiment (see Figure 11).

There remains a need for a more accurate solution of the Boltzmann equation for arbitrary values of \( z \), particularly in the near free molecule regime where the results of Sitarski and Nowakowski are unsatisfactory. In addition, it is desirable to include simultaneous energy transfer.

Momentum Transfer

The drag force on a small particle moving through a surrounding carrier gas also depends on the mean free path of the gas molecules. In the continuum regime the Stokes law applies to the small droplets of interest here; that is, the drag force \( F_D \) is given by

\[ F_D = -6\pi \mu v, \tag{38} \]

where \( \mu \) is the viscosity of the carrier gas, and \( v \) is the steady-state velocity of the sphere.

In the Knudsen regime it is necessary to take into account slip, and Davies (1945) reviewed the early work on the slip correction factor, where the slip correction factor \( f \) is defined by the equation

\[ F_D = -\frac{6\pi \mu v}{1 + f} v. \tag{39} \]

Based on the experiments of Millikan (1920, 1923), Matteut (1925), and Mönch (1933), all of whom used the Millikan oil drop experiment, Davies recommended the expression

\[ f = Kn[1.257 + 0.400 \exp(-1.10Kn^{-1})]. \tag{40} \]

Annis et al. (1972) reexamined the earlier work and reviewed the attempts to solve the BGK model of the Boltzmann equation for momentum transfer in the transition regime.
Based on the solution of Cercignani et al. (1968), they proposed the equation

$$f = \text{Kn}[1.558 + 0.173 \exp(-0.769\text{Kn}^{-1})],$$  \hspace{1em} (41)

where the mean free path in the Knudsen number used is Eq. (41) is given by

$$\lambda_j = 2\mu_j/n_jm_j\bar{c}_j.$$  \hspace{1em} (42)

Annis et al. showed that Eq. (41) gives results for $f$ to within 1% of the numerical results of Cercignani et al. and reproduces Millikan's original equation almost to within experimental error. They also extended their analysis to the mobility of large ions in an electric field, but a discussion of charge effects is deferred to the next section.

Recently Lea and Loyalka (1982) solved the BGK model assuming diffuse reflection at the surface of the sphere to obtain the velocity profiles and drag forces for all Knudsen numbers. They used an integral equation approach that provides the velocity profiles as well as the drag forces. The variational technique of Cercignani et al. gives results only for the latter.
The calculated drag forces are in excellent agreement with those of Cercignani et al. and Aniss et al., and their velocity profiles agree with the calculated results of Sone and Aoki (1976) for the near continuum regime.

Dahneke (1973a–c) investigated drag forces and slip correction factors for nonspherical particles in the continuum, transition, and free molecule regimes. He developed a method for obtaining the slip correction factors for spheres, disks, cylinders, spheroids, and cubes, and he compared his adjusted sphere approximation method with other techniques proposed.

**Charge Effects**

It was mentioned that Aniss et al. considered the mobility of large ions in an electric field. The mobility $K_{ion}$ of an ion in a gas is defined by

$$v = K_{ion}E,$$

where $E$ is the electric field intensity. The force on the ion is $eE$, where $e$ is the ionic charge. Using this result for the force in Eq. (39) and Eq. (43), the ion mobility becomes

$$K_{ion} = (1 + f)e/6\pi\mu a.$$

Aniss et al. developed an expression for the ratio of the ion mobility to the ion mobility in the free molecule regime that is analogous to the slip correction factor.

In a rather different study of charge transport, Iribarne and Thomson (1976) experimentally investigated the evaporation of small ions from evaporating charged droplets. They developed a theoretical argument to establish under what conditions ion evaporation can occur, and they compared those conditions with Rayleigh instability conditions, concluding that ion evaporation should occur only when the drop reaches sizes of order 0.01 μm.

Lord Rayleigh (1945) derived the following condition for the stability of a droplet with charge $q$ and surface tension $\gamma$:

$$\gamma > q^2/(16\pi\alpha^3).$$

If the charged droplet evaporates without losing charges, then a critical radius $a_c$ will be reached below which the drop is unstable. That critical radius is given by

$$a_c = (q^2/(16\pi\gamma))^{1/3}.$$ (46)

Doyle et al. (1964) and Schweizer and Hanson (1971) experimentally investigated this Rayleigh limit, the former using a Millikan chamber and the latter using an electrodynamic balance about which more will be said. The results of Schweizer and Hanson for 1-octanol agreed well with the theoretical limit, and the data of Doyle et al. for water and aniline scatter about the Rayleigh limit.

Berg et al. (1970) used a sealed suspension chamber, described in the experimental section of this paper to study Rayleigh stability, and they showed the existence of metastable states predicted by Cahn (1962) as well as the unstable state of Rayleigh for charged single water droplets.

An additional, and very interesting, charge phenomenon has been studied experimentally and theoretically by Pope (1962). This is the determination of the ionization potential of an organic solid by measuring the threshold for photoemission of electrons by suspending a particle in a Millikan cell in the path of two beams of light of different wavelengths, both shorter than the threshold wavelength. By measuring the potential difference across the Millikan plates required to balance the force of gravity at each wavelength, Pope showed that the photoionization potential can be determined.

**EXPERIMENTAL METHODS**

**Millikan Oil Drop Techniques**

A number of applications of the Millikan oil drop experiment were mentioned, and this section reviews the use of the technique for investigations of transport phenomena.

Millikan himself was quick to realize the difficulties introduced by evaporation and condensation in his experiments, and he shifted his studies from water droplets to less volatile droplets. Gudris and Kulikova (1924) used the
Millikan technique to measure evaporation rates of water in CO₂, air, and H₂-air mixtures. This study and several other investigations involving the use of the Millikan oil drop experiment have been critically reviewed by Fuchs (1959), so we need not elaborate on the earlier work here. The evaporation rates measured by Gudris and Kulikova were considerably smaller than predictions based on Maxwell’s equation, taking into account the Kelvin effect. The gases were saturated with water vapor, so the driving force for evaporation was \( p_s - p_{x} \), where \( p_s \) is the vapor pressure over a flat surface, and \( p_{x} \) is the vapor pressure over curved surface of radius \( a \), which is given by Kelvin’s equation:

\[
p_{x} = p_{s} \exp(2M_{i}/a\rho_{1}RT).
\]  

(47)

In this case the evaporation rate is given by

\[
\frac{da}{dt} = - \frac{D_{ij}M_{i}p_{s}^{2}x}{\rho_{1}RT} \left[ \exp \left( \frac{2M_{ij}}{a\rho_{1}RT} \right) - 1 \right].
\]  

(48)

Nestle (1932) and Schäfer (1932) used the same technique as Gudris and Kulikova to measure the evaporation rates of Hg in vapor-saturated gases. Nestle used CO₂, N₂, and Ar, and Schäfer used H₂ and CO₂. Only some of Schäfer’s data for the Hg–H₂ system agree with theory. It is likely that surface contamination affected most of the results of Nestle and Schäfer, as discussed by Fuchs.

Additional evaporation studies involving the use of the Millikan chamber were performed by Woodland and Mack (1933) with dibutyl tartrate (DBT) and DBP droplets and by Shereshefsky and Steckler (1936), who studied the Kelvin effect for DBP droplets. All of these studies were carried out for the continuum regime, but Monchick and Reiss (1954) used a Millikan condenser to measure the evaporation rates of diamyl sebacate (DAS) in the transition regime. They operated the thermostated chamber at subatmospheric pressures (1.33–13.3 kPa), and they coated the chamber’s surfaces with dicapryl sebacate in some experiments and diundecyl sebacate in others to absorb the DAS vapor, thereby maintaining \( p_{x} \) at nearly zero. Their evaporation rate data followed

\[
\frac{da}{dt} = - \frac{A}{1 + BaP} \exp \left( \frac{2\gamma M_{i}}{a\rho_{1}RT} \right).
\]  

(49)

which has the form of Fuchs’s flux-matching equation [Eq. (31) with \( \Delta = 0 \)], taking into account the Kelvin equation in the flux \( J \). From Eq. (49) a plot of \( (da/dt)^{-1} \exp(2\gamma M_{i}/a\rho_{1}RT) \) versus \( aP \) should yield a straight line, and the data of Monchick and Reiss, though scattered, did yield a straight line on such a plot.

In the limit of very low total pressure \( (P \to 0) \), free molecule evaporation occurs, so we may write

\[
\lim_{P \to 0} \frac{da}{dt} = - \frac{\beta \tilde{c}_{i} p_{s}^{2}x M_{i}}{4\rho_{1}RT} \exp \left( \frac{2\gamma M_{i}}{a\rho_{1}RT} \right).
\]  

(50)

Equation (50) can be used to determine the evaporation coefficient \( \beta \) from the extrapolated value of \( da/dt \) using a Monchick–Reiss plot. As will be shown here, this technique was used by Chang and Davis (1976) and Davis and Ray (1978) to determine the evaporation coefficients of DOP in N₂ and DBS in N₂, respectively.

New applications of the Millikan condenser continue to arise, and the use of the device by Doyle et al. (1964) for investigating the Rayleigh limit of charge has been mentioned. More recently, Sun et al. (1979) reported the use of the Millikan electrostatic method coupled with a diffusion cloud chamber for evaporation and growth studies. A schematic of the apparatus is shown in Figure 4. A supersaturation profile \( (p_{i}/p_{x}) \) versus vertical position) for the diffusing species \( i \) is established by controlling the temperatures of the upper plate (upon which vapor condenses) and the liquid pool over the lower plate. Charged droplets were generated by means of effervescence from an iron wire inserted in the lower liquid pool (an H₃PO₄ solution). In the upper part of the chamber \( p_{i}/p_{x} > 1 \), so droplet growth occurs, and below the plane of unit supersaturation evaporation takes place. By varying the strength and polarity of the electric field, they were able to move droplets from one horizontal plane to another and in and out of the plane of saturation. This method offers better control of the vapor con-
The diffusion cloud chamber and the saturation ratio profile from Sun et al. (1979).

FIGURE 4. The diffusion cloud chamber and the saturation ratio profile from Sun et al. (1979).

centration field around a droplet than does the Millikan oil drop experiment.

The difficulties and inaccuracies associated with measuring rising and falling velocities in a Millikan system have motivated several adaptations of the Millikan chamber, which may be classified as electrostatic and electrodynamic balances.

Electrostatic Balances

The Millikan chamber is, of course, an electrostatic balance in which a charged droplet is suspended in the electric field $E$ between plates a distance $2z_0$ apart. If the buoyant force on the droplet of mass $m$ and charge $q$ is negligible, a force balance on the droplet gives

$$mg = qE = qV/2z_0,$$

where $V$ is the potential difference between the plates. For the flat plate configuration of the Millikan chamber the electrical field is uniform in any horizontal plane between the electrodes. Consider droplets A and B shown in Figure 5. If the droplets have the same mass-to-charge ratio, both droplets can remain suspended if the electric field intensity satisfies Eq. (51). If a small beam of light now passes horizontally through the center of the chamber, only a particle located in the center, say, particle A, will be illuminated by the beam. To ensure that a particle will be positioned at the center of the chamber, it is necessary to modify the apparatus to provide radial and vertical focusing. The devices that have been developed to do this electrostatically are the subject of this section.

Gucker and Egan (1961) developed an instrument to measure the angular variation of light scattered from single aerosol droplets and used it to compare Mie theory with experiments on DOP droplets of about 1 μm radius. A simplified drawing of their apparatus is shown in Figure 6. A polarized light beam entered on side of an enclosed Millikan condenser, and a Rayleigh horn opposite the inlet port trapped the light, preventing backscattering. A window was inserted on one side of the chamber to permit scattered light to be detected by a photometer system that rotated in the horizontal plane. The scattered light was reflected downward to a photomultiplier tube by means of a mirror in the photometer head.

Fletcher's (1914) technique for centering the droplet was used. A small insulated disk was inserted in the center of the top plate. When a droplet drifted off center, the two electrostatic plates were grounded, the disk was electrified, and the droplet was attracted to the centerline. The electric field between the plates was then

FIGURE 5. A simplified diagram of the Millikan condenser.
switched on and the droplet rebalanced. This manually operated feedback system worked well enough for Gucker and Egan to obtain light scattering profiles (intensity versus angle) in reasonably good agreement with Mie theory.

Wyatt and Phillips (1972) developed and commercialized an improved version of Gucker and Egan’s electrostatic balance, the Science Spectrum Inc. Differential II light scattering photometer. The key improvements were the use of an electronic feedback system to balance the charged particle automatically and the incorporation of a laser light source. An exploded view of the Differential II light scattering chamber is shown in Figure 7. Wyatt and Phillips replaced the upper plate electrode of the Millikan chamber with a charged pin, and they grounded the lower plate, thereby maintaining an electrical field that focused the charged particle on the vertical axis of the cell. Vertical centering was accomplished by means of a pin-voltage control system that monitored the particle’s position by detecting the scattered light, which was split by the edge of a mirror, with two phototubes. The ratio of the current from these photodetectors was processed by a log-ratio amplifier and used to change the pin voltage to maintain the particle at the center of the cell. Arnold’s (1979) version of this feedback system is shown in Figure 8.


FIGURE 7. The electrostatic balance and light scattering cell of Wyatt and Phillips (1972).

The Differential II instrument has been used by several investigators for studying light scattering from single particles. Wyatt and Phillips (1972) reported measured intensity profiles for single atmospheric haze particles, bacterial cells, spores, and polystyrene latex (PSL) spheres, and more recently Wyatt (1980) measured the complex refractive index for fly ash particles by comparing the light scattering profiles with Mie theory. Cooke and Kerker (1973) used a Differential II for comparing PSL light scattering with Mie theory, and Davis and Chorbajian (1974) adapted the instrument to measure the evaporation rates of single DOP droplets. Additional light scattering studies were reported by McRae (1982), who determined the refractive index of cigarette smoke droplets, by Marx and Mulholland (1982), who also used the Differential II for measuring the refractive index and size of PSL particles, and by Pluchino et al. (1980). The latter investigators determined the complex refractive index of micron-sized carbon particles using an electrostatic balance they built based on the Wyatt and Phillips design.

The Davis and Chorbajian study of the dynamics of aerosol evaporation using light scattering to follow the size change was con-
Transport with Single Aerosol Particles

continued and expanded upon, as will be seen shortly. Tang and Munkelwitz (1978) also used a Science Spectrum Inc. instrument to investigate particle dynamics. They exposed a suspended particle of NaCl to an aqueous solution of saturated \((\text{NH}_4)_2\text{SO}_4\), and they recorded the light scattering profile as the dry particle transformed into a solution droplet and then grew to its equilibrium size. They showed that the dry NaCl aerosol particle had a light scattering pattern very similar to the Mie theory predictions for a sphere with a diameter equal to the equivalent diameter of the particle.

A novel and very significant application of the electrostatic balance was introduced by Arnold (1979) based on Pope's (1962) determination of the photoionization potential of a suspended particle. Arnold's apparatus, shown in Figure 8, was a Millikan chamber coupled with the Wyatt split-beam feedback circuit, which he developed to measure particle mass and charge with high precision. Using Fletcher's method to center the particle in a vertical laser beam, he balanced a particle with charge \(q_i\) with \(V_i\) applied to the lower plate. Then he exposed the particle to UV radiation to eject one electron, thereby leaving the particle with charge \(q_{i+1}\). Next he rebalanced the particle by changing the voltage to \(V_{i+1}\). From Eq. (51) we may write

\[ \pm e = q_{i+1} - q_i = mg2z_0(1/V_{i+1} - 1/V_i), \]

where \(\pm e\) refers to a positive particle and \(-e\) to a negative one. Thus, the mass is given by the simple equation

\[ m = \frac{e}{2z_0 g} \left( \frac{1}{V_{i+1}} - \frac{1}{V_i} \right). \]  

(53)

The apparatus developed by Arnold was adapted by Arnold et al. (1980) to measure the photophoretic force on a micron-sized particle. For their photophoretic spectrometer they encased the Millikan condenser in a vacuum chamber and made direct measurements of the ratio of the photophoretic force \(F_p\) to the particle weight in milligrams. They reported the action spectrum \((F_p/\text{mg} \text{versus wavelength})\) for Cds in air at a chamber pressure of 11.7 kPa, and they measured \(F_p/\text{mg}\) as a function of Knudsen number.

Evaporation Studies with the Electrostatic Balance

Davis and Chorbajian (1974) were the first investigators to attempt transport process measurements with the electrostatic balance of Wyatt and Phillips, and they were able to estimate the diffusivity of DOP in N\(_2\) using the integrated form of Maxwell's equation and estimates of the vapor pressures of DOP at room temperature from the literature. Setting \(p_i = 0\) in Eq. (9) and
integrating, the evaporation law they used is obtained:
\[ a^2 = a_0^2 - S_{ij}(t - t_0), \]  
where \( S_{ij} = 2D_{ij} \rho_i/\rho_j RT \) and \( a_0 \) is the droplet radius at time \( t_0 \). The radius as a function of the time was obtained by making several light scattering measurements during the course of the evaporation. Typical light scattering data obtained in similar work by Davis and Ray (1977) are shown in Figure 9, where the best fit Mie theory results are also plotted. A plot of \( a^2 \) versus \( t - t_0 \), then, should yield a straight line with slope \( -S_{ij} \); from measurement of the slope, \( D_{ij} \) can be calculated with knowledge of the vapor pressure. The vapor pressure of DOP is extremely low at room temperature, so the data available to Davis and Chorbajian from the literature were unreliable. Thus, the corresponding diffusivities calculated by them are not highly accurate.

Davis and Ray (1977) and Davis et al. (1979) resolved the problem of measuring both the diffusivity and the vapor pressure from a set of evaporation experiments, and they were able to determine Lennard–Jones parameters as well. This was accomplished by measuring the evaporation rates of a species \( i = 1 \) in three different carrier gases \( j = 2, 3, 4 \) at the same temperature at atmospheric pressure (in the continuum regime). From the experimentally determined slopes \( S_{12}, S_{13}, \) and \( S_{14} \) and from the definition of \( S_{ij} \), they obtained the following pairs of slope ratios:
\[ S_{12}/S_{13} = D_{12}/D_{13}, \]  
\[ S_{12}/S_{14} = D_{12}/D_{14}. \]  
(55)  
(56)

Note that the vapor pressure cancels out by using the ratios. Now with the Chapman–Enskog equation, Eq. (21), for \( D_{ij} \), Eq. (55) becomes
\[ S_{12}/S_{13} = \frac{1 + z_{12} \Omega^{(1)}_{13} \sigma_{13}^2}{1 + z_{13} \Omega^{(1)}_{13} \sigma_{13}^2}, \]  
and a similar equation applies for \( S_{12}/S_{14} \) where \( z_{ij} = m_i/m_j \) and \( \Omega^{(1)}_{ij} \) is a function of \( kT/\epsilon_{ij} \).

Using the following combining rules for \( \epsilon_{ij} \) and \( \sigma_{ij} \) there results two equations of the form of Eq. (57) in the two unknowns \( \sigma_{ij} \) and \( \epsilon_{ij} \). For the common light gases used by Davis and his colleagues (He, N2, and CO2) the values of \( \sigma_{ij} \) and \( \epsilon_{ij} \) have been tabulated by Hirschfelder et al. (1954).

Once \( \epsilon_{ii} \) and \( \sigma_{ii} \) have been determined by solving the two equations, \( D_{ij} \) is calculated from Eq. (21), and finally \( p_i^v \) is calculated from the definition of \( S_{ij} \) and its measured value.

In this manner Davis et al. determined the Lennard–Jones parameters \( \sigma_{ii} \) and \( \epsilon_{ii} \), diffusivities, and vapor pressures of DBP, DOP, and DBS. Table 3 summarizes their results, and
Table 3. Diffusivities (at 298 K and 1 atm) and Lennard-Jones Parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parameter</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOP</td>
<td>$\sigma_H = 10.12 , \text{Å}$</td>
<td>0.916 Å</td>
</tr>
<tr>
<td>DOP</td>
<td>$\epsilon_H/k = 622.2 , \text{K}$</td>
<td>58.1 K</td>
</tr>
<tr>
<td>DOP–He</td>
<td>$D_H = 13.2 \times 10^{-6} , \text{m}^2/\text{sec}$</td>
<td></td>
</tr>
<tr>
<td>DOP–N$_2$</td>
<td>$D_H = 3.08 \times 10^{-6} , \text{m}^2/\text{sec}$</td>
<td></td>
</tr>
<tr>
<td>DOP–CO$_2$</td>
<td>$D_H = 1.98 \times 10^{-6} , \text{m}^2/\text{sec}$</td>
<td></td>
</tr>
<tr>
<td>DBS</td>
<td>$\sigma_H = 9.328 , \text{Å}$</td>
<td>1.01 Å</td>
</tr>
<tr>
<td>DBS</td>
<td>$\epsilon_H/k = 664.5 , \text{K}$</td>
<td>76.3 K</td>
</tr>
<tr>
<td>DBS–He</td>
<td>$D_H = 13.6 \times 10^{-6} , \text{m}^2/\text{sec}$</td>
<td></td>
</tr>
<tr>
<td>DBS–N$_2$</td>
<td>$D_H = 3.02 \times 10^{-6} , \text{m}^2/\text{sec}$</td>
<td></td>
</tr>
<tr>
<td>DBS–CO$_2$</td>
<td>$D_H = 1.95 \times 10^{-6} , \text{m}^2/\text{sec}$</td>
<td></td>
</tr>
<tr>
<td>DBP</td>
<td>$\sigma_H = 9.782 , \text{Å}$</td>
<td>1.10 Å</td>
</tr>
<tr>
<td>DBP</td>
<td>$\epsilon_H/k = 695.0 , \text{K}$</td>
<td>97.7 K</td>
</tr>
<tr>
<td>DBP–N$_2$</td>
<td>$D_H = 3.67 \times 10^{-6} , \text{m}^2/\text{sec}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Determined by Davis and Ray (1977) and Davis et al. (1979) by droplet evaporation in the electrostatic balance.

Figure 10 compares the vapor pressures with previously published data. We note that this technique can be used to determine vapor pressures more than five orders of magnitude lower than can be determined by conventional techniques. Furthermore, Lennard–Jones parameters for relatively large molecules can be obtained. Ravindran et al. (1979) compared their results with available estimating procedures for Lennard–Jones parameters and diffusivities.

Davis and his graduate students also carried out a series of investigations on evaporation in the Knudsen aerosol regime. Chang and Davis (1976) operated the electrostatic balance at subatmospheric pressures ($6.80 \leq P \leq 101.3 \, \text{kPa}$) to study DOP evaporating into N$_2$. The Knudsen numbers for their experiments were in the range $0.014 \leq \text{Kn} \leq 0.32$ for droplets in the range $0.3 \leq a \leq 0.6 \, \mu\text{m}$. Davis et al. (1978) reworked the data analysis to take into account new results for the diffusivity and vapor pressure of DOP.

Davis and Ray (1978) performed more carefully controlled measurements using DBS in N$_2$, and they compared their mass flux results as $J/J_K$ with the equations of Fuchs, Fuchs and Sutugin, and others and with Loyalka’s (1973) tabulated results. The apparent agreement among these equations and the data is misleading and fortuitous because Davis and Ray attempted to reconcile the mean free path relations in use. The result was a shift of the abscissa for the graphs of $J/J_K$ versus Kn. More appropriate comparisons made by Davis et al. (1980) show that the equations based on $z < 1$ do not agree with the data for DBS/N$_2$ ($z = 11.22$).

The evaporation rate data for DOP–N$_2$ and DBS–N$_2$ obtained at various total pressures fall on straight lines on a Monchick–Reiss plot, $(da/dt)^{-1}$ versus $aP$. From the intercept at $aP = 0$ for the DOP data and using Eq. (49) together with the vapor pressure reported here, we calculate $\beta = 0.96$. For DBS Davis and Ray (1978) calculated $\beta = 1.07$. Thus, we conclude that $\beta$ is the order of unity for these experiments. The experimental uncertainty is approximately $\pm 10\%$. We should point out that the vapor pressure correction for the Kelvin effect was less than $3\%$ for the droplets used.

We have reexamined the raw data of Davis et al. (1978) to calculate $J/J_c$. Figure 11 shows the data for DOP–N$_2$ and results calculated using the Sitarski–Nowakowski equation, Eq. (37). At intermediate Knudsen numbers, theory and experiment agree very well. Davis et al. (1980) proposed a modification of Eq. (37) to take into
account the collision integral $\Omega_{ij}^{(1,1)}$ in the continuum limit, and their modified equation is in excellent agreement with the data for DBS–N$_2$.

The use of the electrostatic balance together with light scattering has made it possible to perform elegant and fairly precise experiments related to aerosol transport processes, but there are severe limitations associated with it. For relatively rapid processes and for particles smaller than about 0.5 $\mu$m diameter, the feedback system that controls the electric field can lead to oscillations and loss of the particle. A better tool is available for a wider range of conditions, and that is the electrodynamic balance.

**Electrodynamic Balances**

The electrodynamic balance evolved from the electric mass filter of Paul and Raether (1955); it differs from the electrostatic balance in that there are three electrodes used, and both ac and dc fields are applied. Perhaps the simplest version of the device is that of Straubel (1956), and an improved version (Straubel, 1959) is

**FIGURE 10.** The vapor-pressure results of Ray et al. (1979; filled symbols) and their proposed correlating equations compared with data from the literature (open symbols); for DOP (triangles), DBS (circles), and DBS (squares).

**FIGURE 11.** A comparison between the Sitarski–Nowakowski equation (——) for $\beta = 1$ and the experimental flux data of Davis et al. (1978) for DOP evaporating in N$_2$ (chamber pressures: $\circ$, 101.3 kPa; $\Delta$, 33.6 kPa; $\times$, 19.5 kPa; $\square$, 8.3 kPa; $+$, 6.8 kPa).
illustrated in Figure 12. An ac potential is applied to the ring electrode, and a dc field is maintained between the disk electrodes. In the absence of the dc field and viscous forces, a charged particle will oscillate about a point on the centerline somewhat below the midplane between the disks. Viscous damping stabilizes the motion, and the dc field is then used to move the particle to the midplane.

Ataman and Hanson (1969) and Schweizer and Hanson (1971) used Straubel’s design to investigate droplet breakup associated with the Rayleigh limit of charge. Their study indicates that some charge is lost during the evaporation process leading to the Rayleigh limit, and the charge-to-mass ratio at breakup was found to agree very well with the Rayleigh limit.

In their study of the stability of charged droplets, Berg et al. (1970) examined several variations of the electrodynamic balance, and the two principal configurations are shown in Figure 13. They suspended relatively large drops, 100–250 µm diam, using a Dynafax camera for size measurement. A sudden loss of mass and charge was observed to occur at the Rayleigh limit, but they were the first to observe instabilities corresponding to metastabilities predicted by Cahn (1962).

A more sophisticated electrodynamic balance of the Straubel three electrode type was developed and its dynamics analyzed by Wuerker et al. (1959). This balance has become of considerable interest to aerosol scientists in the past few years. An exploded view of the device built by Davis and Ray (1980) for installation in the Science Spectrum photometer is shown in Figure 14.

The device has hyperbolic electrode surfaces for more favorable stability characteristics, and these surfaces are described by the equation

\[ z^2 - \frac{1}{2} r^2 = \begin{cases} \frac{z_0^2}{r_0^2} & \text{for the endcaps,} \\ -\frac{z_0^2}{r_0^2} & \text{for the ring,} \end{cases} \]  \hspace{1cm} (60)

where \(2z_0\) is the distance between the endcap

**FIGURE 12.** Straubel’s (1959) electrodynamic balance.

**FIGURE 13.** Two of the electrodynamic balance configurations of Berg et al. (1970).
The electrodynamic balance of Davis and Ray (1980).

The evaporation rate data of Davis and Ray (1980) for DBS droplets in N₂, obtained with the picobalance (o) and light scattering (Δ), compared with diffusion theory (—).
electrodes at \( r = 0 \), the centerline. The circuitry for the ac and dc fields is essentially that of Straube (1959), shown in Figure 12, except that dc power supplies replace the batteries, and a variable frequency ac source replaces the regular line source.

Wuerker et al. solved the equations of motion for a charged particle suspended in the electric fields and analyzed the stability characteristics of the device. A more comprehensive treatment of both bihemispheric and bihyperbolic electrode configurations was provided by Frickel et al. (1978), who constructed and experimented with instruments of both types. Rubel (1981, 1982) used their bihyperbolic balance for his studies of multicomponent evaporation. Frickel et al. were primarily interested in comparing the two electrode configurations and determining the stability boundaries of the instruments, but they did some experiments on evaporating glycerine droplets with initial diameters of about 100 \( \mu \)m.

Blau et al. (1970) used an electrodynamic balance of the Wuerker et al. type to measure the light scattering intensity functions of DOP, phenyl methyl siloxane, and pentaphenyl ether over the size range 7.5–110 \( \mu \)m diam. Their data were shown to be in good agreement with Mie theory.

Davis and Ray (1980) used the picobalance, designed to operate in the picogram range, to measure the evaporation rates of DBS in \( \text{N}_2 \). They carefully tested the balance by making simultaneous measurements of the dc voltage required to maintain the droplet at the center of the chamber and the light scattering profiles. Figure 15 shows a comparison among the droplet radius history measured by light scattering, that calculated from the droplet mass measured by means of the picobalance, and the predictions from diffusion theory, Eq. (54). The results are in good agreement.

Recently Davis and Ravindran (1982) used the picobalance to measure the real and imaginary components of the refractive index of PSL particles, liquid droplets, and dust particles generated in solar furnace experiments performed to simulate thermonuclear explosions.

Philip et al. (1982) combined the electron-stepping method of Arnold (1979) with the bihyperbolic electrode balance to provide an exciting new method for the measurement of single aerosol particle mass. This development makes it possible to apply the electrodynamic balance to the study of aerosol chemical reactions involving either solid or liquid particles.

Work on single aerosol chemical reactions has been performed by Richardson (1982) very recently. He used Davis's technique of combining the electrodynamic balance with laser light scattering facilities, and he has studied the decomposition of \((\text{NH}_4)_2\text{SO}_4\) under high vacuum in his apparatus.

Other Techniques

Two methods for the study of single small particles have been developed, and these are based on electromagnetic and electrooptic suspension, respectively. Beams (1950) suspended a magnetic sphere (a 100 \( \mu \)m diam steel ball) in a magnetic field using a feedback control circuit to stabilize the position of the particle in the suspension chamber. The feedback circuit controlled the voltage to a solenoid to position the rotating sphere, and he measured rotational speeds of the order of \( 10^6 \) Hz.

Ashkin and Dziedzic (1975, 1977) employed the circuit damping feedback concept of Beams in their optical levitation apparatus, a simplified diagram of which is shown in Figure 16. They demonstrated the suspension by photophoretic forces of spheres of the order of 10 \( \mu \)m diam. A split photodiode detector was used to detect the particle position (height). Where Wyatt and Phillips (1972) used a log-ratio amplifier in their electrostatic balance, Ashkin and Dziedzic used a difference amplifier to amplify the error signal from the split photodiode. The signal was then processed to control the laser beam intensity which levitated the particle. The feedback system was equipped with an error signal differentiator and amplifier so that Beam's error rate damping could be included. The derivative voltage and the error voltage were added to provide the control of the vertical oscillations.

They found that the vertical damping also damped horizontal oscillations due to the converging–diverging beam shape. This device can be used to measure the photophoretic force on a particle with high precision.

CONCLUSIONS AND COMMENTS

The theoretical state of aerosol physics is well developed, particularly where heat and mass transport phenomena can be decoupled. The quasi-steady-state approximation still remains the basis for much theoretical analysis, but it must be questioned when transport processes are rapid and coupled such as in combustion processes.

In the past decade there have been numerous advances in the development of equipment for the study of aerosol physics and aerosol chemistry. The electrostatic, electrodynamic, and electro-optic balances have all reached a sophisticated level of design and reliable operation. There has been a rather recent expansion of interest in the electrodynamic and electrostatic balances, and it is to be expected that further improvements will ensue.

With these new and revitalized experimental tools, it will be possible to investigate in the laboratory many areas of aerosol physics, chemistry, and transport phenomena that have been limited to theoretical analysis.

REFERENCES


