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CHARACTERISTICS OF AGGLOMERATES OF SODIUM OXIDE AEROSOL PARTICLES

Task 7

Topical Report

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Report Date: August 1, 1977

PREPARED FOR THE U. S. NUCLEAR REGULATORY COMMISSION
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CHARACTERISTICS OF AGGLOMERATES OF SODIUM OXIDE AEROSOL PARTICLES

by

J. A. Gieseke, L. D. Reed,
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INTRODUCTION

Accurate macroscopic predictions of aerosol population behavior within enclosed containments are known to depend strongly upon the microscopic characteristics of the individual particles comprising the population. For example, particle shapes and densities have pronounced effects on the settling velocities of individual aerosols. Also, coagulation rates due to mechanisms which produce relative motions between particles within the suspended aerosol are known to depend upon the cross sectional areas of the individual particles. Hence, it has been the primary concern of this study to examine experimentally the microscopic characteristics of sodium oxide aerosols produced in air. The results of these measurements can now be incorporated into the various macroscopic aerosol behavior prediction models.

Experimental studies of sodium oxide aerosols in air are, however, inherently complicated by the extreme reactivity of sodium with the minute amounts of moisture and carbon dioxide normally present in air. Thermodynamic analyses indicate that at temperatures above 1300 F, sodium oxides are unstable and decompose. Previous studies^(1,2) indicate flame temperatures in excess of 1600 F above sodium pool fires. Hence, from a mechanistic point of view, it appears that sodium oxides are formed in cooler regions away from the flame as the sodium vapors cool. In fact, the peroxide has been produced industrially by simply burning sodium in excess amounts of air and collecting the resulting smoke⁽³⁾. The product was well in excess of 90 percent Na₂O₂. From studies of the vapor phase reaction mechanisms at about 500 F, it appears that the superoxide is initially formed:

It has further been suggested that the superoxide then reacts with additional sodium and condenses on available surfaces to form the peroxide:

and

These reactions are complicated by the presence of small amounts of water. In the sodium vapor region of the flame, the sodium may react with the water to form sodium hydroxide and hydrogen:

In regions of the flame about 610 F, a secondary reaction is also probable:

In addition to these reactions, the sodium peroxide may form a series of hydrates. The process is apparently slow but if enough moisture is present and in the absence of CO_2 , a stable octahydrate will be formed, $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$. At slightly elevated temperatures the octahydrate may react with its own water of hydration to form the hydroxide and release oxygen:

Since little is known about the kinetics of these processes, it is not possible to quantitatively predict relative amounts of these species which may comprise individual aerosol particles. However, some qualitative aspects concerning the aerosol formation can be pointed out. Since reactions (4), (5), and (6) all involve the evolution of gases, and reactions (4) and (5) may occur at elevated temperatures and involve the formation of solid products from liquid reactants, it should be no surprise to find porous sodium oxide aerosol formations and possibly hollow-gas-filled particles. Indeed, in the experimental measurements of aerosol densities which are to be described, none approached the theoretical density of sodium monoxide (2.27 g/cm^3), sodium peroxide (2.81 g/cm^3), or sodium

hydroxide (2.13 g/cm^3). Even the smallest particles examined were observed to possess reduced densities.

EXPERIMENTAL APPARATUS

The experimental apparatus used for measuring agglomerate characteristics was composed of two major sections: a sodium oxide aerosol generation system and a Millikan-thermal cell in which the actual measurements on the aerosol particles were performed. The aerosol generation system was chosen to simulate on a small scale the production of sodium oxide aerosols in a sodium pool fire and the Millikan-cell apparatus was chosen for performing measurements because thermal forces as well as agglomerate physical properties could be determined. In addition to the Millikan-thermal cell, agglomerate properties were further characterized through electron microscopy using the aerosols sampled by a new aerosol sampler.

Aerosol Generation System

In the aerosol generation system, sodium was heated well above its melting point (to about 500 C) in a small crucible and under an inert gas atmosphere. Aerosols were then formed by burning this small molten sodium pool as air was introduced into the combustion zone. The sodium oxide aerosol was then directed into a variable volume mixing chamber where agglomerates at various stages in their coagulation aging process were selectively introduced to the Millikan cell apparatus. The system is designed for nominal mass concentrations up to approximately $100 \text{ } \mu\text{g/cc}$, and sodium oxide aerosols over a wide size range were examined.

Millikan-thermal Cell

The actual measurements that were performed on the individual sodium oxide aerosols were done with the Millikan-thermal cell. The

Millikan cell apparatus has a space of adjustable height between two parallel, horizontal plates where the particles were observed. An electrical field can be formed between the plates to facilitate handling of the particles and also to allow accurate measurements of required balancing forces in various phases of the experiment. Furthermore, a well-defined temperature gradient can be produced in the air gap by heating the upper plate and cooling the lower, thus allowing precise measurements of the thermal forces on suspended sodium oxide agglomerates. The space between the plates can be maintained at various pressures so that gas mean free path effects may also be studied.

The Millikan-thermal cell in which the measurements on the sodium oxide agglomerates were performed is similar in design to those used by previous investigators. The cell was made entirely of brass with two threaded end pieces which allow easy access to the actual measuring chamber. Chromel-alumel thermocouples were attached to each cell face. The cell faces are parallel with a 3.505-mm maximum space between them. The faces have diameters of 31.7 mm. A cross-sectional drawing of the Millikan-thermal cell is provided as Figure 1.

The mean free path of the gas in the thermal cell was varied with a vacuum pump. Pressures as low as 250 mm Hg may be created in the cell. The pressure in the cell was measured with a mercury manometer with one branch open to the atmosphere. All other pressure measurements in the system were made with test and standard pressure gages. Filters which are 99.98 percent efficient at collecting $0.3\text{ }\mu\text{m}$ particles were used throughout the system.

Aside from the Millikan cell, the system is of completely stainless steel construction with quartz glass eyepieces and is designed for maximum pressures of approximately 3.0 atmospheres. The combustion chamber has a nominal volume of 500 cm^3 and the mixing chamber consists of two end sections with volumes of 276 cm^3 and four midsections having volumes of 285 cm^3 each. Hence, the mixing chamber volume may be varied from 552 cm^3 to $1,694\text{ cm}^3$. A flow diagram of the entire experimental system is shown in Figure 2 and a photograph of the apparatus is shown in Figure 3.

FIGURE 1. MILLIKAN CELL APPARATUS

FIGURE 2. FLOW DIAGRAM FOR SODIUM OXIDE AGGLOMERATE BEHAVIOR EXPERIMENTS

FIGURE 3. APPARATUS FOR MEASURING SODIUM OXIDE AGGLOMERATE CHARACTERISTICS

The electromotive forces of the thermocouples on the cell faces were measured on a strip chart recorder. All other thermocouple readings were made with a digital indicator which is accurate to ± 1 degree Celsius in the range from -133 C to 1400 C. To provide balancing forces in the thermal cell an electrical potential was applied across the parallel faces with a high voltage supply which has a range of 0 to 1200 volts in steps of 0.10 volts. The light scattered from the aerosol particles was visible through a long focal length (50 X) microscope.

Improved Aerosol Sampler

A new aerosol sampler has been developed and was used for sampling sodium oxide particles for electron microscopy. This sampler is capable of sampling the particles and maintaining them without exposure to undesirable atmospheres such as laboratory air during transfer to an electron microscope. Concepts involved in developing the sampler, design features, and operating procedures can be described as follows.

In the past, electrostatic precipitators and/or thermal precipitators have been widely adopted for aerosol sampling due to their simplicity of design and ease of operation. While both types of precipitators are adequate for many purposes, these conventional methods suffer from the major disadvantage that they do not prevent sample exposure to undesirable ambient atmospheres containing water vapor or reactive gases when microscopy is used for analyzing the samples. In the present sampler, the aerosol is first sampled using conventional thermal precipitation techniques and then maintained in the same atmosphere until the sample is coated in a vacuum for electron microscopy or placed into the microscope from a controlled atmosphere at the loading point. Figure 4 is a schematic diagram of the present sampler. The sampler consists of an aerosol sampling section and sample handling section as shown in the figure.

The aerosol sampling section is similar to the conventional thermal precipitator except in its new configuration. Aerosol particles are introduced into the aerosol inlet port located perpendicular to the

FIGURE 4. SCHEMATIC DIAGRAM OF THE NEW AEROSOL SAMPLER

plane of the figure and subsequently precipitated on an electron microscope grid by thermal forces. A standard automobile cigarette lighter which is heated electrically provides the heat source and is attached to a metal disk of 2 cm diameter. The temperature of the lighter used was measured to be about 500 C at an applied 12 volts. The electron microscope grid is placed on top of the piston which is a part of the sample handling section described below.

The sample handling section is comprised of the piston which holds the microscope and a cylinder having one end closed with a pressure release valve. Upon completion of sampling in the aerosol sampling section, the piston is slid into the cylinder until the sample is hermetically sealed by O-rings from external influences. During this procedure, it is necessary to keep the pressure release valve at the end open such that a part of air in the rear end can escape the cylinder until the piston stops. The stopping position can be adjusted by the valve stem as shown in the figure. The valve is then closed tightly. It should be noted that the sample particles are retained in their original atmosphere. Finally, the handling section or inner cylinder containing the piston is removed from the sampling section for transporting.

If the sample is to be coated prior to viewing in the electron microscope, the handling section is placed in the bell jar of the vacuum coating apparatus. As air in the bell jar is evacuated, the piston is gradually impelled from the cylinder by the trapped residual gas at the rear of the cylinder. The vacuum needed to move the piston and thus to expose the sample, is determined by the O-ring friction. The particular unit built for this study was found to expose the sample at about 4 inches Hg. Once the aerosol particles are coated, they can be freely handled and inserted into an electron microscope for examination.

EXPERIMENTAL TECHNIQUES

In order to ascertain the aerodynamic behavior of agglomerated sodium oxide aerosols, several detailed measurements were performed in the Millikan-thermal cell. The aerodynamic experimental measurements were divided into two categories. The first category involves experiments in which spherical sodium oxide particles were examined. The results from these measurements provide basic information required for direct analyses of results obtained from the second category of experiments in which agglomerates were examined.

Small Particle Measurements

In the first category of experiments, sodium oxide aerosols were produced in a manner such that large numbers of primary aerosol particles were created. A small amount of sodium was burned in a large auxiliary combustion chamber ($1.91 \times 10^5 \text{ cm}^3$) and air was passed directly over the burning sodium to disperse the oxide aerosol cloud immediately. Electron micrographs indicate that spherical primary particles were indeed created in this process. Typical electron micrographs are depicted in Figure 5.

Following the introduction of the spherical sodium oxide aerosol particle into the Millikan-thermal cell, several measurements were performed. Initially, a vertical electric field was established in the cell which either opposed or assisted the downward directed gravitational force on the particle. If it opposed the gravitational force, a sufficient voltage gradient was applied so that the particle rose in the electric field and its rise velocity was recorded. The field was then reversed and the particles' fall time was measured. The difference in the particles' rise and fall velocities may be directly related to its mass. The number of charges on the aerosol was then altered by radiation ionization of the surrounding gas. Rise and fall velocity measurements were again performed. After several charge variations and rise and fall velocity measurements, it was possible to deduce exactly the number of charges on

FIGURE 5. SODIUM OXIDE AEROSOLS PRODUCED IN THE AUXILIARY COMBUSTION CHAMBER

the aerosol corresponding to each rise-fall combination. The rise and fall velocities were measured at several pressures in order to determine the Knudsen number dependence of the particle mobility.

The primary objective of the measurements on the small, spherical sodium oxide aerosol particles was to permit an accurate estimate of the first order slip correction factor for the sodium oxide-air particle material-gas combination. For spherical aerosols, the slip correction may be written to first order as

$$C = 1 + C_m \lambda/R , \quad (7)$$

where C is the slip correction to Stokes law, C_m a dimensionless constant dependent only upon the gas and aerosol particle material, λ the mean free path of the gas, and R the sphere's radius. When, at a given pressure p_1 , an electric field of sufficient magnitude to raise the particle against the force of gravity is established, a steady motion of the particle results as the electrical force on it is just balanced by the gravitational and drag forces. Accordingly, the following equation describing the particle motion applies:

$$\frac{neV}{S} - \frac{6\pi\mu R U_{r1}}{1 + C_m \lambda_1/R} - mg = 0 . \quad (8)$$

Here n is the number of electronic charges e on the aerosol particle, V the applied potential difference, S the plate spacing, m the particle's mass, U_{r1} the rise velocity at pressure p_1 , λ_1 the mean free path of the gas at pressure P_1 , and g the gravitational acceleration. Similarly, when the field is reversed the electrical and gravitational forces are balanced by the drag force and the following equation results:

$$\frac{neV}{S} - \frac{6\pi\mu R U_{f1}}{1 + C_m \lambda_1/R} + mg = 0 . \quad (9)$$

Here U_{f1} is the falling velocity of the particle at pressure p_1 . We note at this point that Equations (8) and (9) contain three unknown quantities: R , m , and C_m . An additional independent equation is supplied when either a rise or a fall velocity at a new pressure, p_2 , is determined

For a rising particle, Equation (8) is rewritten for pressure p_2 :

$$\frac{\text{neV}}{S} - \frac{6\pi\mu R}{1 + C_m} \frac{U_{r2}}{\lambda_2/R} - mg = 0 , \quad (10)$$

where U_{r2} is the measured rise velocity at pressure p_2 and λ_2 the corresponding mean free path of the gas.

These three equations yield the following expressions for the three unknown quantities, m , R , and C_m :

$$m = \frac{\text{neV}}{gS} \frac{(U_{f1} - U_{r1})}{(U_{f1} + U_{r1})} , \quad (11)$$

$$R = \frac{\text{neV}(\lambda_2/\lambda_1 - 1)}{3\pi\mu S(U_{r1} + U_{f1})(\lambda_2/\lambda_1 - U_{r2}/U_{r1})} \quad (12)$$

and

$$C_m = \frac{R}{\lambda_1} \left[\frac{U_{r2}/U_{r1} - 1}{\lambda_2/\lambda_1 - U_{r2}/U_{r1}} \right] . \quad (13)$$

Furthermore, knowledge of R and m from the equations above permits an equivalent spherical mass density, ρ , to be calculated. Accordingly,

$$\rho = \frac{3}{4\pi} \frac{m}{R^3} . \quad (14)$$

Results for several sodium oxide aerosol particles are presented in Table 1. The average slip coefficient was found to be 1.37 for the sodium oxide aerosol in air. It is interesting to note the observed reduced densities for these small spherical particles. Their values tend to corroborate the qualitative chemical reaction kinetics discussed in the introduction.

Large Aerosol Aerodynamic Measurements

After its introduction into the modified Millikan cell apparatus, a single large sodium oxide aerosol particle was initially balanced in an applied electric field. The electric potential difference required to

TABLE 1. RESULTS OF SLIP COEFFICIENT MEASUREMENTS

Particle Number	Particle Radius, μm	Slip Coefficient, C_m	Particle Density, g/cm^3
1	0.244	1.501	0.806
2	0.254	1.743	0.781
3	0.364	1.190	0.746
4	0.181	1.374	1.334
5	0.302	1.703	0.753
6	0.296	1.545	0.821
7	0.268	1.117	0.743
8	0.372	1.088	0.483
9	0.321	1.125	0.239
10	0.241	1.013	0.867
11	0.309	1.410	0.683
12	0.291	1.358	1.031
13	0.289	1.408	1.180
14	0.292	1.384	1.194
15	0.303	1.598	1.108
16	0.305	1.189	1.269
17	0.334	1.590	0.999
Averages:		1.37	0.88

just balance the particle is indirectly proportional to the number of charges on the particle and was recorded. The charge on the particle was then altered by radiation ionization of the suspending gas and the balancing procedure repeated. The required balancing potential difference was again recorded and because of its proportionality relationship to the number of charges on the particle, the following ratio results:

$$\frac{n_1}{n_2} = \frac{V_2}{V_1} , \quad (15)$$

where the subscripts indicate different charge states. Since the n_i must be integers, it is possible after several charge alterations about neutral, to deduce exactly the number of charges on the particle at each balancing potential difference. In each case the gravitational and electrical forces on the aerosol particle were just balanced so that the following force balance expression describing each case may be written

$$mg - \frac{neV_B}{S} = 0 , \quad (16)$$

where V_B is the balancing potential difference.

Following the balancing procedure, the aerosol particle was permitted to settle in the absence of any applied forces other than gravity. The time for the particle to fall over a prescribed distance was measured. In this steady state situation the gravitational force is just balanced by the drag force on the particle. Employment of the Stokes drag expression corrected for gas slippage at the particle-gas interface yields the following force balance expression

$$mg - \frac{6\pi\mu R U_s}{1 + C_m \lambda/R} = 0 \quad (17)$$

where U_s is the measured settling velocity. The assumption of spherical particles is implicit in this form of the Stokes drag expression and appears to be reasonable for the tightly packed sodium oxide aerosol particles. This assumption has been generally verified by numerous electron microscope viewings of deposited agglomerates.

Solution of Equations (16) and (17) for the particle mass and radius yields the following results

$$m = \frac{neV_B}{Sg} \quad (18)$$

and

$$R = \frac{neV_B}{12\pi\mu U_S S} \left(1 + \sqrt{1 + \frac{24\pi\mu U_S S C_m \lambda}{neV_B}} \right) . \quad (19)$$

The particle density is therefore

$$\rho = \frac{3m}{4\pi R^3} . \quad (20)$$

The results of these measurements are depicted in Figure 6.

Comparisons with Previous Studies

Agglomerate behavior of aerosol materials other than sodium has been the subject of considerable previous investigation.* Vomela and Whitby⁽⁵⁾ studied the drag force on chain-like aggregates produced by the exploding wire technique and also by hydrocarbon flames. Stöber⁽⁶⁾ examined the behavior of aggregates of monodisperse polystyrene spheres and Kops⁽⁷⁾ and Kops, et al^(8,9) have studied iron oxide, gold, and copper coagulates.

Most of these authors have presented their results in terms of variously defined agglomerate diameters. In order to compare the current results with these previous studies, it is, therefore, useful to define some of these terms. The Stokes' diameter is defined as the diameter of a sphere having the same bulk density and settling rate as the agglomerate. The equivalent mass diameter is the diameter of a sphere having a mass equal to that of the agglomerate. This corresponds to the size utilized in most analytical aerosol behavior models such as the HAARM-2 code⁽¹⁰⁾. Another common term is the aerodynamic diameter which is the diameter of a unit density sphere having the same settling velocity as the coagulated aerosol.

* An extensive list of references to these investigations is given in Reference (4). The most recent authors are Volmer and Whitby, Stöber and Kops and van de Vate.

FIGURE 6. EFFECTIVE AGGLOMERATE DENSITIES AS A FUNCTION OF PARTICLE MASS

These definitions may be related to the terms used in this study by simply examining these settling rates with the corrections that have been introduced. The settling velocity in terms of the aerodynamic diameter, D_a , results immediately in

$$U_s = \frac{1}{18} \frac{\rho_o D_a^2 g}{\mu}, \quad (21)$$

where ρ_o is unit density. Similarly, the settling velocity in terms of the equivalent mass diameter is obtained by equating the gravitational and fluid drag forces on the agglomerate. Utilizing the density correction, α , and the size correction, f , the force equation becomes

$$\frac{4}{3}\pi \alpha \rho (fr_e)^3 g = 6\pi \mu fr_e U_s, \quad (22)$$

where r_e is the equivalent mass radius. Solving for the settling rate, U_s yields

$$U_s = \frac{2}{9} \frac{\alpha \rho (fr_e)^2 g}{\mu} = \frac{1}{18} \frac{\alpha \rho (fD_e)^2 g}{\mu}. \quad (23)$$

Since the settling velocity of the agglomerate is a fixed quantity, we may equate expressions (21) and (23) to obtain the following relationship:

$$\frac{\rho D_e^2}{\rho_o D_a^2} = \alpha^{-1/3} = f. \quad (24)$$

The relationship between α and f expressed above results immediately from the definitions of α and f as presented in Equation (22).

The data of Kops, et al^(7,8,9) can clearly be divided into two regimes. Kops, et al hypothesized that the first regime corresponded to aggregates comprised of fewer primary particles and possessing branched chain-like structures. Their results were expressed in terms of the aerodynamic diameter of the agglomerates, a proportionality constant k , the number n of primary particles comprising the agglomerate, and the distribution parameters describing the primary particle size distribution. Accordingly,

$$D_a = k n^{1/6} (\rho/\rho_o)^{1/2} D_g \exp(2 \ln^2 \sigma_g). \quad (25)$$

It is implicitly assumed here that the primary particle number distribution over their diameters is log normal with a geometric mean diameter D_g and geometric standard deviation σ_g . The aerosols studied by Kops, et al^(7,8,9) were reportedly modeled accurately by the log normal assumption. This is also true for the primary sodium oxide aerosols observed in this study.

The primary particle size distribution of the sodium oxide aerosol was determined by electron microscopic techniques. Sodium was burned in air which had been passed through an ascarite filter to remove carbon dioxide, and then a Drierite filter to remove most of the water vapor, and finally through a dry ice-acetone bath to bring its temperature down to about -77°C and condense most of the remaining moisture. Samples were then collected on carbon coated electron microscope grids which had been equilibrated in a vacuum under a heat lamp for a minimum of 16 hours prior to use. This total equilibration was accomplished by initially placing the grids in the specially designed air tight thermal precipitator described previously. The precipitator was designed to open automatically under vacuum and to close under atmospheric pressure. The grids were thereby equilibrated in an open position under a vacuum and later closed automatically by introduction of dry air into the equilibration vacuum chamber. Following this equilibration, the precipitator was used to collect a sample by thermal deposition and the closed air-tight apparatus taken to the electron microscope. At this point, the apparatus was placed in a plastic gloved bag which was attached to the electron microscope and filled with air dried as described above. The thermal precipitator was then opened manually and the grids transferred to the electron microscope. Typical electron micrographs obtained by this procedure are presented in Figures 7 and 8. Primary particle size distributions over the average diameter were obtained from a series of similar slides and the results are depicted in Figure 9. The results indicate that the primary particle size distribution may be modeled by a log normal distribution with a geometric mean diameter of $0.45\ \mu\text{m}$ and a geometric standard deviation of 1.47.

Knowing the primary particle size distribution one may relate the equivalent mass diameter to the number of particles comprising an agglomerate. Accordingly,

FIGURE 7. ELECTRON MICROGRAPH OF DRY SODIUM OXIDE PARTICLES

FIGURE 8. ELECTRON MICROGRAPH OF DRY SODIUM OXIDE PARTICLES

FIGURE 9. PRIMARY SODIUM OXIDE AEROSOL SIZE DISTRIBUTION

$$\frac{\rho \pi D_e^3}{6} = n \rho \frac{\pi \overline{D^3}}{6} . \quad (26)$$

Here $\overline{D^3}$ represents the mean diameter cubed of the particles comprising the agglomerate. If it is assumed that particles of all sizes are equally likely to be present in a particular agglomerate, then the primary particle size distribution comprising the agglomerates is equal to that of the primary particles individually suspended. This distribution has been found to be log normal as discussed above and, therefore, may be written as

$$n(D)dD = \frac{N}{\sqrt{2\pi}u} \exp\left\{-\frac{1}{2u} \ln\left(\frac{D}{D_g}\right)\right\} \frac{dD}{D} , \quad (27)$$

where

$$u \equiv \ln^2 \sigma_g . \quad (28)$$

By definition,

$$\overline{D^3} = \frac{\int_0^\infty D^3 n(D) dD}{\int_0^\infty n(D) dD} = D_g^3 \exp\left(\frac{9}{2} \ln^2 \sigma_g\right) . \quad (29)$$

Substituting Equation (29) into Equation (26) relates the equivalent mass diameter to the primary particle size distribution parameters:

$$D_e = D_g n^{1/3} \exp\left(\frac{3}{2} \ln^2 \sigma_g\right) . \quad (30)$$

Solving for D_g and substituting into Equation (25) yields

$$D_a = k n^{-1/6} (\rho/\rho_0)^{1/2} D_e \exp\left(\frac{1}{2} \ln^2 \sigma_g\right) . \quad (31)$$

Rearrangement provides the resulting expression for α

$$\frac{\rho D_e^2}{\rho_0 D_a^2} = k^{-2} n^{1/3} \exp(-\ln^2 \sigma_g) = \alpha^{-1/3} . \quad (32)$$

Hence,

$$\alpha = k^6 n^{-1} \exp(3 \ln^2 \sigma_g) . \quad (33)$$

This equation then provides a direct comparison of values for α measured experimentally in this study with the results of Kops, et al.

The value of k appears to be near to 1.0 for linear aggregates comprised of up to eight monodisperse polystyrene spheres. Stöber's data give $k = 1.077$. An average value taken from Kops⁽⁷⁾ is about 1.23. Utilizing the Kops⁽⁷⁾ result provides the following result for α

$$\alpha = 3.46 n^{-1} \exp(3 \ln^2 \sigma_g) \quad (34)$$

Calculations of the number of primary particles comprising an agglomerate depend on the density of the primary particles. This presents a problem for the case of sodium oxide in air since several species may be present. However, Equation (34) has been compared with our experimental measurements of α in Figure 6 for several primary particle densities. A value of the density near 2.27 g/cm³ appears to give a reasonable fit to the data.

As more primary particles combine, the agglomerate structure gradually attains a three dimensional structure. The number of primary particles added to the structure before this begins to occur probably depends largely upon the magnitude and sign of the electrical charges carried by the primary spheres. If the spheres are charged unipolarly, the linear structure may persist until quite large numbers of primary particles have been added to the structure. On the other hand, if the primary particles have charges of both signs, a more densely packed spherical structure may result. Hence, the resulting agglomerate structure likely depends upon the aerosol material, the charge condition of the gas, and the generation technique employed.

Kops, et al noted a significant difference in agglomerate behavior of the iron oxide aerosol produced by the exploding wire technique when more than about 5×10^3 primary particles were coagulated. In this second regime, their results were presented in the following form:

$$D_a = q n^{1/3} (\rho/\rho_o)^{1/2} D_g \exp\left(\frac{3}{2} \ln^2 \sigma_g\right) \quad (35)$$

where, again, q is a proportionality constant.

Performing similar substitutions and rearrangements as before, yields the following interesting result for α :

$$\alpha = q^6 \quad (36)$$

Hence, the density correction α initially varies as the number of primary particles comprising an agglomerate increases, but eventually reaches a limiting value given by q^6 in terms of Kops notation. Kops⁽⁷⁾ obtained an average value of about 0.35 for q for the iron oxide aerosol while Stöber presented a value near 0.903 for the polystyrene spheres. Our results indicate a value near 0.75 for the sodium oxide aerosol which corresponds to a final value of about 0.18 for α . Of course, this final value for α , and therefore for q , depends upon the final packing density of the agglomerates and, hence, differs for various materials and generation techniques. It likely depends on the electrical charge characteristics of the suspended primary particles.

In summary, our experimental measurements of the aerodynamic behavior of the sodium oxide aerosol seem to be in general agreement with those of previous investigators. In the initial stages of coagulation, the aggregate behavior may be modeled by Equation (34) with an average primary particle density near 2.27 g/cm³. A final limiting value of 0.18 for α appears valid.

Thermophoretic Force Measurements

Following the aerodynamic measurements on the aerosol, a temperature gradient of prescribed magnitude was established in the modified Millikan cell. The potential difference required to balance a particle which had been previously analyzed for mass in the known steady temperature gradient was then recorded. In this steady state situation, the downward directed thermal and gravitational forces are exactly balanced by the applied electrical force on the aerosol particle. Accordingly, the following relationship exists:

$$F_T + mg - \frac{neV_B'}{S} = 0 \quad , \quad (37)$$

where F_T is the thermophoretic force and V_B' the potential difference required to balance the particle in the steady temperature gradient. The

following considerations allow the experimental results to be expressed in a convenient form giving a reduced thermal force calculated from experimentally measured values and as a function only of Knudsen number, λ/R .

The thermophoretic force F_T in the low Knudsen number regime may be written in the following general form

$$F_T = 12\pi\kappa \frac{\mu^2 R}{\rho T} \Omega(\lambda/R) |\nabla T|, \quad (38)$$

where ∇T represents the temperature gradient, T the average gas temperature, κ a constant corresponding to the magnitude of the thermal creep velocity, R the actual particle radius, and Ω represents the pressure variation Knudsen number dependence. Maxwell's⁽¹¹⁾ 1879 derivation of the velocity of creep of a thin layer of gas directly adjacent to an unevenly heated surface yielded $\kappa = 3/4$. However, more recently Derjaquin and Yalamov⁽¹²⁾ have pointed out discrepancies between the Maxwell result and current experimental evidence, and have presented other expressions for the thermal creep which are based on more accurate assumptions concerning molecular collisions near a gas-surface interface. In a more general manner the thermal creep velocity may be written as

$$v_t = \kappa \frac{\mu}{\rho T} (\nabla T)_t \quad (39)$$

where κ is assumed to be a constant between 0.75 and 1.50, and $(\nabla T)_t$ is the tangential component of the temperature gradient along the surface. Use of this expression in the development of a thermophoretic force expression yields the general form presented in Equation (38). Utilizing the ideal gas equation of state and relating pressure to gaseous mean free path yields the following rearrangement of Equation (38):

$$F_T = 12\pi\kappa \frac{\mu^2 R^2 \bar{R}_g T_o}{M P_o \lambda_o T} \Omega(\lambda/R) |\nabla T|. \quad (40)$$

Here, $\bar{R}_g$ is the universal gas constant, M the molecular weight of the gas, and λ_o the gaseous mean free path corresponding to pressure P_o and temperature T_o .

In the limit of infinite Knudsen number an expression for the thermophoretic force may be developed based on gas kinetic theory. Derjaguin and Bakanov⁽¹³⁾ and Waldmann⁽¹⁴⁾ have independently developed the following expression for the free molecular thermophoretic force:

$$F_T' = \frac{32}{15} \frac{R^2 k_{tr}}{\bar{c}} |\nabla T|, \quad (41)$$

where k_{tr} is the translational component of the gaseous thermal conductivity, and $\bar{c}$ is the mean molecular velocity. Mathematically,

$$k_{tr} = \frac{15}{4} \frac{k\mu}{m'} \quad (42)$$

and

$$\bar{c} = \sqrt{\frac{8kT}{\pi m'}} \quad (43)$$

where k is the Boltzmann constant and m' the molecular mass of the gas. Substituting Equations (42) and (43) into (41) yields

$$F_T' = \sqrt{\frac{8\pi k}{m'}} R^2 \mu |\nabla T|. \quad (44)$$

Utilizing Equation (44), a dimensionless or reduced thermophoretic force expression may be developed by dividing it into Equation (40). Thereby, the following expression results

$$F_T^* = \sqrt{\frac{144\pi}{8kMTA}} \frac{\bar{R}_g T_o \mu \kappa}{P_o \lambda_o} \Omega(\lambda/R), \quad (45)$$

where A is Avogadro's number. Under standard conditions and with the Maxwell $\kappa = 3/4$, this expression may be written more simply as

$$F_T^* = 4.74 \Omega(\lambda/R). \quad (46)$$

This then defines a reduced thermal force as a ratio of force at existing conditions to force at infinite Knudsen number which is a function only of Knudsen number, λ/R .

For comparing experimental results with theory, it is evident that the term $\Omega(\lambda/R)$ as determined experimentally and as derived from theory can be used to give theoretical and experimental values for F_T^* .

Substitution of Equation (40) into (37) and solving for the Knudsen number dependence, yields the following result based on experimental measurements:

$$\Omega = \frac{ne(V_B' - V_B)MP_o \lambda_o T}{12\pi\kappa\mu^2 R^2 \frac{R}{g} T_o S |\nabla T|} \quad (47)$$

This expression is utilized to transform the experimental measurements to a useful form. Comparison of Equation (40) with the theoretical thermophoretic force expression derived by Brock⁽¹⁵⁾ yields the following analytical expression for the Knudsen number dependence:

$$\Omega = \left(\frac{\lambda/R}{1 + 3C_m \lambda/R} \right) \left(\frac{k_f/k_s + C_t \lambda/R}{1 + 2C_t \lambda/R + 2k_f/k_s} \right) \quad (48)$$

Results from the experimental measurements are compared with theory as given by Brock in terms of the reduced thermophoretic force, F_T^* , in Figure 10 as a function of λ/R and for a range of parametric variations of assumed gas particle interface conditions and ratios of gas to particle thermal conductivities. The Maxwell value of 0.75 was utilized for the thermal creep coefficient κ .

The results seem to indicate reasonable agreement with the Brock expression. However, because of the porous and possibly hollow structure of the agglomerates, their effective thermal conductivities probably vary significantly, producing considerable variation in the thermal force data. It is interesting to note in Figure 10 that all of the cases using room air were significantly more affected by the thermal gradient. This may be due to a decrease in their effective thermal conductivities, due either to porosity differences, chemical differences, or both.

FIGURE 10. REDUCED THERMOPHORETIC FORCE AS A FUNCTION OF KNUDSEN NUMBER

CONCLUSION

In summary, aerodynamic and thermophoretic force measurements have been performed on aggregated sodium oxide aerosols in air using a modified Millikan cell apparatus. The effective density measurements were found to be in reasonable agreement with the empirical correlations developed by Kops, et al. The effective density reached a limiting value of about 18 percent of the material density of Na_2O for agglomerates comprised of about 50 - 100 primary particles. Measurements performed on relatively small particles indicated that the primary particles also possessed significantly reduced densities and may have a porous or hollow structure. The modified Millikan cell apparatus was found to be particularly suited for thermophoretic force measurements. These measurements were performed over a wide range of Knudsen numbers. The results were found to agree with the Brock continuum-slip theory when the thermal conductivity ratio of the gas to the agglomerate was set to about 0.10.

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