MASTER

92

COO-1018

ENGINEERING EXPERIMENT STATION

UNIVERSITY OF ILLINOIS

March 1, 1959

Technical Report No. 16
(Research and Development Report)

THE AGGLOMERATION OF SOLID
AEROSOL PARTICLES

By

H. F. Johnstone, Technical Director

Contract No. AT(11-1)-276
U. S. Atomic Energy Commission

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ENGINEERING EXPERIMENT STATION

UNIVERSITY OF ILLINOIS

March 1, 1959

Technical Report No. 16
(Research and Development Report)

THE AGGLOMERATION OF SOLID
AEROSOL PARTICLES

By

H. F. Johnstone, Technical Director

Contract No. AT(11-1)-276
U. S. Atomic Energy Commission

This report is based on a thesis submitted by George A. Sehmel for the Master of Science Degree in Chemical Engineering in the Graduate College at The University of Illinois, August 1956. Mr. Sehmel was a research assistant on the contract from September 1955 to June 1956.

DISTRIBUTION LIST

<u>Copies</u>		<u>Copy No.</u>
1	Dr. M. D. Thomas, Stanford Research Institute	1
5	Argonne National Laboratory	2-6
1	Armed Forces Special Weapons Project (Miss Collie)	7
1	Army Chemical Center (Technical Library)	8
1	Army Chemical Corps (Fort Detrick)	9
3	Atomic Energy Commission, Washington (Technical Library)	10-12
1	Battelle Memorial Institute (H. W. Russell)	13
3	Brookhaven National Laboratory (Dennis Puleston)	14-16
1	Navy Department Bur. Med. (Code 74)	17
2	Carbide and Carbon Chemicals Company, ORNL (K-25)	18-19
2	Carbide and Carbon Chemicals Company, ORNL (Y-12 Area)	20-21
5	Oak Ridge National Laboratory (E. B. Struxness)	22-26
1	AEC, Chicago Patent Group	27
5	AEC, Chicago Operations Office (Milton Klein)	28-32
1	Chief of Naval Research, Washington (Code 209)	33
5	DuPont Company, Atomic Energy Division (F. M. Burns)	34-38
2	General Electric Company (ANPP)	39-40
5	General Electric Company, Richland (Miss M. G. Freidank)	41-45
1	AEC Hanford Operations Office (K. L. Englund)	46
2	Dr. Philip Drinker, Harvard School of Public Health	47-48
1	Harvard University, Office for Govt. Contracts (H. A. Thomas)	49
5	AEC Idaho Operations Office (J. L. Schwennessen)	50-54
1	Iowa State College (Ray Fisher)	55
1	Dr. Abel Wolman, Johns Hopkins University	56
1	Atomic Energy Division, Kaiser Engineers (P. D. Bush)	57
3	Knolls Atomic Power Laboratory (J. J. Fitzgerald)	58-60
2	AEC Los Alamos Field Office	61-62
6	Los Alamos Scientific Laboratory	63-68
1	Mallinckrodt Chemical Works	69
1	Professor Rolf Eliassen, Massachusetts Institute of Tech.	70
1	Massachusetts Institute of Technology (A. R. Kaufman)	71
2	AEC Mound Laboratory	72-73
1	National Bureau of Standards (R. D. Huntoon)	74
2	National Lead Company of Ohio (R. Heatherton)	75-76
1	Naval Radiological Defense Lab (Technical Information Branch)	77
1	Naval Research Laboratory (E. A. Ramskill)	78
1	Mr. C. E. Lapple, Stanford Research Institute	79
2	Phillips Petroleum Company, Atomic Energy Division (D. Paige)	80-81
2	AEC Savannah River Operations Office, Wilmington (D. Darrow)	82-83
3	AEC Savannah River Operations Office, Augusta (Karl Herde)	84-86
2	AEC Albuquerque Operations Office (E. Mathews)	87-88
1	AEC Research and Operations Division, Schenectady (Ball)	89
1	AEC Patent Branch, Washington (R. A. Anderson)	90
1	USPHS, Taft Center, Cincinnati (A. Rossano)	91

5	AEC Technical Information Service, Oak Ridge	92-96
1	UCLA Medical Research Laboratory (S. L. Warren)	97
3	University of California Radiation Laboratory (M. D. Thaxter)	98-100
1	UCLA (Leonard Baurmash)	101
2	University of Rochester, Atomic Energy Project	102-103
3	Westinghouse Electric Corporation, Atomic Power Division	104-106
2	Arthur D. Little, Inc. (W. J. Smith)	107-108
2	Dow Chemical Company, Rocky Flats (R. Walker)	109-110
5	AEC New York Operations Office	111-115
1	Dr. William P. Yant, Mines Safety Appliances Company	116
1	Dr. Lyle Gilbertson, Air Reduction Company	117
1	North American Aviation, Inc., Atomic Energy Res. Dept. (Jarrett)	118
1	RAND Corporation (E. H. Plesset)	119
3	Atomic Energy Project, Chalk River (Librarian)	120-122
1	Naval Research Laboratory (F. P. Anderson)	123
1	Naval Medical Research Institute, Div. of Atomic Medicine	124
1	Sandia Corporation, Albuquerque (Dale N. Evans)	125
1	Library of Congress, Acquisitions Department	126
1	Picatinny Arsenal Technical Information Section	127
1	Stanford Research Institute, Air Res. Lab., (Mrs. Heppell)	128
1	Army Chemical Center, Medical Division (Mrs. Helen Marquand)	129
171	Files, and for internal use	130-300

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. THEORETICAL	5
III. EXPERIMENTAL	11
The Millikan Cell	11
Cascade Impactor Measurements	13
IV. CALCULATIONS FROM THE MILLIKAN CELL DATA	19
Calculation of Mass	19
Calculation of Stokes' Diameter and Density of Agglomerates	21
V. COMPARISON OF MILLIKAN CELL DATA AND ELECTRON MICROGRAPHS OF AGGLOMERATES	28
Magnesium	28
Magnesium Oxide	28
Antimony	36
Bismuth	36
Copper Sulfate	36
Graphite	43
Iron	43
Tungsten	43
Polystyrene	43
Ammonium Chloride	51
Practical Considerations	51
VI. SUMMARY	55
VII. NOMENCLATURE	56
VIII. BIBLIOGRAPHY	57

LIST OF FIGURES

Figure		Page
1	CUNNINGHAM FACTOR FOR SMALL PARTICLES	3
2	CUNNINGHAM FACTOR FOR PARTICLES LARGER THAN 0.25-MICRON RADIUS	4
3	NEBULIZER FOR DISPERSING AEROSOLS	9
4	MILLIKAN CELL USED FOR MEASURING PARTICLE SIZE AND DENSITY	10
5	RELATIONSHIP OF CD^2/ρ AND MASS FOR AMMONIUM CHLORIDE AGGLOMERATES FORMED FROM UNIFORM PARTICLES, 0.3 - 0.8 MICRONS DIAMETER	14
6	DETERMINATION OF MASS OF COPPER SULPHATE AGGLOMERATE FROM MILLIKAN CELL DATA	18
7	RELATIONSHIP BETWEEN CD^2/ρ AND MASS FOR SPHERICAL PARTICLES IN AIR AT ROOM TEMPERATURE	22
8	RELATIONSHIP OF CD^2/ρ AND MASS FOR MAGNESIUM AGGLOMERATES	24
9	RELATIONSHIP OF CD^2/ρ AND MASS FOR MAGNESIUM OXIDE AGGLOMERATES	25
10	ELECTRON MICROGRAPHS OF MAGNESIUM AGGLOMERATES	26
11	ELECTRON MICROGRAPHS OF MAGNESIUM OXIDE AGGLOMERATES	27
12	ELECTRON MICROGRAPHS OF ANTIMONY AGGLOMERATES	29
13	RELATIONSHIP OF CD^2/ρ AND MASS FOR ANTIMONY AGGLOMERATES	30
14	RELATIONSHIP OF CD^2/ρ AND MASS FOR BISMUTH AGGLOMERATES	31
15a	ELECTRON MICROGRAPHS OF ANHYDROUS COPPER SULFATE	32
15b	ELECTRON MICROGRAPHS OF COPPER SULFATE PENTAHYDRATE AGGLOMERATES	33
16	RELATIONSHIP OF CD^2/ρ AND MASS FOR PENTAHYDRATE COPPER SULFATE AGGLOMERATES	34
17	RELATIONSHIP OF CD^2/ρ AND MASS FOR ANHYDROUS COPPER SULFATE AGGLOMERATES	35
18	ELECTRON MICROGRAPHS OF GRAPHITE AGGLOMERATES	37
19	RELATIONSHIP OF CD^2/ρ AND MASS FOR GRAPHITE AGGLOMERATES	38

LIST OF FIGURES (Continued)

Figure		Page
20	ELECTRON MICROGRAPHS OF IRON AGGLOMERATES	39
21	RELATIONSHIP OF CD^2 AND MASS FOR IRON AGGLOMERATES	40
22	RELATIONSHIP OF CD^2 AND MASS FOR TUNGSTEN AGGLOMERATES	41
23	ELECTRON MICROGRAPHS OF TUNGSTEN AGGLOMERATES	42
24	RELATIONSHIP OF CD^2 AND MASS FOR POLYSTYRENE AGGLOMERATES FORMED FROM SPHERES OF 1.171 MICRON DIAMETER	44
25	ELECTRON MICROGRAPHS OF POLYSTYRENE AGGLOMERATES FORMED FROM SPHERES 1.171 MICRON DIAMETER	45
26	ELECTRON MICROGRAPHS OF POLYSTYRENE AGGLOMERATES FORMED FROM SPHERES OF 0.333 MICRON IN DIAMETER	46
27	RELATIONSHIP OF CD^2 AND MASS FOR POLYSTYRENE AGGLOMERATES FORMED FROM SPHERES OF 0.333-MICRON DIAMETER	47
28	RELATIONSHIP OF CD^2 AND MASS FOR AMMONIUM CHLORIDE AGGLOMERATES FORMED FROM A HETEROGENEOUS PRIMARY SIZE	48
29	ELECTRON MICROGRAPHS OF AMMONIUM CHLORIDE AGGLOMERATES FORMED FROM A CONTROLLED PRIMARY SIZE	49
30	ELECTRON MICROGRAPHS OF AMMONIUM CHLORIDE AGGLOMERATES FORMED FROM A HETEROGENEOUS PRIMARY SIZE	50
31	PARTICLE-SIZE DISTRIBUTION OF AMMONIUM CHLORIDE AEROSOL, DETERMINED FROM JET-IMPACTOR DATA AND FROM A MICROSCOPE COUNT	52
32	PARTICLE-SIZE DISTRIBUTION OF AMMONIUM CHLORIDE AEROSOL, DETERMINED FOR TWO DEGREES OF AGGLOMERATION	53

LIST OF TABLES

Table		Page
1	Properties of Materials Studied	8
2	Measurements on a Particle of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the Millikan Cell	16
3	Voltages Required for Balancing Forces on Tungsten Particles	20

I. INTRODUCTION

An important property of aerosols of solid particles is the variation of size and density. Such aerosols may be composed of unitary particles or agglomerates formed by coagulation. The agglomerates may have any geometric configuration and a void space. Hence, their density will be lower than that of the primary particles from which they are formed and their size distribution will not be definable in terms of unitary particle diameters. The Stokes-Cunningham equation for the free-fall terminal velocity, as a function of the diameter and the density of a particle, has been used to determine the size distribution of agglomerates for a number of systems from simultaneous measurements of mass and free-fall velocity. A modification of Millikan's oil drop apparatus was used. It consisted of two enclosed horizontal plate electrodes between which the velocity of fall under gravity and the velocity of rise under electric field could be observed. The method has been employed by Wells and Gerke (15) to find the size distribution of an aerosol of known density and uniform charge, though it must be observed that Kunkel (5, 6) has shown that there are sometimes wide variations of the charge on the particles of an aerosol. Whytlaw-Gray and Patterson (16, 17) used the apparatus to determine the mass and diameter of some agglomerates from a series of rising velocities under different field strengths and electronic charges. Rotzeig and Fuchs (14) measured the zigzag paths of particles moving vertically under the influence of a rapidly reversing field of constant voltage and found the particle velocities from their data.

In the present study, experiments were made with a wide variety of substances using a modification of Whytlaw-Gray and Patterson's method in which the free-fall velocity was determined and the mass was estimated both by balancing the gravitational and electrostatic forces and from rising velocities under constant field strength. The results were compared with

the shape and structure of the aerosols shown by electron microscopy. The variation of the Stokes' (or drag) diameters was found by combining the results with cascade-impactor and microscope measurements.

Figure 1. Cunningham factor for small particles

Figure 2. Cunningham factor for particles larger than 0.25-micron radius

II. THEORETICAL

Stokes' Law is applicable to unaccelerated motion in a continuous medium. For particles smaller than 1 micron radius in air at ordinary temperatures and pressures the medium is not continuous and a correction must be applied. Cunningham and others (3, 4, 9, 13) expressed the effect by an additional factor C in the equation

$$F = mg = \frac{3\pi\mu D v_g}{C} \quad (1)$$

where

$$C = 1 + \frac{2A\lambda}{D} \quad (2)$$

The values of $2A\lambda$ shown in Figures 1 and 2 were calculated from the constants derived experimentally by Mattauch (9), Ehrenhaft and Wasser (4), and Reiss (13).

From Equation (1)

$$v_g = \frac{g}{3\pi\mu} \frac{Cm}{D} \quad (3)$$

v_g is the free-fall terminal velocity.

In the simple case of spheres, $m = \pi D^3 \rho / 6$

and

$$CD^2 \rho = \frac{18\mu v_g}{g} \quad (4)$$

It is evident that the quantity $CD^2 \rho$ can be obtained for spheres directly by measuring the free-fall terminal velocity.

The mass of the particle is determined from the rising times under a constant electric field with several different total charges on the particle. The particle reaches its terminal rising velocity rapidly under the influence

of the electric field. Stokes' Law can be applied again and the force balance now includes a term for the electrical force:

$$neX - mg = \frac{3\pi D\rho v_e}{C} \quad (5)$$

If the values of e , X , m , g , ρ , and C are constant, and if the orientation of the particle is constant for all values of v_e , the equation is linear,

$$v_e = an - b \quad (6)$$

When the forces of gravity and the electric field are equal, i.e., when $v_e = 0$, n is the charge on the particle necessary for the balance between the two forces. Thus, a straight line is determined from a series of rising velocities for different values of n , and the mass of the particle can be found by extrapolation of the line to $v_e = 0$. From Equation 5,

$$m = \frac{neX}{g} \quad (7)$$

If the particle is not charged, $n = 0$ and $(v_e)_0 = -b$. The term $(v_e)_0$ is the velocity of the particle falling under gravity with the same orientation as that in which it rose under the electric field. The results of the present work show that the actual velocity under gravity tends to be lower than that obtained from the intercept $-b$.

The use of Equation 6 requires the determination of the charge corresponding to each rising velocity. There should be an equal increment in v_e for each additional unit charge on the particle. Several rising velocities must be measured in order to establish the value of the increment for the effect of one electron charge. Since increments in velocity must be related by whole numbers, the slope of Equation 6 is found readily. The value of each charge must be determined by extrapolating the line and finding the

intercept on the velocity axis. For spheres, the intercept $(v_e)_0$ is v_g ; for agglomerates, the experimental results show that $(v_e)_0 \geq v_g$. If $(v_e)_0 \neq v_g$, it is necessary to plot the rising velocities for the smallest possible value of n .

Another way to determine the mass of an agglomerate is to balance the gravitational and the electrical forces on the particle by adjusting the field strength. In this case,

$$mg = n_1 eX_1 = n_2 eX_2 = \dots \quad (8)$$

The value of n for each field strength is then determined easily from the ratios of the products of $n_1 eX_1$, $n_2 eX_2$, etc.

Table 1. Properties of Materials Studied

<u>Substance</u>	<u>Density gm/cc</u>	<u>Crystalline form</u>	<u>Shape of primary particles shown by electron micrograph</u>	<u>Source</u>
Antimony	6.68	hexagonal	irregular fragments	Cenco -- "powdered metal"
Ammonium chloride (heterogeneous)	1.53	cubic	irregular fragments	Baker -- "reagent grade"
Ammonium chloride (homogeneous)	1.53	cubic	indefinite	Baker -- "reagent grade"
Bismuth	9.80	hexagonal	no micrograph	Baker -- "granular"
Copper sulfate pentahydrate	2.26	triclinic	indefinite	Mallinckrodt -- "crystals"
Copper sulfate anhydrous	3.60	rhombic	prisms	dehydrated pentahydrate
Iron	7.86	cubic	indefinite	E. M. Sergeant Pulp and Chemical Co., Inc. -- "dust"
Graphite	2.25	cubic	cubes (?)	U. S. Graphite Co. -- "Air floated Mexican graphite"
Magnesium	1.74	hexagonal	irregular fragments	Burning Mg ribbon
Magnesium oxide	3.67-3.75	cubic	cubes of various sizes	Burning Mg ribbon
Polystyrene latex	1.05	spheres	uniform spheres	Dow-Corning -- 1.171- micron spheres with a standard devi- ation of 0.013 microns, and 0.333- microns spheres with a standard devi- ation of 0.007 microns
Tungsten	19.3	cubic	irregular, with some cubes	dust from shattered solid

FIG. 3. NEBULIZER FOR DISPERSING AEROSOLS

FIG. 4. MILLIKAN CELL USED FOR MEASURING PARTICLE SIZE AND DENSITY

III. EXPERIMENTAL

In order to reveal the variables most important in agglomeration, the materials for aerosol production were chosen so that their physical and chemical properties differed widely. The properties are shown in Table 1. A LaMer generator (8) was used for dispersing ammonium chloride. Uniform particles of a desired size could be produced by this device so that agglomerates of the same substance with different primary particle size could be compared. Magnesium oxide smoke was formed by blowing air through a flask in which magnesium ribbon was burned. All the other aerosols were dispersed from a nebulizer obtained from the Vaponefrin Company. This is shown diagrammatically in Figure 3. The polystyrene spheres were dispersed from a dilute suspension in water and the others as dry powders.

The Millikan Cell

The Millikan cell was obtained from the Central Scientific Company and is shown diagrammatically in Figure 4. It consisted of two enclosed horizontal brass plates 15 cm. in diameter and 3 mm. apart, connected to a battery through a reversing key. The aerosol being studied was blown into the space above the top plate which has three small holes near the center. Aerosol particles fell through these holes and were illuminated by a beam of light through a window between the plates. A second window was diametrically opposite and was used for positioning the light source. A third window was located at an angle of 20 degrees from the second and was used for observing the particles through a low-power microscope equipped with a scalar eyepiece.

The apparatus was provided with a device for changing the charge on the particles. By means of a button beneath the cell a small amount of radioactive material could be raised above the surface of the lower plate to

ionize the surrounding air. The chance of the particle to capture ions of either charge was increased by the higher concentration of ions in the air.

The voltage was provided by 45-volt "B" batteries. The potential across the plates of the cell could be varied from 45 to 540 volts. Two 100,000 ohm decade resistance boxes were used as voltage dividers for fine adjustment of the field strength.

In making the measurements, the small holes in the upper plate of the cell were left uncovered until particles were observed between the plates. A particle was chosen and the voltage was applied by closing the reversing key. If the particle could be made to move up and down, the entry of further particles was stopped by closing the shutter over the holes in the upper plate. The particle was then moved up and down while the others in the field of vision were removed by impaction on the plates.

The velocity of rise and fall of the particle was found by measuring the time required to traverse a fixed distance on the calibrated eyepiece of the microscope. Ten measurements of the free-fall velocity were made. Velocities in the range from 0.0013 to 0.069 cm./sec. were measured. The range was limited by Brownian motion of the very small particles at the lower extreme and by the difficulty of keeping sufficient charge on a particle at the higher limit.

When the mass was measured by balancing forces, the maximum voltage was applied first. Then, by the use of the radioactive source, the charge on the particle was decreased until it rose very slowly under the electric force. Finally, the voltage was decreased until the particle was balanced. This procedure was repeated at four or five lower voltages.

When a constant field strength was used, a set of preliminary measurements was necessary to determine the voltage producing velocities in the

range mentioned above. The number of charges was calculated by the method described below. The particles changed charge and velocity by collision with ions but the radioactive source was used to reestablish conditions until each different rising velocity had been determined ten times.

For either method, higher accuracy was attained when the particle under observation had less than 7 unit charges.

Cascade Impactor Measurements

The cascade impactor (12) is an instrument for measuring the distribution of particle size by passing an aerosol through a series of jets from which the particles impinge in glass cups or other impaction collectors. The size of the jets decreases progressively and the particles are thereby separated into size groups. The impactor was used on aerosol agglomerates formed from primary particles of ammonium chloride 0.3 to 0.8 micron in diameter. A series of three rectangular jets followed by a glass wool filter was employed. About 0.3 mg. of ammonium chloride was collected in a period of 15 minutes. The mass distribution was found by dissolving each fraction in 50 ml. of water and determining the amount of ammonia with Nessler's reagent (1, 2).

Two determinations of the size distribution of the particles were made with the impactor. In one, a 3-foot section of 1/2-in. Tygon tubing was inserted between the LaMer generator and the impactor. A sample of this material was collected for one minute on a Millipore filter. In the other determination, a 25-ft. length of tubing was used. The difference of 0.22 min. in the coagulation time provided for a different degree of agglomeration.

The size distribution of the Millipore filter sample was determined by viewing the filter under a microscope equipped with a Porton graticule in the microscope eyepiece (11). The eyepiece was a 15x Bausch and Lomb

Figure 5. Relationship of $CD^2 \rho$ and mass for ammonium chloride agglomerates formed from uniform particles, 0.3 - 0.8 microns diameter

Density of pure substance, $\rho = 1.53 \text{ g./cc.}$

Equation of experimental line, $CD^2 \rho = 1.5m^{0.46}$

Hyperplane. It was used with a 97x Bausch and Lomb oil-immersion objective. The graticule had nine circles ranging in size from 0.35 to 5.76 microns.

The particle count was made in the following manner: Five 5-mm. circular sections of the 100-square centimeter Millipore Filter were cut out with a cork borer. One of these was from the center of the filter. The other four were cut from the center of each quadrant. Four subsections of each section were chosen at random and around 5000 particles were counted. A mass distribution was determined from the count by using the average apparent densities from the curve of $CD^2 \rho$ vs. mass for ammonium chloride agglomerates (Figure 5) obtained with the Millikan cell. The results of these tests are discussed in Section V.

Table 2. Measurements on a Particle of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the Millikan Cell

Voltage: Run A -- 221 volts; Run B -- 90 volts; Plate Spacing: 0.3 cm.

Air Viscosity: 1.83×10^{-4} poises at 25°C

Distance travelled: 0.076 cm.; *0.038 cm.; **0.152 cm.

1	2	3	4	5	6	7	8
t_g	t_e	t_e (mean)	v_e	Δv_e	Δn	$\frac{\Delta v_e}{\Delta n}$	n
Seconds	Seconds	Seconds	cm./sec.		number of electrons		
Run A							
9.0	6.2	6.5	6.4	6.3	0.0121		4
9.3	6.1	6.3	6.2				
9.2	6.4	6.1	6.3				
8.9	6.4						
8.9							
9.2	11.4	10.7	11.3	11.1	0.00685		3
9.3	10.8	11.0	11.5				
8.8	10.9	11.2	11.4				
9.2	10.6						
9) 81.8							
9.1	*25.3	24.5	24.8	23.8	0.00160		2
	25.3	20.8	24.2				
	24.1	20.7	22.9				
v_g	25.3						
cm./sec.							
0.0084							

$$\begin{array}{r} 2 \overline{) 0.01050} \\ 0.00525 \end{array}$$

for $v_e = 0.00160$ cm./sec., $\frac{v_g + v_e}{\Delta v_e / \Delta n} = 1.90$, thus $n = 2$ unit charges

and from Figure 6, $(v_e)_0 = 0.0089$ cm./sec. and $n_A = 1.70$ unit charges

Table 2. (continued)

[illegible]

for $v_o = 0.0138$ cm./sec., $\frac{v_g + v_e}{\Delta v_e / \Delta n} = 10.8$, thus $n = 11$ unit charges

and from Figure 6, $(v_e)_0 = 0.0090$ cm./sec. and $n_B = 4.34$ unit charges

thus $(v_e)_o/v_g = D_e/D_g = 0.93$

Figure 6. Determination of mass of copper sulphate agglomerate from Millikan cell data

IV. CALCULATIONS FROM THE MILLIKAN CELL DATA

Calculation of Mass

The measured falling times of a particle in the Millikan cell are listed in the first column of Table 2. The distance travelled divided by the average of these values gives the terminal velocity listed at the bottom of Column 1. The rising velocities under the electrostatic force were determined in a similar way from the rising times given in the next two columns. The average rising velocities are shown in Column 4. The differences between successive rising velocities are shown in Column 5. These increments in velocities must be an integral multiple of the change in velocity caused by one electron charge. If the value of Δn were not readily apparent, the refinement of using the increment of the increments could be used.

The exact number of electrons for each rising velocity is required for the final solution. A first approximation of these values may be calculated by assuming that the Stokes' diameter under the electric field is the same as the diameter under gravity. Thus, the quantity $(v_g + v_e)$ should be an integral multiple of the change in velocity per unit charge. This division was performed and the results were rounded off to the next highest integer. The values of 2 and 11 were determined from the data given in Table 2.

When v_e is zero, the particle is balanced between the electrical and the gravitational forces. Values of n_A and n_B may then be found from the graph of Equation 6 (Figure 6). They were 1.70 and 4.34 charges, respectively. When multiplied by the respective field strengths, the values are proportional to the gravitational forces:

$$m = \frac{neX}{g} = \frac{neV}{300 \text{ gL}} = \frac{4.80 \times 10^{-10} \text{ nV}}{980 \times 0.3 \times 300} = \frac{nV \times 10^{-12}}{183.6} \text{ grams.}$$

$$m_A = \frac{(1.70)(221) \times 10^{-12}}{183.6} = 2.05 \times 10^{-12} \text{ grams.}$$

$$m_B = \frac{(4.34)(90) \times 10^{-12}}{183.6} = 2.12 \times 10^{-12} \text{ grams.}$$

with

$$m_{av.} = 2.08 \times 10^{-12} \text{ grams.}$$

The two measurements are within 2 percent of the average value. The average value of $(v_e)_0$ is 0.00936 cm./sec., which is larger than the value of v_g of 0.00837 cm./sec. Since v_g is inversely proportional to the Stokes' diameter, two different diameters are obtained for this agglomerate. This is caused by a difference in orientation of a non-spherical particle when the center of charge is not at the center of mass.

The second method for the determination of the mass was by balancing the electrical and gravitational forces. Table 3 shows data for one of the experiments on tungsten particles.

Table 3. Voltages required for balancing forces on tungsten particles

Voltage required for balancing	$\frac{V_1}{V}$	Charge, no. of electrons	nV
$V_1 = 235$	1.00	2	470
153	1.54	3	459
115	2.04	4	460
94	2.50	5	470
			4 <u>1859</u>
			465

At first the largest voltage is assumed to correspond to a particle charge

of one electron. If this voltage is divided by each other voltage, the value of n is usually apparent, since nV is constant. From Equation 9

$$m = \frac{nV \times 10^{-12}}{183.6} = \frac{465 \times 10^{-12}}{183.6} = 2.53 \times 10^{-12} \text{ g.} \quad (10)$$

Calculation of Stokes' Diameter and Density of Agglomerates

Calculations, using the free-fall velocity of the copper sulfate pentahydrate particle, follow: from Equation 4

$$CD^2 \rho = \frac{18 \mu v_g}{g} = \frac{(18)(1.83 \times 10^{-4})(0.00837)}{980} = 2.81 \times 10^{-8} \frac{\text{g.}}{\text{cm.}} \quad (11)$$

If the diameter is desired, Equation 1 shows

$$\frac{D}{C} = \frac{mg}{3\pi \mu v_g} = \frac{(2.08 \times 10^{-12})(980)}{3\pi (1.83 \times 10^{-4})(0.00837)} = 1.41 \times 10^{-4} \text{ cm.} \quad (12)$$

The Cunningham factor is found by trial and error in Figure 2, assuming that the correction is applicable when the Stokes' diameter for non-spherical particles is used. Thus,

$$C = 1 + \frac{2A\lambda}{D} = 1 + \frac{1.81 \times 10^{-5}}{1.57 \times 10^{-4}} = 1.115$$

From Equation 12

$$D = 1.57 \text{ microns} \quad (13)$$

The apparent density from Equation 11 is

$$= \frac{2.81 \times 10^{-8}}{CD^2} = \frac{2.81 \times 10^{-8}}{(1.115)(1.57 \times 10^{-4})^2} = 1.04 \text{ g./cc.} \quad (14)$$

The normal density of copper sulphate pentahydrate is 2.28 g./cc.

The results of the Millikan cell measurements are shown in a series of figures which follow, as plots of $CD^2 \rho$ vs. mass on logarithmic

FIG. 7. RELATIONSHIP BETWEEN $CD^2\rho$ AND MASS FOR SPHERICAL PARTICLES IN AIR AT ROOM TEMPERATURE.

coordinates. The equations of the lines have the form, $CD^2\rho = A(m)^B$. They are given for each substance below the corresponding figure. The broken lines represent the relationship between $CD^2\rho$ and mass for single spheres having the densities of the pure substances. The influence of the Cunningham factor, C , makes the line slightly curved. These lines have a slope of $2/3$ and hence the value of B is $2/3$. The value of A depends on the density of the pure substances from which the aerosols were dispersed. The data for any aerosol composed of agglomerates of uniform shape and packing should in fact fall on a line of slope $2/3$. Figure 7 is a nomogram by which the mass and values of $CD^2\rho$ can be found for a spherical particle of any diameter and density within the range of this study.

Figure 8. Relationship of $CD^2\rho$ and mass for magnesium agglomerates

Density of pure substance, $\rho = 1.74$ g./cc.

Equation of experimental line, $CD^2\rho = 1.2m^{0.37}$

Figure 9. Relationship of $CD^2 \rho$ and mass for magnesium oxide agglomerates.

Density of pure substance, $\rho = 1.74$ g./cc.

Equation of experimental line, $CD^2 \rho = 0.94m^{0.42}$

5 μ

Figure 10. Electron micrographs of magnesium agglomerates

2 μ

Figure 11. Electron micrographs of magnesium oxide agglomerates

V. COMPARISON OF MILLIKAN CELL DATA AND ELECTRON MICROGRAPHS OF AGGLOMERATES

There is no apparent correlation between the normal densities of the substances used in the experiment and the apparent densities of the agglomerates. Nevertheless, certain conclusions may be drawn regarding the state of agglomeration when the Millikan cell data are considered in relation to shape and structure as revealed by electron microscopy. Electron micrographs were made of representative agglomerates for each type of substance. These samples were obtained by placing a membrane on a grid over the holes in the top plate of the Millikan cell and introducing the aerosol in the usual manner. Several micrographs are shown as examples of the extent of correlation between the state of agglomeration and the Millikan cell data.

Magnesium

It will be noted in Figure 8 that the slope of the line representing $CD^2 \rho$ vs. mass for magnesium is low compared to the slopes of the corresponding lines for other substances shown in the figures. This is explained by the electron micrographs in Figure 10 which show many loosely packed agglomerates composed of thin flakes, or needles. For this type of primary particle it is conceivable that the percentage of void space increases rapidly as agglomeration proceeds; hence, the larger agglomerates are expected to have decreasing density with increasing mass.

Magnesium Oxide

As in the case of Figure 8 for magnesium, Figure 9 for the oxide shows a low slope. Loosely packed and chain-like structures of magnesium oxide are seen in the micrographs in Figure 11. These agglomerates are composed of heterogeneous primary particles. Presumably the void space increases rapidly as agglomeration proceeds leading to decreasing density with increasing mass.

5μ

Figure 12. Electron micrographs of antimony agglomerates

Figure 13. Relationship of CD^2_{ρ} and mass for antimony agglomerates

Density of pure substance, $\rho = 6.68$

Equation of experimental line, $CD^2_{\rho} = 2.1m^{0.71}$

Figure 14. Relationship of $CD^2 \rho$ and mass for bismuth agglomerates

Density of pure substance, $\rho = 9.8 \text{ g./cc.}$

Equation of experimental line, $CD^2 \rho = 1.9m^{0.69}$

5 μ

Figure 15 (a). Electron micrographs of anhydrous copper sulfate.

10 μ

Figure 15 (b). Electron micrographs of copper sulfate pentahydrate agglomerates

Figure 16. Relationship of CD^2_{ρ} and mass for pentahydrate copper sulfate agglomerates

Density of pure substance, $\rho = 2.28$ g./cc.

Equation of experimental line, $CD^2_{\rho} = 1.8m^{0.66}$

Figure 17. Relationship of $CD^2\rho$ and mass for anhydrous copper sulfate agglomerates

Density of pure substance, $\rho = 3.60$ g./cc.

Equation of experimental line, $CD^2\rho = 2.0m^{0.64}$

Attention is directed to the lower portion of the experimental line in Figure 9. Seven points represent data of Whytlaw-Gray and Patterson, who also measured agglomerates formed from burning magnesium ribbon (17). The agreement with the results of the present work is excellent.

Antimony

The micrographs for antimony (Figure 12) show that there was little agglomeration of the particles dispersed from the nebulizer. The agglomerates which did form appear to be composed of the smallest particles. Most of the larger particles appear to be unitary with irregular shapes and surfaces. The graph of $CD^2\rho$ for antimony (Figure 13) confirms this observation. It approaches the normal density curve for the particles of higher masses. This is to be expected if the large masses are unitary and if the irregular shape is the only property which decreases the terminal velocity.

Bismuth

Since bismuth particles did not adhere to the electron-microscope grid these were studied under an optical microscope where the primary particles appeared to be quite heterogeneous. As in the case of antimony (Figure 13), the graph of $CD^2\rho$ vs. mass for bismuth (Figure 14) approaches the normal density line at higher masses, suggesting a similar explanation to that given in the case of antimony.

Copper Sulfate

The electron micrographs of the anhydrous and the hydrated forms of copper sulfate are shown in Figure 15. The agglomerates appear to be formed from a small number of primary particles. The Millikan cell data in Figures 16 and 17 deviate only slightly from the line based on the normal densities.

5μ

Figure 18. Electron micrographs of graphite agglomerates

Figure 19. Relationship of CD^2_{ρ} and mass for graphite agglomerates

Density of pure substance, 2.25 g./cc.

Equation of experimental line, $CD^2_{\rho} = 1.4m^{0.61}$

5 μ

Figure 20. Electron micrographs of iron agglomerates

Figure 21. Relationship of $CD^2 \rho$ and mass for iron agglomerates

Density of pure substance, $\rho = 7.87 \text{ g./cc.}$

Equation of experimental line $CD^2 \rho = 2.2m^{0.65}$

Figure 22. Relationship of $CD^2 \rho$ and mass for tungsten agglomerates

Density of pure substance, $\rho = 19.3 \text{ g./cc.}$

Equation of experimental line, $CD^2 \rho = 1.7m^{0.59}$

5 μ

Figure 23. Electron micrographs of tungsten agglomerates

Graphite

The micrographs for graphite are shown in Figure 18. There are a large number of agglomerates which appear to be closely packed. In Figure 19 the experimental points for the Millikan cell data fall on a line parallel to the normal density line. Therefore, it may be concluded that the agglomerates, regardless of size, had similar void fractions.

Iron

The micrographs for iron are shown in Figure 20. A substantial number of large and small unitary particles are present and shapes appear very irregular. The Millikan data line shown in Figure 21 approaches, at high masses, to the line calculated from normal density reflecting the influence of large unitary masses. In view of the overall difference between the lines it must be supposed that considerable agglomeration is, in fact, present at all sizes.

Tungsten

The Millikan cell data for tungsten is shown in Figure 22. The points are widely scattered and the line of best fit is farther from the normal density line than is the case of any other substance. The electron micrographs (Figure 23) show agglomerates composed of many small particles and a wide range of sizes and void fractions. In such circumstances, the void fractions of the agglomerates will be as variable as the range of particle sizes and shapes. This accounts for the scatter of the points in Figure 22. The total void fraction will be proportionately high for all sizes of agglomerates; thus the lines are widely separated but parallel.

Polystyrene

Figure 24 shows Millikan cell data for agglomerates formed from polystyrene spheres of 1.71 micron diameter. As required, the two lines

Figure 24. Relationship of $CD^2 \rho$ and mass for polystyrene agglomerates formed from spheres of 1.171 micron diameter

Density of pure substance, $\rho = 1.05 \text{ g./cc.}$

Equation of experimental line $CD^2 \rho = 1.8m^{0.57}$

Figure 25. Electron micrographs of polystyrene agglomerates
formed from spheres 1.171 micron diameter

Figure 26. Electron micrographs of polystyrene aggregates
formed from spheres 0.333-micron ~~in~~ diameter

Figure 27. Relationship of $CD^2\rho$ and mass for polystyrene agglomerates formed from spheres of 0.333-micron diameter

Density of pure substance, $\rho = 1.05$ g./cc.

Equation of experimental line, $CD^2\rho = 1.5m^{0.56}$

Figure 28. Relationship of $CD^2 \rho$ and mass for ammonium chloride agglomerates formed from a heterogeneous primary size

Density of pure substance, $\rho = 1.53 \text{ g./cc.}$

Equation of experimental line, $CD^2 \rho = 1.1m^{0.28}$

5 μ

Figure 29. Electron micrographs of ammonium chloride agglomerates formed from a controlled primary size

5μ

10μ

Figure 30. Electron micrographs of ammonium chloride agglomerates formed from a heterogeneous primary size

converge at the mass of the unitary particles. They diverge as the mass of the agglomerates increases, but the difference is always small because the particles are uniform in size and shape and hence are tightly packed. The micrographs (Figure 25) agree with this interpretation. The case of polystyrene spheres of 0.333 micron diameter is shown by the micrographs in Figure 26, and by the Millikan cell data in Figure 27. The same observations that were made for spheres of 1.71 micron diameter apply.

Ammonium Chloride

Aerosols of homogeneous ammonium chloride particles (0.3-0.8 micron diameter) and of heterogeneous particles were studied. Both the Millikan cell data (Figures 5 and 28) and the electron micrographs (Figures 29 and 30) indicate that the heterogeneous aerosol forms larger and more variable agglomerates than does the homogeneous.

The velocities of agglomerated ammonium chloride particles in the Millikan cell decreased during a period of 1/2 to 1 hour. Several particles were observed for which the velocity decreased gradually two to three fold. The agglomerates may have been breaking up because of nitrogen oxides formed in the arc discharge of the LaMer generator. The phenomenon was not noticed when the concentration of nitrogen oxides was decreased by allowing the gas to diffuse out of the cell. There appeared to be a minimum concentration of nitrogen oxides for peptization. Kohlschutter and Ehlers (7) observed the peptization of smoke agglomerates by carbon dioxide.

Practical Considerations

A variation in drag diameters caused by particle orientation for non-spherical forms is significant in electrical precipitation. For example, a spherical particle would have a ratio of diameters calculated from the

Figure 31. Particle-size distribution of ammonium chloride aerosol, determined from jet-impactor data and from a microscope count

Figure 32. Particle-size distribution of ammonium chloride aerosol, determined for two degrees of agglomeration

rising and falling velocities of 1.0. An irregularly-shaped particle would have a ratio less than 1. If both were equally charged and at the same distance from the wall of a precipitator, the second would have a velocity equal to the reciprocal of the ratio of its diameters times the velocity of the spherical particle. Thus, the velocity of the irregularly shaped particle would be greater than the spherical particle and the efficiency of the electrical precipitator would be higher for the particles of irregular shape.

Figure 31 shows the size distribution of ammonium chloride aerosol formed from primary particles of 0.3 to 0.8 microns in diameter. These distributions were calculated by using the jet impactor data and a microscope count. The two outer lines show the results when the normal density is assumed to hold for the agglomerates. No agreement was found between the distributions derived by the two methods. The inner line was calculated on the basis of the line of Figure 5, which indirectly expresses the variation of the density with the mass of the agglomerates. Excellent correlation of the jet impactor and the microscope count data was found when this curve was used. Thus, the cascade impactor can be used with the CD^2 curves obtained from the Millikan cell measurements to determine the actual mass and size distribution of aerosols when they contain agglomerates.

The mass distributions for two different degrees of agglomeration are shown in Figure 32.

VI. SUMMARY

The effective diameter, porosity, and uniformity of agglomerates formed from several types of aerosols were measured by means of a Millikan cell. The results were compared with electron micrographs of the agglomerates.

1. When an agglomerate is composed of particles of uniform size and shape the void space is minimal and its effective density is close to that of the primary particles from which it is formed. In this case the free-fall velocity of the agglomerate is proportional to the two-thirds power of its mass.

2. When the primary particles are not uniform in size and shape there are wide variations in the density of the agglomerates and a plot of CD^2 vs. mass differs considerably from the line calculated from the normal density of the substance.

3. When the primary particles have irregular shapes there is a difference between the drag diameter of the agglomerate determined from the rising and falling velocities. This has a practical significance in the efficiency of electrical precipitation of such aerosols.

4. The cascade impactor can be used for determining the size distribution of agglomerates when Millikan cell data also are available.

VII. NOMENCLATURE

A = constant in Cunningham correction, dimensionless

C = Cunningham correction factor = $1 + \frac{2A\lambda}{D}$, dimensionless

D = drag diameter of particle determined from Stoke's Law, $F = \frac{3\pi\mu Dv}{C}$

D_e = drag diameter of particle when $v = v_e$

D_g = drag diameter of particle when $v = v_g$, D is used unless emphasis of the force of gravity is desired

e = value of unit electric charge, esu

F = force acting on body, dynes

g = gravitational acceleration, cm./sec.²

$g.$ = mass, grams

L = plate spacing in Millikan cell, cm.

m = mass of particle, grams

n = number of unit electric charges on a particle

t_e = time of rise over measured distance in electric field, sec.

t_g = time of free fall for measured distance, sec.

V = applied potential, volts

v = relative velocity between particle and fluid, cm./sec.

v_e = velocity of rise in an electric field, cm./sec.

v_g = terminal gravitational settling velocity, cm./sec.

X = strength of electric field, esu/cm.

Δ = difference

λ = mean free path of the gas molecules, cm.

μ = viscosity of the gas, poises

ρ = apparent density of a particle calculated on the basis of a sphere of diameter D_g and the particle mass

VIII. BIBLIOGRAPHY

- (1) American Public Health Association, "Standard Methods for the Examination of Water, Sewage and Industrial Wastes," 10th ed., p. 144, Prepared and published jointly by American Public Health Association, American Water Works Association and Federation of Sewage and Industrial Wastes Association, New York, 1955.
- (2) Beeghly, H. F., Ind. Eng. Chem. Anal. Ed., 14, 137 (1942).
- (3) Cunningham, E., Proc. Roy. Soc. (London), A83, 357 (1910).
- (4) Ehrenhaft, J. and Wasser, E., Z. Phys., 37, 820 (1926).
- (5) Kunkel, W. B., J. Appl. Phys., 21, 820 (1950).
- (6) Ibid. p. 833.
- (7) Kohlschutter, V. and Ehlers, C., Z. Electrochem., 18, 373 (1912).
- (8) LaMer, V. K. and Sinclair, D., Chem. Revs., 44, 245 (1949).
- (9) Mattauch, J., Z. Phys., 32, 439 (1925).
- (10) Millikan, R. A., Phys. Rev., 2, 109 (1913).
- (11) Patterson, H. S. and Cawood, W., Trans. Faraday Soc., 32, 1084 (1936).
- (12) Ranz, W. E. and Wong, J. B., Ind. Eng. Chem., 44, 1371 (1952).
- (13) Reiss, M., Z. Phys., 39, 623 (1926).
- (14) Rotzeig, B. and Fuchs, N., Acta Physicochim. U.R.S.S., 5, 893 (1936).
- (15) Wells, P. V. and Gerke, R. H., J. Amer. Chem. Soc., 41, 312 (1919).
- (16) Whytlaw-Gray, R. and Patterson, H. S., Proc. Roy. Soc. (London), A113, 302 (1926).
- (17) Whytlaw-Gray, R. and Patterson, H. S., "Smoke," p. 106, Edward Arnold and Co., London, 1932.