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THEORY OF A DIFFUSION BATTERY

By

Wendell DeMarcus
Jess W. Thomas

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THEORY OF A DIFFUSION BATTERY

Wendell DeMarcus
Jess W. Thomas

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ABSTRACT

A diffusion battery consists of a number of long, narrow rectangular channels arranged in parallel, through which an aerosol moves in streamline flow. The object of the work described in this report was to develop an equation relating the fractional penetration of aerosol with the diffusion constant of the aerosol.

An equation has been developed which allows the calculation of the diffusion constant from known operating parameters in the case of negligible settling due to gravity; and a second equation developed to permit calculation of the settling velocity in case of particle removal due to both diffusion and gravity. A method for calculating the particle size and mass from the diffusion constant and settling velocity is given.

THEORY OF A DIFFUSION BATTERY

I. Introduction

The "diffusion battery" is primarily a device for measuring the diffusion constant of aerosols (smokes) dispersed in air. From the measured diffusion constant, the particle size of the aerosol may be calculated.[1] It is also possible to use the battery for determination of the settling velocity of the particles due to gravity. This permits the calculation of the mass of the particle. Rodebush[2] was probably the first to use the term "diffusion battery" since his apparatus consisted of 40 parallel rectangular plates, somewhat resembling an automobile battery.

A sketch of a typical diffusion battery is shown in Figure 1. It consists of a battery of long, narrow, parallel channels, through which the aerosol moves in streamline flow.

The battery may be used in either of two positions. One of the positions, as indicated on the sketch, has the short dimension of the channels perpendicular to the direction of gravity. The other position, obtained by turning the battery on its side, has the short dimension parallel to the direction of gravity.

To measure the diffusion constant of the aerosol with the apparatus, the short dimension of the channel is placed perpendicular to gravity, and the fractional penetration of the aerosol measured at a known flow rate. The mechanism is as follows: As the aerosol travels through the channel in streamline flow, those particles near the wall of the channel diffuse over to it and are removed from the air stream. This sets up a concentration gradient in the cross section of the channel, and the particles then move by diffusion in the direction of decreasing concentration, that is, toward the wall, and a certain fraction of the particles are removed from the air stream. The fraction removed for the air stream, hence the percentage penetration, is a function only of the diffusion constant of the aerosol, provided the effect of gravity is negligible. This is almost always the case when the battery plates are parallel to gravity.

---

1. Langmuir, Irving, "Filtration of Aerosols and Development of Filter Materials" (Part IV), OSRD-865, Sept. 4, 1942.
2. Rodebush, W. H., C.E. Holley, Jr., B. A. Lloyd, "Progress Report on Filter Penetration by Aerosols of Very Small Particle Size" Univ. of Illinois, OSRD-2050, Nov. 24, 1943.

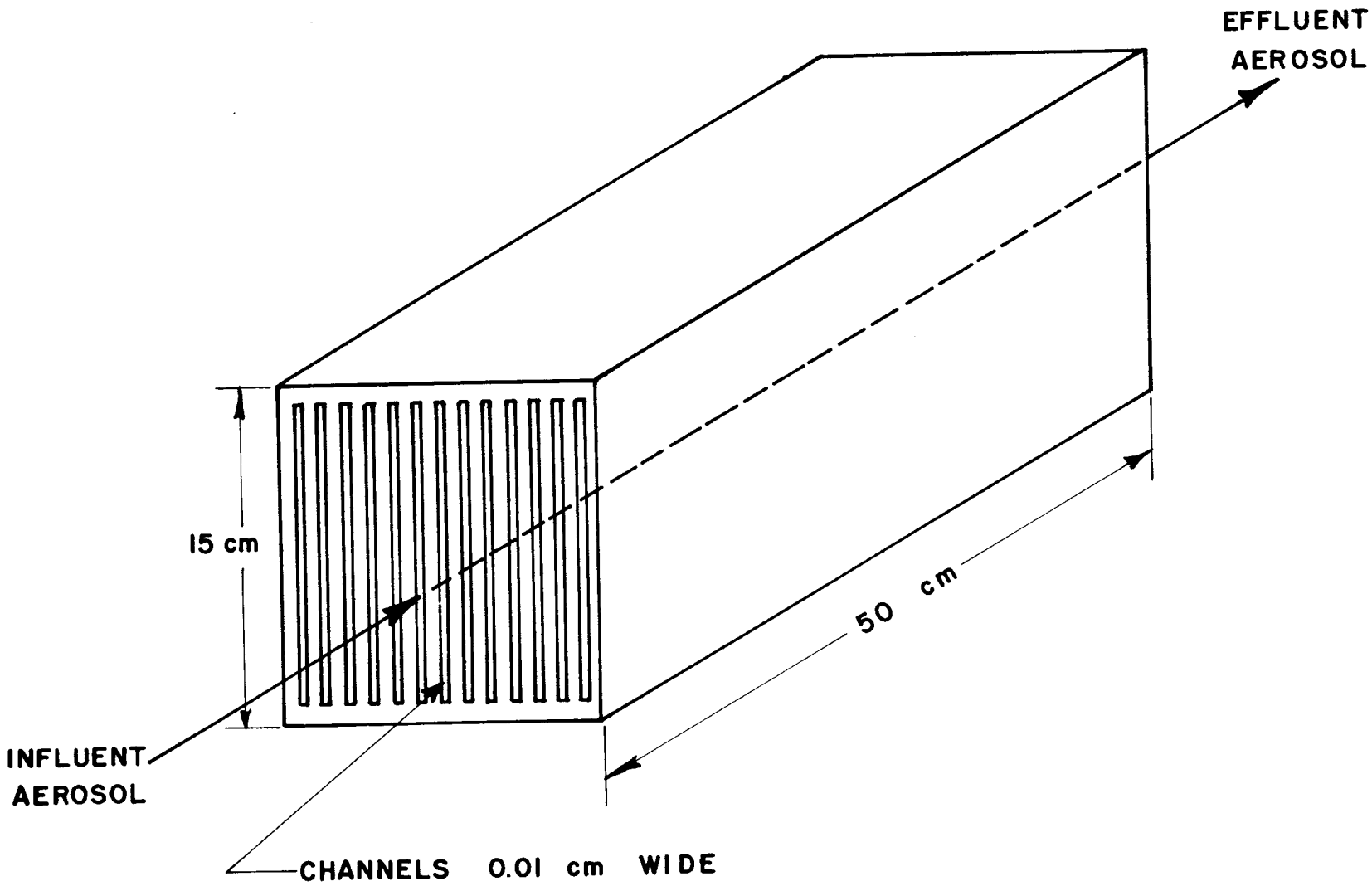

FIGURE I. TYPICAL DIFFUSION BATTERY

To measure the settling velocity of the particles, the battery is used with the short dimension of the channels parallel to gravity, and the percentage penetration again determined. Frequently, in this case, both diffusion and settling contribute appreciably to particle removal, and the resulting differential equations are difficult to solve.

Probably the first work done relating the diffusion constant with the fraction of diffusing particles penetrating the battery was done by Townsend[3] in 1900. Townsend used a circular tube as his battery, to determine the diffusion constant of ions in air.

In 1935 Nolan and Guerrini,[4] with the aid of Timoney, developed an equation for a rectangular battery such as is described here. However, their equation is not valid when the penetration is nearly 100%.

For this reason it was decided to re-derive the basic equation for the case of negligible effect due to gravity. After the work was complete, a later paper by Nolan and Nolan[5] was found, which confirms very closely the final equation given here. This is given below:

$$\frac{J(s)}{J(o)} = 0.915e^{-2.83S} + 0.059e^{-33.5S} + 0.026e^{-227S}$$

$\frac{J(s)}{J(o)}$ = fraction of aerosol penetrating battery

$$S = \frac{4DL}{3Qa}$$

D = diffusion constant of aerosol, cm^2/sec

L = length of battery in direction of flow, cm

a = one half the channel width, cm

Q = flow rate through one channel, cm^3/sec per unit height of channel

3. Townsend, J.S. "The Diffusion of Ions into Gases," Transactions Royal Society, 193-A, 125-158 (1900).
4. Nolan, J.J., and V.H. Guerrini, "The Diffusion Constants and Velocities of Fall in Air of Atmospheric Condensation Nuclei," Proc. Royal Irish Academy, 43, 4-24 (1935).
5. Nolan, J.J., and P.J. Nolan, "Diffusion and Fall in Atmospheric Condensation Nuclei," Proc. Royal Irish Academy, 45, p. 47 (1938).

This equation applies when the channels are placed parallel to gravity, and is valid when the influence of gravity can be neglected. For a battery of the dimensions shown in Figure 1, calculations show that gravity is negligible for a particles of 0.3 microns radius or less.

It was also decided to attempt to develop an equation for the case of the channels perpendicular to gravity, where both gravity and diffusion contribute to particle removal. A formal solution has been obtained, and the numerical values of the lowest eigenvalues have been calculated.

Subsequent sections of this paper give the mathematical theory of the diffusion battery. Implicit assumptions in the derivation of the equations are:

(1) The aerosol is homogeneous with respect to particle size
(2) All particles which contact the wall of the channel adhere
(3) The effect of turbulence in the entrance to the channels is negligible
(4) The pressure drop across the battery is small
(5) The diffusion of the particles is not affected by electrostatic changes on the particles or battery wall.

II. Derivation of General Equations

The diffusion battery considered below consists of a large number of rectangular channels of lateral dimensions 2a, 2b and longitudinal dimension L. It is sufficient to consider only one channel. The dimension b is very much greater than the dimension a so that for many purposes one may consider b as infinite and deal with the case of parallel planes. As origin of coordinates, we take the center of the front entrance of the channel with the axis of X perpendicular to the long width of the channel and axis of Y perpendicular to the short width of the channel. The axis of Z we take positive into the channel. Thus the channel is bounded by segments of the planes

$$x = a$$
$$x = -a$$
$$y = b$$
$$y = -b$$
$$z = 0$$
$$z = L$$

In operations, air containing dust or smoke particles is forced through the channel at low rates. Neglecting entrance effects, the flow will be laminar; and disregarding this entrance effect and edge effects of the long width, the velocity profile will be parabolic. Let V (x) be the velocity at a point x

centimeters from the central plane of the channel and V_c the velocity at the central plane. Then it is well known[6] that

$$V(x) = V_c \ (1 - x^2/a^2)$$

for a viscous fluid. Let Q be the volume of air per second flowing through unit height of the channel. Then we have

$$Q = \int_{-a}^{a} V_c \ (1 - x^2/a^2) \ dx = \frac{4a}{3} \ V_c \quad .$$

We can thus express the velocity profile in terms of Q,

$$V(x) = \frac{3Q}{4a} \ (1 - x^2/a^2).$$

Let the diffusion coefficient of the dust or smoke particles in the air be D and let ϕ (x, y, z) be the number of particles per unit volume at the point x, y, z. Then diffusion alone will give rise to a current density vector whose components are

$$\overrightarrow{(J_x)}_D = -D \ \partial\phi/\partial x,$$

$$\overrightarrow{(J_y)}_D = -D \ \partial\phi/\partial y,$$

$$\overrightarrow{(J_z)}_D = -D \ \partial\phi/dz;$$

or

$$\overrightarrow{(J)}_D = -D \text{ grad } \phi .$$

In addition there will be a net current density in the Z direction due to convection of amount

$$\overrightarrow{(J_z)}_C = 3Q/4a \ (1 - x^2/a^2) \phi ,$$

and a current due to the influence of gravity directed vertically downwards whose magnitude will be

$$\vec{v}_g \phi$$

6. Lamb, Sir Horace, Hydrodynamics, Sixth Edition, p 582, Dover Publications, 1945.

where $\vec{v_g}$ is the terminal velocity of free fall for the particles considered. As mentioned in the introduction, there are two experimental arrangements of primary interest. The first arrangement has the direction of gravity parallel to the axis of negative y and its effect is negligible since the dimension in this direction is large. In the second case the force of gravity is in the negative x direction. The necessary partial differential equations relevant to the problem can now be written down by applying the equation of continuity, viz

$$\frac{\partial \phi}{\partial t} + \operatorname{div} \vec{J} = 0$$

or more explicitly

$$\frac{\partial \phi}{\partial t} - D\nabla^2\phi + \frac{3Q}{4a}(1 - x^2/a^2)\frac{\partial \phi}{\partial z} + v_g \operatorname{div}(\phi\vec{g}) = 0.$$

In the above, $\vec{g}$ is a unit vector in the direction of gravity and ∇^2 is the Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

If we consider a steady state of the arrangement in which the effect of gravity can be neglected we have

$$D\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2}\right) = \frac{3Q}{4a}(1 - x^2/a^2)\frac{\partial \phi}{\partial z}.$$

Neglecting diffusion effects in the y and z directions further reduces this to

$$D\frac{\partial^2\phi}{\partial x^2} = \frac{3Q}{4a}(1 - x^2/a^2)\frac{\partial \phi}{dz}.$$

Let $x = ax'$, $s = \frac{4D}{3Qa}z$.

In terms of the new variables x' and s we have, for $\phi(x', s)$

$$\frac{\partial^2\phi}{\partial x'^2} = (1 - x'^2)\frac{\partial \phi}{\partial s}$$

If the direction of gravity is along the negative axis of x, by neglecting diffusion in the Y Z plane one obtains

$$D\frac{\partial^2\phi}{\partial x^2} = \frac{3Q}{4a}(1 - x^2/a^2)\frac{\partial \phi}{\partial z} - v_g\frac{\partial \phi}{\partial x}.$$

Again letting $x = ax'$, $s = \frac{4D}{3aQ} z$, the equation becomes

$$\frac{\partial^2 \phi}{\partial x'^2} + \frac{a}{D} v_g \frac{\partial \phi}{\partial x'} = (1 - x'^2) \frac{\partial \phi}{\partial s} .$$

If we assume that the streamline flow is established exactly at $z = 0$ and that the entrant air contains a uniform concentration of particles, the boundary conditions are

$$\phi(\pm a, z) = 0 \qquad z > 0$$

$$\phi(x, 0) = 1 \qquad -1 < x < +1$$

or in terms of x' and s

$$\phi(\pm 1, s) = 0$$

$$\phi(x', 0) = 1.$$

The first boundary condition expresses the fact that particles impinging on the walls of the battery adhere thereto.

The quantity which is measured experimentally is the ratio of the total current of particles leaving the battery to the total current entering the battery. Let $K(s)$ be the total number per unit time crossing the plane $s =$ const. Then $K(s)$ is proportional to the quantity $J(s)$ where

$$J(s) = \int_{-1}^{1} \phi(x, s) \, (1 - x^2) \, dx.$$

III. Solution of the Boundary Value Problem When the Effects of Gravity are Negligible

The partial differential equation to be solved is

$$\frac{\partial^2 \phi}{\partial x^2} = (1 - x^2) \frac{\partial \phi}{\partial s}$$

with the boundary conditions

$$\phi(x, 0) = 1,$$
$$\phi(1, s) = 0,$$
$$\phi(-1, s) = 0$$

where we have dropped the prime on x. We note that there are solutions to the partial differential equation of the form

$$\phi(x, s) = \psi(x)e^{-as}$$

where a is constant. The differential equation for $\psi(x)$ is then

$$\frac{d^2\psi}{dx^2} + a(1 - x^2)\psi = 0$$

and the boundary conditions are

$$\psi(1) = \psi(-1) = 0.$$

This is an eigenvalue problem with a discrete spectrum of eigenvalues a_i. Let the function corresponding to the eigenvalues a_i be $\psi_i(x)$. We shall now show that the sequence of functions $\{\psi_i\}$ is orthogonal in the interval $-1 \leqq x \leqq +1$ with weight function $\rho(x)$ where

$$\rho(x) = 1 - x^2.$$

The differential equations for $\psi_i(x)$ and $\psi_j(x)$ are

$$\frac{d^2\psi_i}{dx^2} + a_i(1 - x^2)\psi_i = 0,$$

$$\frac{d^2\psi_j}{dx^2} + a_j(1 - x^2)\psi_j = 0.$$

Multiplication of the first equation by ψ_j, the second by ψ_i and subtraction of the results gives

$$\left\{\psi_j \frac{d^2\psi_i}{dx^2} - \psi_i \frac{d^2\psi_j}{dx^2}\right\} + (a_i - a_j)(1 - x^2)\psi_i\psi_j = 0.$$

The term in curly brackets above is the derivative of

$$\psi_j \frac{d\psi_i}{dx} - \psi_i \frac{d\psi_j}{dx}.$$

Accordingly if we integrate the foregoing expression from -1 to +1 we get

$$\left.\psi_j \frac{d\psi_i}{dx} \quad \psi_i \frac{d\psi_j}{dx}\right|_{-1}^{1} + (a_i - a_j)\int_{-1}^{1}(1 - x^2)\psi_i(x)\psi_j(x)dx = 0.$$

Since both ψ_i and ψ_j vanish at $x = \pm 1$ we have

$$(a_i - a_j) \int_{-1}^{1} (1 - x^2)\psi_i \, \psi_j \, dx = 0.$$

This is the required orthogonality relation.

We now assume that the set of eigenfunctions $\{\psi_i\}$ and the set of eigenvalues $\{a_i\}$ are known. In addition we suppose that the eigenfunctions have been normalized, i. e.

$$\int_{-1}^{1} (1 - x^2) \, \psi_i^2 \, (x) \, dx = 1.$$

The formal solution for $\phi(x, s)$ can now be written down

$$\phi(x, s) = \sum_{\nu=1}^{\infty} a_\nu \psi_\nu(x) e^{-a_\nu s}.$$

The problem is solved if we can determine the constants a_ν so that

$$\phi(x, 0) = \sum_{\nu=1}^{\infty} a_\nu \psi_\nu(x) = 1.$$

Multiplication of the two members of the preceding equation by $(1 - x^2)$ $\psi_n(x)$ gives

$$\sum_{\nu=0}^{\infty} a_\nu (1 - x^2) \psi_\nu(x) \psi_n(x) = (1 - x^2) \psi_n(x)$$

and integration from -1 to +1 gives further

$$a_n = \int_{-1}^{1} (1 - x^2) \, \psi_n(x) \, dx$$

the coefficients of all the other constants being zero by virtue of the orthogonality of the functions.

It is of interest to examine the behavior of the function

$$J(s) = \int_{-1}^{1} (1 - x^2)\, \phi(x, s)\, dx.$$

We have formally

$$J(s) = \int_{-1}^{1} (1 - x^2) \left\{ \sum_{\nu = 1}^{\infty} a_\nu \psi_\nu(x)\, e^{-a_\nu s} \right\} dx$$

$$= \sum_{\nu = 1}^{\infty} a_\nu^2\, e^{-a_\nu s}.$$

At $s = 0$ we have

$$J(0) = \sum_{\nu = 1}^{\infty} a_\nu^2 = \int_{-1}^{1} (1 - x^2)\, \phi^2(x, 0)\, dx$$

$$= \frac{4}{3}.$$

Therefore

$$\frac{J(s)}{J(0)} = \frac{3}{4} \sum_{\nu = 1}^{\infty} a_\nu^2\, e^{-a_\nu s}.$$

This completes the formal solution of the problem. We are now concerned with obtaining the eigenvalues and eigenfunctions needed.

Since the function $f(x) = 1$ is even in the interval $-1 \leqq x \leqq +1$, no odd eigenfunctions will appear in its expansion. Accordingly for the present we seek only solutions for which

$$\psi(0) = 1,$$

$$\left(\frac{d\psi}{dx}\right)_{x=0} = 0.$$

These two conditions above completely define the value of the solution to

$$\frac{d^2\psi}{dx^2} + a\,(1 - x^2)\psi$$

at the points $x = \pm 1$. Denote this value by

$$F(a) = \psi_a(1)$$

The desired eigenvalues are the roots of $F(a) = 0$.

Several values of $F(a)$ can be obtained by direct integration of the differential equation. Let $\psi(x) = \phi(x)\, e^{-(1/2)\sqrt{a}\, x^2}$. The differential equation for $\phi(x)$ is

$$\frac{d^2\phi}{dx^2} - 2\sqrt{a}\, x \frac{d\phi}{dx} + (a - \sqrt{a})\phi = 0$$

and putting $t = a^{1/4}\, x$ gives

$$\frac{d^2\phi}{dt^2} - 2t\frac{d\phi}{dt} + (\sqrt{a} - 1)\phi(t) = 0.$$

This is Hermite's differential equation[7] and if $\sqrt{a} - 1 = 2n$ where n is an integer, solutions are Hermite Polynomials of degree n. We need even solutions so that we restrict ourselves to $\sqrt{a} = 4n + 1$, $(n = 0, 1, 2)$. The solutions are then

$$\phi = H_{2n}\,[(4n + 1)^{1/4}\, x]$$

or

$$\psi = H_{2n}\left\{(4n + 1)^{1/4}\, x\right\} e^{-(2n + \frac{1}{2})\, x^2}$$ wherein H_{2n} is the Hermitian Polynomial of degree 2n. The even Hermitian Polynomials for the first few orders are given below;

$$H_o(u) = 1,$$

7. Courant, R., and D. Hilbert, Mathematische Physik, p. 440, Springer, Berlin, (1931).

$$H_2(u) = 4u^2 - 2,$$

$$H_4(u) = 16u^4 - 48u^2 + 12.$$

The solutions obtained do not yet give values for $F(\alpha)$ since we do not necessarily have $\psi(0) = 1$. The correction solutions are

$$\frac{H_{2n}\left\{(4n+1)^{1/2}\ x\right\}}{H_{2n}(0)}\ e^{-(2n+1/2)x^2}$$

We have thus evaluated infinitely many values of the function $F(\alpha)$ whose roots we desire.

Suppose that

$$\psi(x) = \sum_{n=0}^{\infty} a_n(\alpha)\, x^n$$

The differential equation gives the recursion relations for the $a_n(\alpha)$ as

$$(n+2)(n+1)\, a_{n+2}(\alpha) + \alpha\left[a_n(\alpha) - a_{n-2}(\alpha)\right] = 0.$$

Dropping the argument α and rearranging we get

$$a_{n+2} = -\frac{\alpha}{(n+1)(n+2)}\left[a_n - a_{n-2}\right].$$

Our boundary conditions give

$$a_0 = 1,$$
$$a_1 = 0.$$

The value of $F(\alpha)$ is then

$$F(\alpha) = \sum_{n=0}^{\infty} a_n(\alpha),$$

where the $a_n(\alpha)$ are computed from the recursion formula above. Following we give the first two roots of $F(\alpha) = 0$ and the set of a_n corresponding thereto which define the eigenfunctions.

$\alpha = 2.827764$

n	a_n
0	1.000000
2	- 1.413882
4	.568824
6	- .007071
8	.038160
10	- .007071
12	.000969
14	- .000125
16	.000013
18	- .000001

$$\psi_1(x) = \sum a_n x^n$$

$\alpha = 32.147265$

n	a_n
0	1.000000
2	- 16.073633
4	45.739217
6	- 66.237136
8	64.280955
10	- 46.619996
12	27.008805
14	- 13.005300
16	5.359767
18	- 1.929368
20	.616647
22	- .177159
24	.046230
26	- .011048
28	.002436
30	- .000498
32	.000095
34	- .000017
36	.000003

$$\psi_2(x) = \sum a_n x^n$$

Further solutions can be found in the same manner but the number of constants required in the expansion rapidly becomes prohibitively large.

A second method of obtaining solutions makes use of a variational principle. Consider all sectionally smooth functions $\phi(x)$ for which simultaneously

$$\int_{-1}^{1} (1 - x^2)\, \phi^2(x)\, dx = 1,$$

$$\phi(\pm 1) = 0,$$

and consider the value of the integral

$$I(\phi) = \int_{-1}^{1} \left(\frac{d\phi}{dx}\right)^2 dx,$$

for every function of the class defined above. Then the eigenfunctions $\psi_i(x)$ are those functions $\phi_i(x)$ which give stationary values to $I(\phi)$. We make use of this in the following manner:

Using the Schmidt orthogonalization process,[8] we construct a sequence of even polynomials $F_{2n}(x)$ which individually satisfy the boundary conditions

$$F_{2n}(\pm 1) = 0,$$

and in addition,

$$\int_{-1}^{1} (1 - x^2)\, F_{2n}(x)\, F_{2n}(x)\, dx \begin{cases} = 0 & m \neq n \\ = 1 & m = n \end{cases}.$$

As an approximation for $\psi(x)$ we take

$$\psi^*(x) = \sum_{n=1}^{N} A_n F_{2n}(x) .$$

The value of $I(\psi^*)$ will then be a homogeneous quadratic form in the variables $A_1, A_2, \ldots, A_N$; i.e. of the form

8. Courant, R. and D. Hilbert, Mathematische Physik, p. 41, Springer, Berlin, (1931).

$$I = C_{11} A_1^2 + C_{12} A_1 A_2 + C_{22} A_2^2 + \cdots$$

$$+ C_{N-1,N} A_{N-1} A_N + C_{NN} A_N^2$$

where the C_{ij} are constants. The condition that

$$\int_{-1}^{1} (1 - x^2) \left[\psi^* (x) \right]^2 dx = 1$$

will be expressible also as a quadratic function of the A, viz.

$$S = S_{11} A_1^2 + S_{22} A_2^2 + \ldots + S_{NN} A_N^2 = 1$$

since the polynomials are orthogonal among themselves.

We thus need to minimize the function I of the N variables A_i subject to the constraining relation $S(A_1, A_2, \ldots, A_N) = 1$. To accomplish this we make use of Lagrange's undetermined multiplier. This leads to the following equations for a minimum of I;

$$C_{11} A_1 + C_{12} A_2 + \ldots + C_{1N} A_N + \alpha S_{11} A_1 = 0,$$

$$C_{12} A_1 + C_{22} A_2 + \ldots + C_{2N} A_N + \alpha S_{22} A_2 = 0,$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$C_{1N} A_N + C_{2N} A_2 + \ldots + C_{NN} A_N + \alpha S_{NN} A_N = 0,$$

$$S_{11} A_1^2 + S_{22} A_2^2 + \ldots + S_{NN} A_N^2 = 1.$$

The N homogeneous equations for the N unknowns A_i have a nontrivial solution if and only if the determinant

$$D = \begin{vmatrix} C_{11} + \alpha S_{11} & C_{12} & \ldots & C_{1N} \\ C_{12} & C_{22} + \alpha S_{22} & & C_{2N} \\ \cdots & \cdots & \cdots & \cdots \\ C_{1N} & \ldots & & C_{NN} + \alpha S_{NN} \end{vmatrix}$$

is zero. Solving the equation D = 0 involves finding the roots of a polynominal of the Nth degree. For each value of the N values α which made D = 0 we can solve for

$$\frac{A_2}{A_1}, \frac{A_3}{A_1}, \ldots \frac{A_N}{A_1}$$

and finally determine A_1 from the condition

$$S = A_1^2 \left\{ S_{11} + S_{22} \frac{A_2^2}{A_1^2} + \ldots + S_{NN} \frac{A_N}{A_1^2} \right\} = 1$$

The approximate eigenvalues are thus determined and the approximate eigenfunctions likewise.
The function

$$\frac{J(s)}{J(0)}$$

obtained for their use is given below:

$$\frac{J(s)}{J(0)} = .91489\, e^{-2.827785s}$$

$$+ .059245\, e^{-33.5s}$$

$$+ .025865\, e^{-227.672s}$$

The last method of solution we present is similar in technique to the standard perturbation methods. In essence it is an expansion in Fourier Series. We start with the solutions to the simple boundary value problem

$$\frac{d^2u}{dx^2} + \lambda u = 0$$

with boundary conditions $u(\pm 1) = 0$. The solutions are of two types. Even functions

$$u_m = \cos (m + 1/2)\pi x \qquad m = 0, 1, 2, \ldots$$

with eigenvalues $\lambda_m = (m + 1/2)^2 \pi^2$ and odd functions

$$u_m = \sin m\pi x \qquad m = 1, 2, \ldots$$

with eigenvalues $\lambda_m = m^2 \pi^2$. For reasons already stated we dismiss the odd functions from consideration so that in the sequel u_m will always denote the cosine function. Now we turn to the differential equation for the mth eigenfunction of the equation

$$\frac{d^2\psi_m}{dx^2} + a_m (1 - x^2)\, \psi_m = 0$$

and expand ψ_m in terms of the orthonormal set $\{u_n\}$

$$\psi_m = u_m + \sum_{n \neq m} \beta_{nm} u_n \quad .$$

The second derivative of ψ_m is

$$- \lambda_m u_m - \sum_{n \neq m} \lambda_n \beta_{nm} u_n$$

by virtue of the differential equations satisfied by the u_n. Accordingly the differential equation becomes

$$-\lambda_m u_m - \sum_{n \neq m} \beta_{nm} u_n + \alpha_m (1 - x^2) u_m$$

$$+ \alpha_m (1 - x^2) \sum_{n \neq m} \beta_{nm} u_n = 0.$$

If we multiply throughout by u_m and thereafter integrate from -1 to 1 using the orthogonality of the u_n we get

$$-\lambda_m + \alpha_m (1 - C_{mm}) - \alpha_m \sum_{n \neq m} \beta_{nm} C_{mn}$$

In the above we have made use of the definition

$$C_{mn} = C_{nm} = \int_{-1}^{1} x^2 u_m u_n \, dx$$

One notes that the C_{mn} are determined from this relation once and for all. If, instead of multiplying the differential equation throughout by u_m, we multiply throughout by u_s $(s \neq m)$ and integrate the result we obtain

$$-\lambda_s \beta_{sm} - \alpha_m C_{sm} + \alpha_m B_{sm} - \alpha_m \sum_{n \neq m} \beta_{nm} C_{ns} \; .$$

Rewriting the two equations we have

$$\alpha_m = \frac{\lambda_m}{1 - C_{mm} - \sum_{n \neq m} \beta_{nm} C_{mn}} \quad ,$$

$$\beta_{sm} = \frac{\alpha_m}{\alpha_m - \lambda_s} \left[C_{sm} + \sum_{n \neq m} \beta_{nm} C_{ns} \right].$$

The form in which we have written the equations suggests a method of successive approximations to solve the equations for α_m and the β_{sm} $(s \neq m)$.

As a zero approximation we take $\beta_{sm}^{(0)} = 0$ $(s \neq m)$. The first approximation for α_m is then

$$\alpha_m^{(1)} = \frac{\lambda_m}{1 - C_{mm}},$$

and the first approximation to β_{sm} is

$$\beta_{sm}^{(1)} = \frac{\alpha_m^{(1)}}{\alpha_m^{(1)} - \lambda_s} \left[C_{sm} \right].$$

In general the (K + 1) approximation for α_m is

$$\alpha_m^{(K+1)} = \frac{m}{1 - C_{\lambda m} - \sum_{n \neq m} \beta_{nm}^{(K)} C_{mn}},$$

and similarly for the $\beta_{sm}^{(K+1)}$

$$\beta_{sm}^{(K+1)} = \left\{ \frac{\alpha_m^{(K+1)}}{\alpha_m^{(K+1)} - \lambda_s} \right\} \left\{ C_{sm} + \sum_{n \neq m} \beta_{nm}^{(K)} C_{ns} \right\}.$$

The results of calculations using the above formulae agree exactly with the results obtained by the power series method, thus affording a check on the results.

IV. Integration of the Partial Differential Equation Including the Effects of Gravity.

For this case the partial differential equation becomes

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{a v_g}{D} \frac{\partial \phi}{\partial x} = (1 - x^2) \frac{\partial \phi}{\partial s}$$

Before integrating this equation, it is of interest to solve the problem in the limiting case of $\frac{av_g}{D} >> 1$. We may then neglect the term involving the second partical derivative and deal only with the simple equation

$$\frac{av_g}{D} \frac{\partial \phi}{\partial x} - (1 - x^2) \frac{\partial \phi}{\partial s} = 0 .$$

We have

$$\frac{dx}{ds} = \frac{\frac{\partial \phi}{\partial s}}{\frac{\partial \phi}{\partial x}} = - \frac{av_g}{D(1 - x^2)} ,$$

or

$$(1 - x^2)\, dx = - \frac{av_g}{D}\, ds ,$$

which integrates to

$$x - \frac{x^3}{3} = - \frac{av_g}{D} s + x_o - \frac{x_o^3}{3} .$$

Thus particles describe the family of curves in the x, s plane described by the above equation with parameter x_o being the initial value of x. The path traced by a particle which initially entered at x = 1 is given by

$$x - \frac{x^3}{3} + \frac{av_g}{D} s = \frac{2}{3}$$

and at s the function $\phi = 1$ for $-1 \leqq x \leqq \tau$ and $\phi = 0$ for $\tau \leqq x \leqq 1$ where

$$\tau - \frac{\tau^3}{3} + \frac{av_g}{D} s - \frac{2}{3} = 0 .$$

Hence

$$J(S) = \int_{-1}^{\tau} (1 - x^2)\, dx = \tau - \frac{\tau^3}{3} + \frac{2}{3} .$$

From the preceding equation

$$\tau - \frac{\tau^3}{3} = \frac{2}{3} - \frac{av_g s}{D},$$

and therefore

$$J(S) = \frac{4}{3} - \frac{av_g s}{D}$$

On recalling that $3Q$ as $= 4D$ and using $J(o) = \frac{4}{3}$ there results

$$\frac{J(S)}{J(0)} = 1 - \frac{v_g z}{Q}$$

If the length of the battery L is greater than Q/v_g, no particles will penetrate.

Returning to the equation

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{av_g}{D} \frac{\partial \phi}{\partial x} = (1 - x^2) \frac{\partial \phi}{\partial s}$$

and again putting $\phi(x, s) = \psi(x)\, e^{-\alpha s}$, one obtains

$$\frac{d^2\psi}{dx^2} + \frac{av_g}{D} \frac{d\psi}{dx} + \alpha(1-x^2)\psi = 0.$$

The relevant boundary conditions are

$$\psi(\pm 1) = 0.$$

Next put

$$\psi(x) = \tau(x)\, e - \frac{av_g}{2D} x \ .$$

The differential equation for $\tau(x)$ is

$$\frac{d^2 \tau}{dx^2} - \left(\frac{av_g}{2D}\right)^2 \tau + \alpha(1 - x^2)\tau = 0 \ .$$

Again, we need solutions which vanish at $x = \pm 1$, and therefore we have once more an eigenvalue problem giving rise to eigenvalue α_i. This time we may not ignore the odd eigenvalue. We express $\phi(x, s)$ as the sum

$$\phi(x, s) = \sum_{=0}^{\infty} A_i\, e^{-\frac{av_g}{2D} x}\, \tau_i(x) e^{-\alpha_i s} \ .$$

If we multiply both sides by $e^{(av_g/2D)x}$ $(1-x^2)\zeta_i(x)$ and integrate from -1 to 1 after putting s = o we obtain

$$\int_{-1}^{1} e^{(av_g/2D)x}(1-x^2)\zeta_j(x)\,dx = A_j\int_{-1}^{1}(1-x^2)\zeta_j^2(x)\,dx.$$

This form is necessary because it is the function $\zeta_j(x)$ and not the corresponding $\psi_j(x)$ which form an orthogonal family. (The orthogonality proof is exactly like the corresponding one when gravity was considered negligible.)

The numerical work involved in a complete solution of the problem would be much greater than for the corresponding case of $v_g = o$ since one more parameter has to be included. Therefore below we present only the first two eigenvalues as a function of

$$\sigma^2 = \left(\frac{av_g}{2D}\right)^2.$$

Several numerical pairs of eigenvalue as function of σ^2 were obtained with σ^2 varying from 0 to 10. Over this range the smallest eigenvalue can be represented satisfactorily by the formula

$$\alpha_0 = 2.827764 + 1.141113\,\sigma^2 - .001332\,\sigma^4,$$

and the second eigenvalue α_1 by

$$\alpha_1 = 13.485758 + 1.339451\,\sigma^2 - .002109\,\sigma^4.$$

Thus for $s > 0$ $J(s)$ will be essentially a constant times $e^{-\alpha_0 s}$, since the second eigenvalue, for $0 < \sigma^2 < 10$, is always much greater than the smallest eigenvalue. Thus, for all practical purposes, we may write,

$$J(s) = K_1\,e^{-\alpha_0 s}$$

where K_1 is an unknown constant.

This is equivalent to writing

$$\frac{J(s)}{J(o)} = K_2\,e^{-\alpha_0 s}$$

$$\ln \left\{ \frac{J(s)}{J(o)} \right\} = K_3 - \alpha_o s$$

Since $S = \frac{4DL}{3Qa}$, it is possible experimentally to vary S by changing the flow rate Q through the battery, obtaining a value of $\frac{J(S)}{J(o)}$, the fractional penetration through the battery, for each value of S. By plotting the natural logarithm of $\frac{J(S)}{J(o)}$ against S, α_o is obtained as the slope of the curve. From the value of α_o, σ^2 is calculated and from this, the quantity $\frac{v_g}{D}$ obtained. Since the value of D can be determined by use of the battery in the position where gravity is negligible, v_g, the settling velocity of the particles, may be obtained.

V. Use of Battery for Assessing a Homogeneous Liquid Aerosol

Essentially, use of the battery and the equations developed herein allow one to determine the diffusion constant D of the aerosol and the ratio $\frac{v_g}{D}$. Langmuir[1] gives the relation between the diffusion constant of the aerosol and the particle radius:

$$D = \frac{KT}{6\pi\eta r}\left[1 + A\frac{\lambda}{r}\right],$$

$$A = A_o + B e^{-C\frac{r}{\lambda}}$$

r = radius of the particle,
D = diffusion constant of aerosol, cm^2/sec,
K = Boltzman's constant (1.38×10^{-16} ergs/^oC),
T = absolute temperature, ^oK,
η = viscosity of air at T, cgs units,
λ = mean free path of air molecule, cm, at T.

Many investigators, particularly Millikan,[9] have measured the ABC constants, but the values reported vary and also depend on the value of λ, the mean free path, used in each particular case.

9. Millikan, R. A., "The General Law of Fall of a Small Spherical Body Through a Gas," Physical Review, 22, 1-23.

From the values and formulae given by Partington[10] and Kennard[11] we may take the modern value of the mean free path of an air molecule at 20°C, 760 mm, to be 6.47×10^{-6} cm. Langmuir[1] summarized the results of previous investigators and gave $A_0 = 0.62$, $B = 0.22$, $C = 2.2$. Langmuir used an obsolete value of the mean free path, 1.31×10^{-5} cm at 20°C, 760 mm. Correcting his results to the modern value of the mean free path, there is obtained,

$$A_0 = \frac{1.31 \times 10^{-5}}{6.47 \times 10^{-6}} (0.62) = 1.25,$$

$$B = \frac{1.31 \times 10^{-5}}{6.47 \times 10^{-6}} (0.22) = 0.44,$$

$$C = \frac{6.47 \times 10^{-6}}{1.31 \times 10^{-5}} (2.2) = 1.09 .$$

Using the value of D found by use of the diffusion battery, r, the radius of the particle, may be calculated by the above equation.

The quantity $\frac{v_g}{D}$, determined by use of the battery, permits the calculation of the mass of the particle by the following relationship:

$$\frac{v_g}{D} = \frac{mg}{KT} ,$$

where m is the mass of the particle and g the acceleration of gravity. This relationship may be derived as follows: For a homogeneous aerosol, statistical thermodynamics shows that in the equilibrium state the concentration of particles ϕ as a function of height Z in a uniform gravitational field is given by

$$\phi \sim e^{-\frac{mgz}{KT}} .$$

The one dimensional diffusion equation in a gravitational field predicts a net current upwards of the amount

$$\vec{J}_z = -D \frac{\partial \phi}{\partial z} - v_g \phi$$

10. Partington, J. R., "An Advanced Treatise on Physical Chemistry," London, Longmans (1949).
11. Kennard, E. H., "Kinetic Theory of Gases," New York, McGraw-Hill (1939).

In the steady state the current is zero and hence

$$\phi = \phi_{(o)} \cdot e^{-\frac{v_g}{D} Z}$$

Comparison of the two exponential terms yields the identity

$$\frac{v_g}{D} = \frac{mg}{KT}$$

When using the battery to assess a homogeneous aerosol, the density of the aerosol particle will be known. Since it is possible by use of the battery, to obtain both the size and mass of the particle, it is possible to check the validity of the method and equations by comparing the density of the particle as given by the battery to the known density.

Another check on the battery performance and equations may be made by holding all conditions constant except the flow rate, and comparing the experimental rate of change of battery penetration with flow rate to that predicted from the equations given herein.