DIFFUSION COEFFICIENTS OF CHARGED AEROSOL PARTICLES.

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1. INTRODUCTION.

The diffusion coefficient (D) of aerosol particles in the sub-micron size range can be determined by measuring the ratio of the particle concentration at the entrance and exit of rectangular or cylindrical channels. (Nolan, Nolan and Gormley (1938) and Gormley and Kennedy (1949)). Fuchs (1964) drew attention to the effect of image forces on the deposition of charged particles on surfaces and the consequent over estimation of D as measured by these methods. His criticism of the work of Nolan and O'Connor (1955) is discussed fully in a paper by Anderson, Nolan and O'Connor (1968) who showed that the inclusion of image forces in the calculation of the diffusion coefficients did not alter the results significantly, unless the particles were highly charged particles only.

The present paper presents the results of some experiments made to measure the diffusion coefficients of homogeneous aerosol particles when charged and uncharged.

Nolan and O'Connor (1955) produced the aerosol particles by bubbling filtered air through distilled water. The particles were heterogeneous with an average radius of $1.52 \times 10^{-6}$ cm and on production they were practically all charged, some with over 100 electronic charges. For the ions of lower mobilities the concentration of positive and negative ions were about equal but the negative ions predominated at the higher mobilities. For the purpose of the present investigations a simple aerosol was needed, which ideally would be monodisperse, controllable in size and concentration, and capable of being highly charged with ions of one sign. The main problem is that it becomes difficult to measure the diffusion coefficient of particles which are large enough to acquire a substantial charge only by a diffusion charging process.

2. APPARATUS.

(i) Aerosol Generator: A monodisperse aerosol generator was constructed following the design of Liu, Whitby and Yu (1966). The liquid dicycyl phthalate (DOP) was atomized by high pressure filtered air, the droplets were evaporated and allowed to recondense. The operating conditions, particularly the atomizing pressure, could be regulated to produce an aerosol of any desired size and concentration. The generator, which is simple to construct, takes about 10 minutes to reach steady operation and gives satisfactorily reproducible results. On production less than ten per cent of the aerosol particles were electrically charged.
(ii) Ion Generator: High concentrations of small ions of one sign were produced by a sonic-jet ion generator similar to that of Whitby (1961). A rectified voltage in the range 2.5 to 3.5 kV was applied to a needle whose point was about 0.18 cm from an orifice of 0.159 cm diameter in a grounded brass plate. Dried, filtered air at about two atmosphere pressure swept ions formed near the needle point away at sonic velocities through the orifice. The generator gave a steady production of ions of either sign in the concentration range \(10^9\) to \(10^{11}\) ions per cm\(^3\).

(iii) Aerosol Charger: Aerosol particles become charged when mixed intimately for a time with a high concentration of small ions which attach themselves to the particles by a diffusion process by virtue of their thermal energies. In the present experiments negative ions from the sonic-jet ion generator were ejected downwards through a conical passageway along the axis of a lucite cylinder and mixed with the aerosol particles which entered from an annular slot. The mixture then entered a mixing chamber of 36.3 litres volume where it remained until the particles had time to become charged adequately.

(iv) Particle Counter: The particle concentration was determined by a Nolan-Pollak photo-electric nucleus counter, constructed and operated according to the instructions of Pollak and Matnieks (1959). It is based on the principle of the attenuation of a beam of light by the fog formed by the adiabatic expansion of a moistened sample of the aerosol.

The other apparatus used in these experiments was either standard commercial equipment or specially constructed apparatus which will be described later in the text. Airflow were usually measured by calibrated rotameters.

3. EXPERIMENTAL PROCEDURES.

The size of aerosol particles can be determined by measuring the fraction of them that becomes charged when they are brought to a state of equilibrium charge distribution by an intense source of small ions of both signs. (Keeffe, Nolan, and Rich, 1959). This was achieved by passing the aerosol through a region ionized by alpha particles from a foil of americium 241 with an activity of about \(2 \times 10^{-4}\) curies. The aerosol then passed between the plates of a cylindrical condenser into a photoelectric nucleus counter. With no potential difference across the condenser the counter measured \(Z\) the total particle concentration. With a large potential difference across the condenser it measured \(N_0\), the concentration of uncharged particles emerging. A number of successive measurements of \(Z\) and \(N_0\) were made and the size of the particles was related to the mean value of \(N_0/Z\).
The size of aerosol particles may also be determined from their diffusion coefficient $D$. Nolan and Guerrini (1935) obtained $D$ for condensation nuclei by measuring the fraction of them that penetrated a series of narrow rectangular channels. The ratio of the concentration of particles emerging from the channels ($Z_v$) to that entering them ($Z$) is related to $D$ by the formula of Nolan, Nolan and Cormley (1938),

$$Z_v/Z = 0.9099 \exp(-x) + 0.0531 \exp(-11.4x)$$

where $x = 3.77 \frac{C b L D}{a Q}$.

The dimension of a channel are length $= L$ cm, height $= b$ cm, width $= 2$ cm, $C$ = number of channels, $Q$ = Total volume of air (cm$^3$) passing through all the channels per second.

The relationship between $D$ and $x$ may be written $D = x f Q$ where $f = a/3.77 G b L$.

To obtain an easily measurable diffusion loss for the rather large particles used in the present investigations, with reasonably convenient airflow, a diffusion battery with a small value of the constant $f$ was required. The "giant" diffusion battery of Pollak and Metnieks (1959) was obtained by courtesy of Professor T. Murphy, School of Cosmic Physics, Dublin. The dimensions of the battery were $L = 60$ cm, $b = 25.1$ cm, $2a = 0.0436$ cm and $c = 30$ channels. The volume of the end pieces was six litres. The value of $f$ was $1.43 \times 10^{-7}$. This was determined experimentally by comparison with a diffusion battery with $f = 2.698 \times 10^{-7}$.

For greater convenience and accuracy in measuring $Z$ with the same counter as $Z_v$, the aerosol was passed through a wide tube in parallel with the diffusion battery and of equal volume to it. Thus particle losses due to coagulation and diffusion in the connecting tubing were the same for $Z_v$ and $Z$. A series of alternate readings of $Z_v$ and $Z$ were made at constant $Q$ and the mean value of $Z_v/Z$ obtained. Even with the "giant" battery the value of $Z_v/Z$ was sometimes greater than 0.8 and the low loss formula of Kennedy (Nolan and Kenny, 1953)

$$Z_v/Z = 1 - 0.7652 x^{2/3} + 0.0531 x + 0.0075 x^{4/3}$$

was used. The airflow $Q$ was usually 2 litres per minute. The aerosol emerging from the generator was first diluted by filtered air. It was diluted further by, mixing with the air from the ion generator. The airflow emerging from the mixing chamber was about 40 litres per minute. Most of this was allowed to escape to the atmosphere but a fraction, usually less than 5 litres per minute was directed through either the cylindrical condenser, the diffusion battery or the equal volume tube (E.V.T.) into the particle counter.

The usual sequence of an experiment was to allow the particle generator reach steady operating conditions producing particles of the required size and concentrations and to arrange all airflows at their desired values. With no high voltage on the ion generator needle most
of the particles emerging from the mixing chamber were uncharged. Several alternate readings of $Z$ and $Z_v$ were taken and $D$ calculated from $Z_v/Z$. With conditions as before a negative high voltage was applied to the needle so that practically all the particles become charged. A series of values of $Z$ and $Z_v$ were again taken and $D$ for the charged particles calculated. The effect of charging the particles can be seen by comparing the values of $D$ obtained.

4. RESULTS.

The results of three typical experiments were given in the following table:

<table>
<thead>
<tr>
<th>Expt. Number</th>
<th>Ion Generator</th>
<th>Airflow 1/min.</th>
<th>Particles per cm$^3$</th>
<th>Penetrating Fraction $Z_v/Z$</th>
<th>Diffusion Coefficient $D \times 10^{-3}$ cm$^2$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>off</td>
<td>3</td>
<td>22,400</td>
<td>0.786</td>
<td>11.30</td>
</tr>
<tr>
<td></td>
<td>on</td>
<td>3</td>
<td>22,600</td>
<td>0.662</td>
<td>22.75</td>
</tr>
<tr>
<td>11.</td>
<td>off</td>
<td>2</td>
<td>10,150</td>
<td>0.895</td>
<td>2.863</td>
</tr>
<tr>
<td></td>
<td>on</td>
<td>2</td>
<td>9,100</td>
<td>0.722</td>
<td>11.294</td>
</tr>
<tr>
<td>111.</td>
<td>off</td>
<td>2</td>
<td>29,200</td>
<td>0.746</td>
<td>9.754</td>
</tr>
<tr>
<td></td>
<td>on</td>
<td>2</td>
<td>25,800</td>
<td>0.650</td>
<td>15.886</td>
</tr>
</tbody>
</table>

It is clear from the above that charging the nuclei causes some of them to be deposited by electrostatic forces thus increasing their apparent diffusion coefficient. The effect is most marked in the case of the larger particles which acquire larger charges.