Measurement of the Mobility and the Diffusion Coefficient of Ultrafine Radioactive Particles in the Air

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ABSTRACT

The mobilities and diffusion coefficients of the decay products of a natural radioactive gas, $_{86}Tn^{220}$, and of an artificial radioactive gas, $_{36}Kr^{88}$, have been measured in filtered air. The study of the mobility of these radioactive ions has demonstrated the presence of four groups of ions, ThB^+ and Rb^+.

Assuming that the different groups of ions correspond to an increase in the dimensions of these ions, it has been found that the agglomeration velocity of the most rapid ions increases with the irradiation of the air.

Under the same conditions, measurements have been made of diffusion coefficients of neutral particles.

1. Introduction

The radioactive particles which can be found in the atmosphere come principally from thoron and radon. Through alpha or beta disintegration, these gases give rise to metallic atoms which are isotopes of Pb, Bi or Po. When an alpha particle is emitted, the recoil nucleus is ionized (Scüczs and Delfosse, 1965). During its slowing down, the nucleus is subjected to charge-exchange reactions with the medium. In air, when reaching thermal energy, this particle is still ionized (Renoux, 1965). It can then recombine with negative ions, or being an atom of a heavy metal, it can agglomerate with gaseous molecules or fasten onto the aerosol particles which are present. Since these interactions are functions of the concentration of ions, gaseous impurities and aerosols present, many different types are possible.

Jacobi *et al.* (1959) and Lassen and Weicksel (1961) made theoretical analyses of the attachment times of ultrafine particles onto atmospheric aerosols, obtaining values ranging from 20 to 80 sec. In the same manner for radioactive particles with diameters <10 Å, Chamberlain and Dyson (1956) found attachment times between 9 and 44 sec.

Junge (1963) could thus define a "primary" lifetime which corresponds to the time leading up to the attachment of the ultrafine radioactive particles onto larger particles, this time being a function of the average size of the atmospheric aerosols (Chapuis, 1966).

We have studied the behavior and properties of radioactive particles during this primary lifetime when their diameters range from several angstroms to several tens of angstroms. Our experiments were made in a filtered atmosphere in order to eliminate the aerosols present in the air and to have reproducible conditions. Radioactive particles with diameters >30 Å were not detected under our experimental conditions.

Measurements were made of the mobility of radioactive ions and the diffusion coefficient of radioactive neutral particles. These two series of measurements enabled us to follow the evolution of these particles in filtered air.

2. Measurements of ionized particles

Erikson (1924, 1925) first measured the mobilities of radioactive ions. He found two groups of positive ions with mobilities of 4.35 and 1.55 $cm^2\ sec^{-1}\ V^{-1}$, the ions of the first group transforming into the ions of the second group in 1/50 sec. Briggs (1926) found a single group of ions with a mobility of 1.6 $cm^2\ sec^{-1}\ V^{-1}$, while Wilson (1922), with the help of a cloud chamber, observed that ThA^+ ions moved about twice as fast as the gaseous ions of the air.

Having previously measured the mobility of the ThB^+ ions, we showed that there are two groups of ions having different mobilities (Blanc *et al.*, 1963). A series of more precise determinations made by the group headed by Prof. Bricard, and by our group, enabled us to define the mobility spectrum of the ThB^+ ions (Bricard *et al.*, 1965, 1966; Fontan *et al.*, 1966).

Using the same experimental apparatus, we have also measured the mobility of Rb^+ ions produced by beta disintegration of the artificial radioactive gas $_{36}Kr^{88}$.

a. Principle of the apparatus

As shown in Fig. 1, air (or any other gas) containing the radioactive gas is filtered to remove the aerosols it contains; it then enters an airtight disintegration chamber (100 liters) where particles are created, 90% of which are ionized (Renoux, 1965). The apparatus used to measure the mobilities, a Zeleny tube, is placed at the exit of the disintegration chamber. The mobility

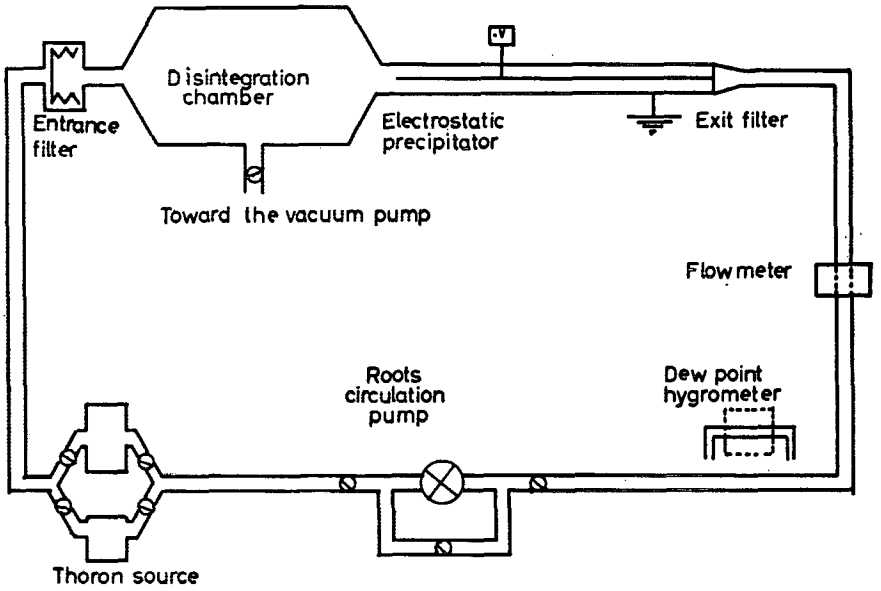

FIG. 1. Diagram of the installation used for measurements on charged particles.

spectrum of the ions is deduced from the distribution of the alpha or beta activity of a wire placed along the axis of the precipitator. The experiment is performed in a closed circuit, made of stainless steel, where a vacuum of 10^{-2} torr can be created.

The experiments were carried out with filtered atmospheric air, as well as with a gaseous mixture (20% O_2, 80% N_2, by volume) having a purity of 99.995%. Water vapor concentration inside the circuit was 500 ppm; other impurities were not measured. It must be noted, however, in this respect, that the neoprene gaskets and the Roots-type circulation pump could have introduced organic vapors into the system.

b. Results of the mobility measurements

A series of measurements (Fig. 2) enabled us to deduce the existence of four groups of ions in the case of ThB^+, these results being in agreement with those obtained in non-filtered air for ThB^+ by Bricard *et al.* (1966) with an Erikson precipitator. Four groups of ions were also obtained with Rb^{88+} under the same experi-

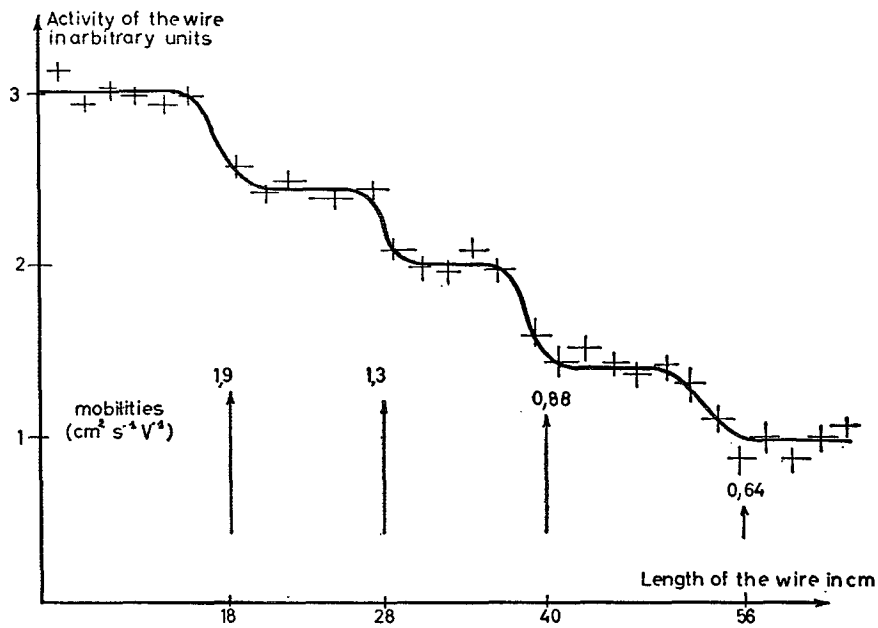

FIG. 2. Measured mobilities in air of thorium B ions at atmospheric pressure.

TABLE 1. Measured mobilities (cm^2 sec^{-1} V^{-1}) of ThB^+ and Rb^+ ions.

	Ion groups			
	I	II	III	IV
ThB^+	2	1.3	0.95	0.55
Rb^+	2.2	1.5	1	0.65

mental conditions (Fig. 3). In each case the four groups are identified as I, II, III, IV, where ion speeds decrease with group number. Table 1 summarizes the measured mobility values (cm^2 sec^{-1} V^{-1}) for the different groups of ions, to an accuracy of 10%.

c. Results of ion agglomeration time measurements

After reaching the thermal level 90% of the ThB atoms are ionized (Renoux, 1965), as compared to 95% for Rb. These ions are then subjected to recombination with negative ions and to agglomeration. Since the concentrations of negative and positive ions inside the disintegration chamber have always been less than 1.5×10^6 ions cm^{-3}, we need not be concerned with such phenomena as the re-ionization of a particle by transfer of charge, the Penning effect, and fixation onto an ionized particle.

Our interpretation of these results is that the fastest ions (group I) can transform themselves into ions of weaker mobility by means of either of the following processes, γ designating the agglomeration velocity of the ions and having the same dimensions as the velocity of a chemical reaction:

$$\text{ions (I)} \xrightarrow[\gamma_A(\text{I})]{} \text{ions (II)} \xrightarrow[\gamma_A(\text{II})]{}$$

$$\text{ions (III)} \xrightarrow[\gamma_A(\text{III})]{} \text{ions (IV)}, \quad \text{(A)}$$

$$\text{ions (I)} \xrightarrow[\gamma_B(\text{I})]{} \begin{cases} \text{ions II} \\ \downarrow \\ \text{ions III} \\ \downarrow \\ \text{ions IV} \end{cases} \quad \text{(B)}$$

where

$$\gamma_A(\text{I}) = \gamma_B(\text{I}) = \gamma(\text{I}).$$

The agglomeration velocity $\gamma(\text{I})$ of ions (I) is the most important since it remains the same in processes A and B. One will find in Fontan *et al.* (1967) the solution to equations giving the concentration of ions I and of ions II, III, and IV in process A, which is the simplest mathematical formulation of the problem.

Knowing γ, one can then find the agglomeration time $\tau(=\gamma^{-1})$ of the ions, i.e., the time at which the ionic concentration decreases by a factor of e when agglomeration is the only process involved in ion removal (Kondrat'ev, 1964). Fig. 4 shows that $\tau(\text{I})$ slowly diminishes with the irradiation rate of the gas; its value of a few seconds is about the same as that for $\tau_A(\text{II})$ and $\tau_A(\text{III})$.

These values are much larger than those measured by Erikson (1929) in air. This very long time characterizes a much slower transformation.

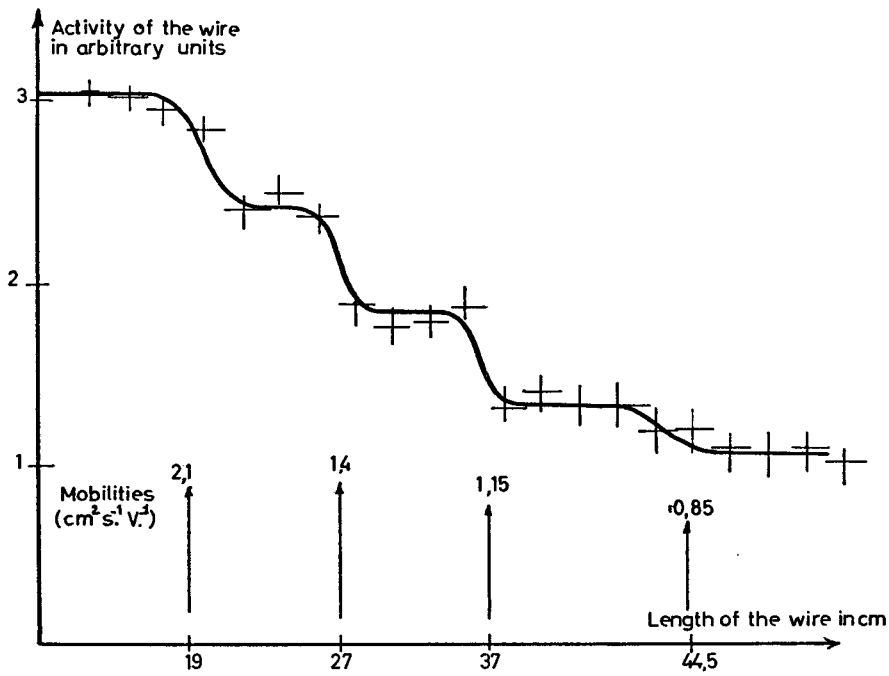

FIG. 3. Measured mobilities in air at atmospheric pressure of rubidium 88 ions.

d. Air under irradiation

In a separate experiment a source of two curies of tritium, adsorbed on a metallic tungsten target, was placed at the entrance of the disintegration chamber inside an electrostatic precipitator which stops all the ions formed by the β-rays emitted by the source. With this arrangement only the neutral particles are carried with the air through the system. The study was made with thoron in very weak concentration. In a non-irradiated atmosphere, the characteristic agglomeration time of ions (I) was about 1.5 sec, while the lifetime of ions (I), which takes into account agglomeration and recombination, was about 1 sec.

While one thus observes the disappearance of ions (I), the total number of ions remains constant. This means that the Penning effect, if it exists, is negligible compared to the agglomeration increase.

3. Measurements of neutral particles

Chamberlain and Dyson (1956) measured the diffusion coefficient of the active deposit of radon in a filtered atmosphere by studying the deposit of RaA particles on the wall of a tube. The radon activity was weak and the radon daughters were primarily in the form of ions. His measured value of 5×10^{-2} cm^2 sec^{-1} corresponds to ions whose mobility is 2.2 cm^2 sec^{-1} V^{-1}.

With a stronger irradiation Megaw and Wiffen (1961) showed that there is a formation of neutral particles having larger dimensions. From a study of ThB neutral particles older than 5 min, Madelaine (1965) and Bricard *et al.* (1966) noted an enlargement of the particles with time.

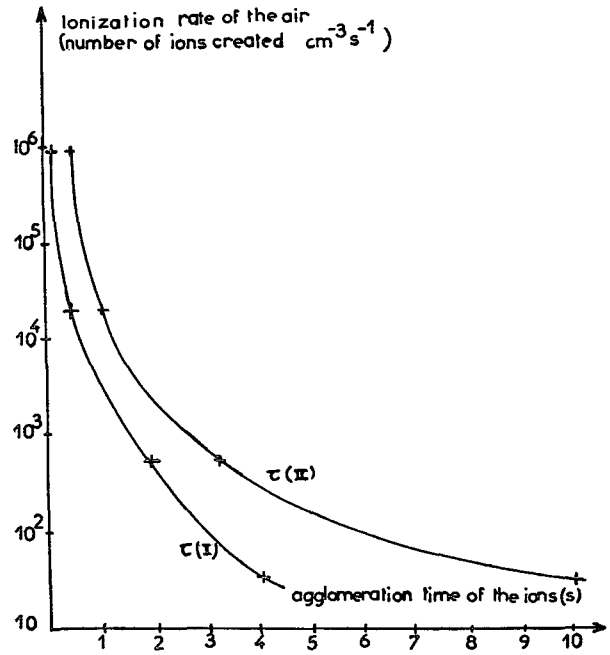

FIG. 4. Variation of the agglomeration time of radioactive ions as a function of the ionization rate of the air.

For our observations, installations were set up which permitted us to measure the diffusion coefficient for particles in two maximum age ranges: 1) from 5–30 sec and 2) from 30 sec to 10 min. These two installations enabled us to follow the full evolution of a radioactive aerosol and made it possible for us to compare the evolution of neutral particles with that of charged particles.

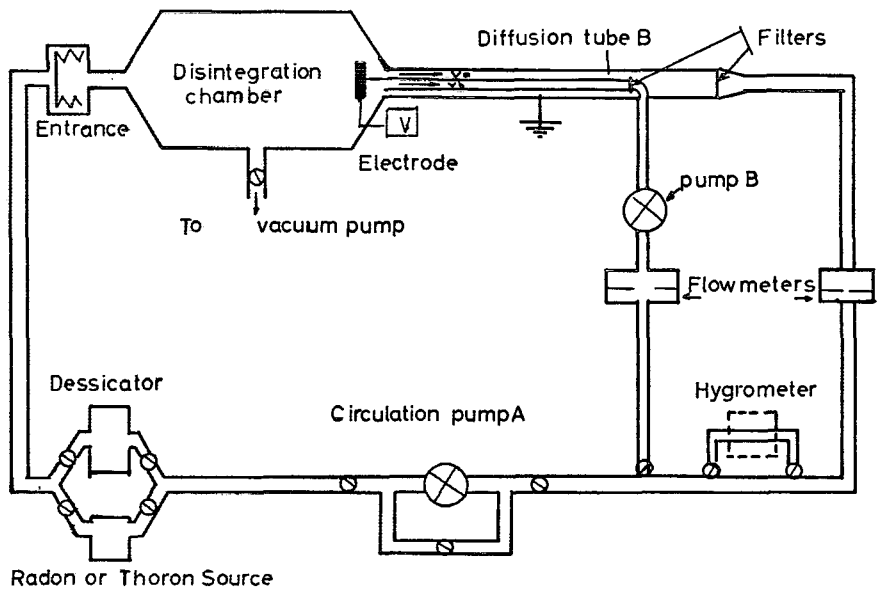

FIG. 5. Diagram of the installation with diffusion tube used for measurements on neutral particles in the age range from 5–30 sec.

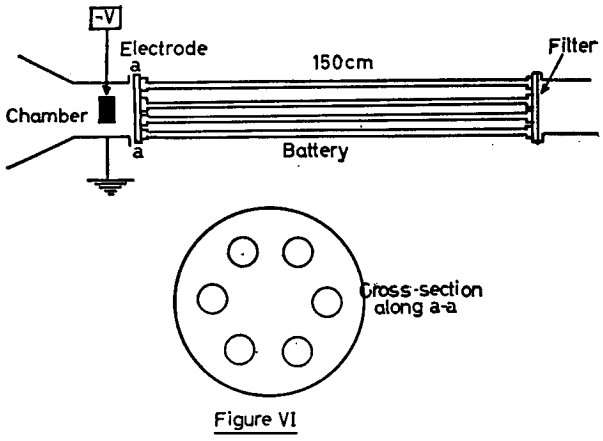

FIG. 6. Diagram of the diffusion battery used for measurements on neutral particles in the age range from 30 sec to 10 min.

a. Description of the measurement installations

1) Particles whose maximum age is included between 5 and 30 sec (Fig. 5).

The circuit is fed by two circulation pumps, A and B, pump B not being used under certain conditions. The air is then drawn in through B because of the differential pressures introduced by a set of valves. The speeds V_A and V_B are about the same. The air charged with radioactive gas is filtered to remove the aerosols it contains and then goes into an airtight chamber (100 liters) where radioactive disintegration gives rise to particles, 90% of which are ionized. These particles recombine with the negative ions of the air. The apparatus which measures the diffusion coefficient is placed at the exit of the disintegration chamber ahead of a charged electrode V which permits only the neutral particles to enter the tube T_B. The measurement of the radioactivity of the T_B walls then enables one to determine the diffusion coefficient of these particles. The tube is made of very thin stainless steel (1/10 mm thick). The radioactive particles emit 2 MeV β-rays which go through the wall of the tube and are counted by a Geiger counter, the window of which is collimated. By using a valve system passage time could be varied between 5 and 30 sec.

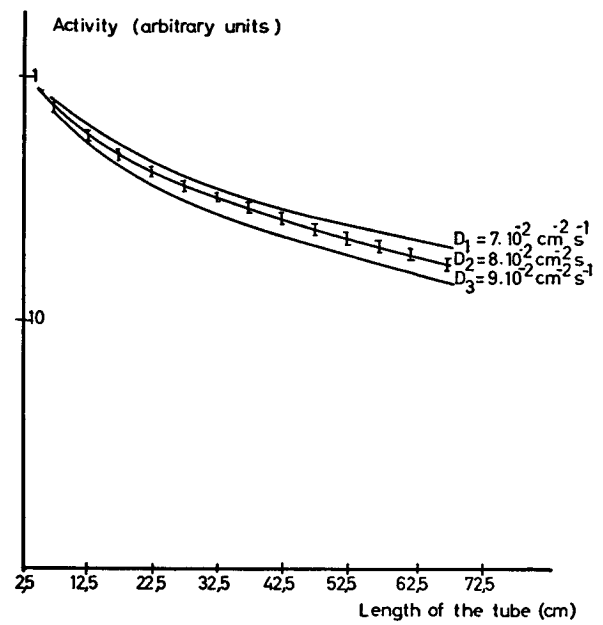

FIG. 7. Range of experimental points and theoretical curves of the activity deposit of neutral particles along the walls of a battery tube for a flow in the tube of 50 cm sec^{-1} for different coefficients of diffusion. The age of the particles was 1 min.

2) Particles whose maximum age is older than 30 sec (Fig. 6).

In this installation a diffusion battery made of six tubes similar to that used by Fuchs and Sutugin (1963) is placed at the exit of the disintegration chamber. These tubes are similar to those used in the last experiment. One measures the activity deposited on the wall of one of the tubes while air circulates in all of them.

The experiments were made with radioactive particles resulting from the disintegration of thoron and of radon. A filter placed at the exit of T_B or the battery makes it possible to determine the proportion of the untrapped particles. The ions are stopped by an electrode placed ahead of the battery.

b. Results

The vertical line segments in Fig. 7 show the variation of the activity deposited along the wall of a diffusion-battery tube for a 50 cm sec^{-1} velocity in the tube, the particles being 1 min old. In addition, several theoretical curves have been drawn showing the variation of the deposited activity for three monodispersed aerosols, $D_1 = 7\times10^{-2}$ cm^2 sec^{-1}, $D_2 = 8\times10^{-2}$ cm^2 sec^{-1} and $D_3 = 9\times10^{-2}$ cm^2 sec^{-1}, these curves being based on calculations found in Twomey (1962). According to the results of Chamberlain and Dyson (1956) entrance effects are preponderant when one observes a deposit uniform in density along the length of establishment. This was not the case in our experimental curves, as shown by the alignment of the experimental points along the theoretical curve D_2 which was plotted without taking into consideration the length of establishment.

Fig. 8 shows the variation of the average value of D and radius r with the age of the particle. Our results agree with those of Madelaine (1965) and of Billard *et al.* (1967) for particles whose radii are greater than 5 Å.

4. Interpretation of the results

The study of ionized or neutral radioactive particles carried out in filtered air shows that these particles agglomerate. While it is difficult in our present state of knowledge to determine precisely the nature of these

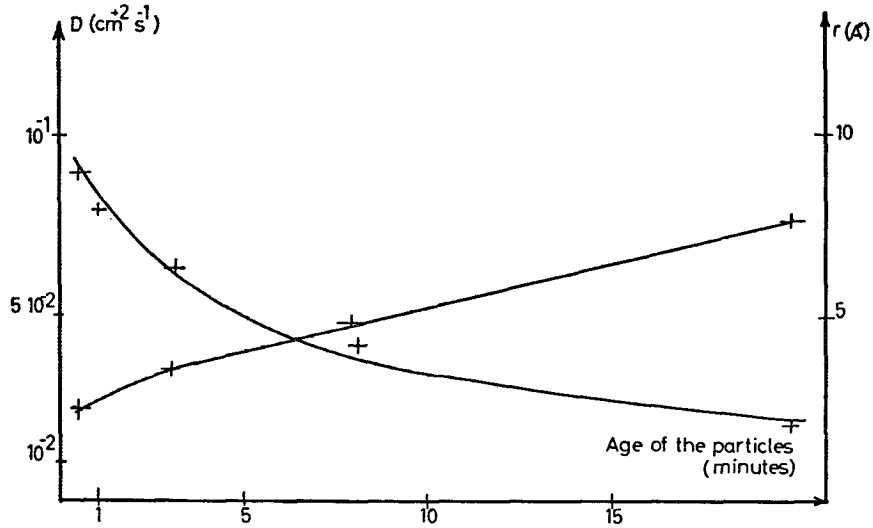

FIG. 8. Variation of the average value of the diffusion coefficient D (curve decreasing with time) and the average value of the particle radius (curve increasing with time) of neutral particles as a function of the age of the particles.

agglomerates, it is possible to hypothesize and to compare our results with those obtained with ions of a different nature.

Our mobility spectra of radioactive ions ThB^+ and Rb^+ indicated the presence of four groups of ions. Measurements made by others of the mobilities of non-radioactive atmospheric ions have given results close to ours for small positive ions. Thus, using the condensator-aspirator method, Erikson (1929) found positive ions whose mobility is 1.85 $cm^2\ sec^{-1}\ V^{-1}$. More recently, Siksna and Lindsay (1959) found three groups of positive ions in air irradiated by tritium β-rays. This is a result identical with that obtained by Chapman (1937) in the case of ions formed in air by the spraying of water.

According to Loeb (1967), the first group of ions found for ThB^+ could correspond to the primary ion Pb^+, whose theoretical mobility in air is 2.15 $cm^2\ sec^{-1}\ V^{-1}$, actual measurements of the mobility of Pb^+, or of any other non-radioactive ion in air or any other gas, having never been made to our knowledge. While Rb^+ ions have often been studied, they were produced in a very different fashion by a Kunsman source in an atmosphere where all trace of O_2 was excluded (Bacconnet, 1965; Tyndall, 1938). In addition, the age of the Rb^+ ions was much shorter (10^{-3}–10^{-6} sec) than in our experiments.

The theoretical mobility of a non-agglomerated Rb^+ ion in air would be 2.4 $cm^2\ sec^{-1}\ V^{-1}$. While the measured mobilities of ions (I), ThB^+ or Rb^+, thus appear to be slightly lower than the theoretical mobilities, more accurate experimental measurements are necessary before exact comparisons can be made. We nevertheless believe that ions (I) are not the "primary," "non-agglomerated" ions, because they are older than 10^{-1} sec.

The maximum value of the ion radius is about 12 Å (group IV). Under the conditions which we worked, the concentration of ions whose radii >12 Å is less than 2% of the total concentration of ions. The study of the evolution of the fastest ions (group I) shows that these ions undergo a slow transformation, of about 1 sec, accelerated by the irradiation of the gas.

We made several experiments with A, O_2 and N_2 where the concentration of radioactive gas was 6 atoms $liter^{-1}$ and the concentration of impurties was of the same order as that of the 99.995% pure initial mixture (20% O_2, 80% N_2, by volume). The results gave essentially the same values for the mobilities, the relative importance of the different groups of ions being the same as in O_2 as in N_2. In argon, however, ions (I) disappear faster. This does not eliminate a possible action of O_2 which can react even when it is present in a small quantity.

These phenomena can be compared with those observed on large ions by Vassails (1948), on small ions by El Nadi (1958) and on Aitken nuclei by numerous authors (Went, 1966; McGreevy and O'Connor, 1962; Verzar and Evans, 1954).

The comparison between neutral particles and ions is interesting, since, in effect, the neutral particles, whose diffusion coefficients were measured, are recombined ions. Fig. 8 shows the variation of the average value of the particle radius as a function of the maximum age of the particles.

We recall that these results were obtained by neglecting the length of establishment. They seem, however, to show that 1) recombination breaks up the agglomerates so that seemingly we are dealing with dissociative recombination, and 2) neutral particles seem to grow at a slower rate than ionized particles. Thus, after 1 min the diffusion coefficient is still 8×10^{-2}

$cm^2 sec^{-1}$ (for an irradiation corresponding to 1.5×10^{-3} rad, i.e., a concentration of thoron of 1.5 atoms cm^{-3}). After an aging of 5 min, Madelaine found for the active deposit of thoron a diffusion coefficient of 2.6×10^{-2} cm^2 sec^{-1} for an irradiation of 0.1 Rad of thoron, corresponding to 110 atoms cm^{-3}. A diffusion coefficient of 2.6×10^{-2} cm^2 sec^{-1} corresponds to neutral particles whose radius is 6 Å or to ions which have a mobility of about 1.0 cm^2 sec^{-1} V^{-1}.

5. Conclusion

The study of neutral and ionized radioactive particles produced by the disintegration of a radioactive gas enables one to follow the behavior of certain heavy atoms in air. The observed behavior for the two types of particles was quite different with the neutral particle appearing to develop more slowly than the ion.

We intend to specify the role of impurities and to take the same measurements in a controlled atmosphere. The introduction of known quantities of impurities ought to enable us to study the formation of Aitken nuclei around these heavy metallic atoms.

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