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Air Ions and Aerosols

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All charged airborne particles the motion of which is subject to electric forces and under average conditions does not depend on weight and inertia are called air ions or atmospheric ions.

The only directly measurable characteristic of an air ion mobility is equal to the mean velocity of an air ion in an electric field of unit intensity. The basic unit of mobility in the system of SI is $m^2\ V^{-1}\ s^{-1}$. $1\ cm^2\ V^{-1}\ s^{-1} = 10^{-4}\ m^2\ V^{-1}\ s^{-1} = 100\ mm^2\ V^{-1}\ s^{-1}$ is not recommended as a unit.

The partial concentration of a group of air ions (k_1, k_2) is calculated as a ratio of the partial charge density made up by the air ions of that group to the elementary charge:

$$n\ (k_1,\ k_2) = \rho\ (k_1,\ k_2)/e. \qquad (1)$$

$e = 1.6 \times 10^{-19}$ C. The group of air ions (k_1, k_2) designates all air ions whose mobility is greater than k_1 and smaller than k_2. The concentration of air ions is measured in the units m^{-3} or mm^{-3}.

Formula (1) is justified if each air ion carries one elementary charge. Although this is not the case at small mobilities, in practice formula (1) is applied universally. For this reason the concentration of large air ions (in particular that of artificially produced large air ions) is a conventional quantity. Strictly speaking, it is better to avoid the concept of concentration and to speak of the partial density of a charge expressed in $e \times m^{-3}$, which gives the same numerical value.

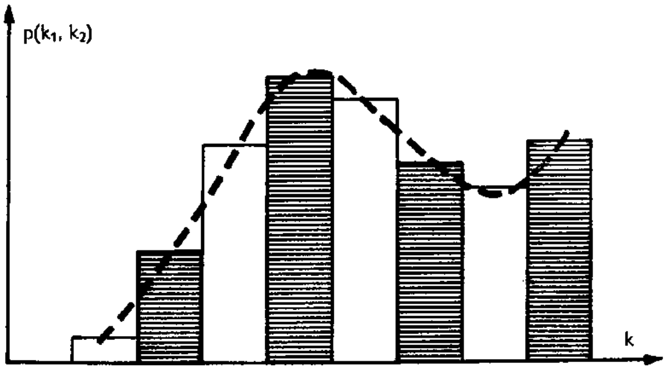

Fig. 1 - Diagram of the spectrum of air ions (example).

Partial concentrations of the neighbouring groups of air ions (k_1, k_2), (k_2, k_3), etc. represent the spectrum of air ions which may be presented in the form of a diagram (see example in Fig. 1). By detailing the diagram up to the limit, one attains the spectral function, which is calculated as $n(k) = n(k,\ k + dk)/dk$ whose diagram is shown in Fig. 1 by a dotted line.

Quantities corresponding to positive or negative air ions are distinguished by the signs + or —. The predominance of the one or the other charge is expressed by the coefficient of unipolarity

$$\eta\,(k_1, k_2) = \frac{n_+\ (k_1, k_2) - n_-\ (k_1, k_2)}{n_+\ (k_1, k_2) + n_-\ (k_1, k_2)} \times 100\%. \qquad (2)$$

In an absolutely dry and clean air there are only monomolecular ions of oxygen with a mobility of $220\ mm^2\ V^{-1}\ s^{-1}$ (Maushart, 1958). But already in the presence of a small amount of humidity the positive as well as negative air ions having an age of more than 0.1 sec. consist of a few up to a score of molecules of H_2O. Such cluster ions are called small air ions, with a mobility within the limits of 40 to 220 $mm^2\ V^{-1}\ s^{-1}$. Information concerning the spec-

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trum of mobilities and the structure of small air ions is scarce (Segal, 1962; Bricard *et al.*, 1966). Cluster ions are rather unstable, they disintergrate in an intense electric field. This makes the accurate measurement of their mobilities difficult.

When the air contains even a negligible quantity of metal vapour, e.g. mercury vapour, positive air ions — due to the Kallmann-Rosen effect — include an atom of metal in their basis (Loeb, 1960). According to Kuda (1960) a negative charge may change to highly electronegative molecules of NO_2 and halogens even at an exceedingly small concentration ($\sim 10^{-6}\%$) of the admixture.

Under normal conditions electroconductivity of the air is nearly completely due to small air ions, and there is almost a functional interdependence between the concentration of small air ions and the conductivity (Jonassen and Wilkening, 1965). If the mean mobilities $\bar{k}_+$ and $\bar{k}_-$ are in the neighbourhood of 120 and 170 $mm^2\ V^{-1}\ s^{-1}$ (atmospheric air), one obtains the following formulas

$$n_+\ (50\ mm^2\ V^{-1}\ s^{-1},\ \infty)/\ /mm^{-3}/\ \sim\ 52\ \lambda_+\ /pSm^{-1} \qquad (3)$$

$$n_-\ (50\ mm^2\ V^{-1}\ s^{-1},\ \infty)/\ /mm^{-3}/\ \sim\ 36\ \lambda_-\ /pSm^{-1}$$

The symbol with the unit in slanting brackets designates the numerical value of a quantity in the units indicated.

Air ions with mobilities of 20 to 40 $mm^2\ V^{-1}\ s^{-1}$ have not been plausibly observed. Air ions with a mobility below 20 $mm^2\ V^{-1}\ s^{-1}$ are charged aerosol particles. Classification of aerosol particles according to size is represented in Table 1.

TABLE 1

Radius	Subgroup	Group
< 1 nm	small	submicroscopic
1 to 10 nm	intermediate	
10 to 100 nm	large	
0.1 to 1 μm	ultrafine	microscopic
1 to 10 μm	fine	
10 to 100 μm	coarse	
> 0.1 mm	macroscopic	

Small submicroscopic particles are small air ions. They exist only in a charged state, and some investigators do not regard them as aerosol particles. Intermediate submicroscopic particles may be neutral or carry one elementary charge, rarely two charges. In a charged state they have a mobility of 0.6 to 20 $mm^2\ V^{-1}\ s^{-1}$ and are called intermediate air ions. These ions are only occasionally present and appear in relatively small numbers. On the other hand, large submicroscopic particles are very common. In a charged state they carry one, rarely two or three, elementary charges, have a mobility of 0,01 to 0.6 $mm^2\ V^{-1}\ s^{-1}$ and are called large air ions. Ii the atmosphere there are mostly particles whose $k = 0.03$ to $0.06\ mm^2\ V^{-1}\ s^{-1}$. These particles are known as Langevin air ions. Air ions with $k = 0.01$ to $0.025\ mm^2\ V^{-1}\ s^{-1}$ are sometimes called ultralarge.

Neutral submicroscopic particles are by some physicists called condensation nuclei or Aitken particles. The sizes of neutral submicroscopic particles are measured by the diffusion method (Metnieks, 1965).

In view of their small mobility, microscopic particles are usually not regarded as air ions. Only the artificially charged microscopic particles may acquire a mobility that can be compared with the mobility of large and even intermediate air ions. The charge of such particles may include a few thousand elementary charges.

Fine microscopic aerosols are used for the inhalation of medicines. Ultramicroscopic aerosols (e.g. tobacco smoke) are again exhaled and are, therefore, unsuitable for inhalation. However, coarse particles settle already in the upper respiratory tract, and do not reach the bronchi and alveoli.

It is not possible to produce aerosols with all particles neutral. The state of equilibrium which aerosol reach in the bipolarly ionized atmosphere is characterized by a minimum degree of electrification. Charge distribution of particles in a state of equilibrium (Fuchs, 1963; Bricard *et. al.*, 1965) and dependence of mobility on the charge and the radius (Metnieks and Pollak, 1961; Fuchs and Stechkina, 1963) is well known. This makes it possible to apply the data on measuring the spectrum of mobilities of air ions in equilibrium for the calculation of the size spectrum.

Aerosols whose particles are charged considerably in excess of the level of thermal equilibrium are called electroaerosols. Electroaerosols may have a unipolar charge, which imparts to them special properties of application.

Detailed information on air ions may be found in the writings of Israel (1957) and Loeb (1960); on aerosols, in those of Fuchs (1955), Green and Lane (1964) and Junge (1963).

Rise of Air Ions

The ionization volume q is measured by the number of pairs of air ions arising in unit volume per unit time.

In nature $q = 0.002$ to 0.03 mm^{-3} s^{-1}. Cosmic rays give us the values $q = 0.002$ m^{-3} s^{-1}, γ -radiation of soil (on land) — 0.002 to 0.005 mm^{-3} s^{-1}; the rest is the result of the radiation of radioactive admixtures of the air (emanations and products of their disintegration).

Of ionizing radiation used for the production of artificial air ionization, the most suitable are α-rays whose energy is 4 to 9 MeV and whose path length in the air is 25 to 90 mm, respectively. A short path length enables one to use all the energy of α-rays for ionization. To establish the number of ion pairs produced in a second, it is necessary to multiply the number of α-particles emitted within a second by the energy /MeV/ and by the number 3000. The same rule is true for β-rays on condition that the mean energy of rays (not the maximum one) is taken into account and that the particles are completely absorbed in the air to be ionized. The latter condition is often not fulfilled since the path length of hard β-rays (e.g. from the preparation Sr^{90}) is ~ 7 m. For this reason preparations emitting soft rays (e.g. tritium) are more convenient (energy up to 0.018 MeV, path length up to 4 mm).

If the activity of the preparation is expressed in curies, the number of particles per second equals activity (in curies) × × coefficient of utilization × 3.7×10^{10}.

The path length of γ-rays in the air runs into hundreds of metres. Volume if ionization near a preparation is

$$q/\mathrm{mm}^{-3}\ \mathrm{s}^{-1}/ = \frac{M\,/\,\mathrm{mg} — \mathrm{e\ kv\ Ra}\,/}{2\ (r\ /\mathrm{m}/)^2}, \qquad (4)$$

where M stands for the activity of the preparation and r for the distance travelled.

The dose rate of X— and γ-radiation for one roentgen per hour is $q = 580$ mm^{-3} s^{-1}.

All radiations produce symmetrical-bipolar ionization. To obtain unipolarly ionized air, it is necessary to separate air ions in an electric field (Martin, 1954).

The wave lengths of ultra-violet rays of a mercury vapour lamp are too long to have directly an ionizing effect. The slight generation of air ions by the quartz lamp is due to the photo-effect and to chemical reaction in the air. The photo-effect arises on the surface upon which the UV- rays fall and produces only negative air ions. The rays of a quartz lamp do not produce the photo-effect on any surface. To obtain good results, zinc or zinc-coated tin is to be recommended.

Calculation of the intensity of ion-formation in a self-maintained gas discharge by the formula I/e results in enormous figures. However, not all ions can be removed from the discharge zone. An exception is the corona discharge which has been described in detail by Kaptsov (1947) and Loeb (1965). The electrode producing a corona discharge may be a point or a fine wire to which is applied a voltage of at least a few thousand volts. Electrons and positive ions are formed in the fine luminous zone over the electrode but only air ions having a charge of the same polarity as the electrode can leave this zone. The intensity of air ion production is limited only by the speed of the removal of ions from the corona electrode.

Thermal ionization of the air starts at a temperature of approximately 4000 °C. The use of a wire (heated up to 1000 °C) as a source of air ions is based on another phenomenon — surface ionization (Zandberg and Ionov, 1959). Some experimental data on surface ionization in the air were presented in the report by Martin (1952).

All these methods of ionization cause the simultaneous formation of small quantities of nitrogen oxides and of ozone. Only small air ions are being produced (a heated surface may also emit intermediate air ions), which may form large ones by coagulation with aerosol particles.

To obtain electroaerosols by the method of charging particles with small air ions, it is necessary to apply a sufficiently intense electric field. The extreme obtainable charge of a not very small conductive particle with the radius r in a field having the intensity E will be

$$q\ /e/ = 2\ E\ /\mathrm{kVm}^{-1}/ \times (r\ /\mu\mathrm{m}/)^2, \qquad (5)$$

A detailed discussion of the problem of charging particles was published by Kaptsov in 1947.

When spraying it is usually more expedient to charge particles by the induction method, also called the method of contact charging. If the electric field over the orifice induces a surface charge on the surface of the orifice, the detaching droplets are charged. The formula for a rough computation of the charge of a conductive droplets coincides with formula (5) if the multiplier 2 in the formula is replaced by 0.5. Liquids, the product of whose resistivity and dielectric constant exceeds 10 MΩm, lend themselves badly to induction charging by ordinary sprayers (Tammet, 1963).

When liquids are sprayed, charges arise also without applying an external electric field (Lenard or balloelectric effect), but these charges are small and cannot be regulated. The symmetrical-bipolar balloelectric effect can be explained entirely by fluctuations in the charge density of the liquid to be sprayed (Natanson, 1951). The unipolar balloelectric effect is due to the presence of a double layer on the surface of the liquid (Loeb, 1958).

The literature contains some additional data on the rise of air ions, e.g. ionization of gases in a flame, ionization through agitation of air through a liquid and ionization caused by a rapid evaporation of salt water (Björnsson *et. al.*, 1967, etc.).

Travel and Decay of Air Ions

The task of directing air ions to a predetermined place is considerably more complicated than the generation of air ions. The theory of air ionizers is primarily the theory of the movement of air ions.

Three mechanisms of the motion of air ions are known: *1.* transfer by the motion of the air; *2.* motion in an electric field, and *3.* diffusion. There is no « natural » way of motion which cannot be reduced to these mechanisms.

It is well established that the diffusion of air ions is an extremely slow process. Diffusion is called forth by Brownian motion. The mean value of the causal travel or motion of an air ion in a particular direction within the time period t is:

$$\Delta x\ /mm/ =$$

$$= 0.01 \sqrt{k\ /\mathrm{mm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}/ \times T\ /^\circ\mathrm{K}/ \times t\ /s/.} \qquad (6)$$

Calculation in accordance with this formula shows that diffusion plays a considerably smaller part than other factors in the movement of air ions.

Transfer by the motion of the air proceeds without inertia. In a turbulent airflow the mechanism of transfer is able to reduce the concentration of air ions by mixing ionized air with neutral air. For instance, in the flow of a turbulent jet of a relatively weakly ionized air out of a small orifice, the concentration of air ions on the axis of the jet is — due to dilution — inversely proportional to the distance from the orifice (Salm and Tamm, 1963).

In an electric field air ions travel along the lines of force. In the absence of the electric field of a space charge the electric field cannot increase or reduce the concentration of air ions. The air ion concentration along the lines of force in the absence of rise or decay of air ions is strictly constant (Cagniard, 1943). In the presence of a considerable space charge one observes electrostatic scattering of air ions which leads to the decay of the concentration. The time of decay of the concentration of unipolar monomobile air ions by a half of the original one is inversely proportional to the mobility and concentration of air ions. The formula for small air ions is as follows:

$$\tau\ /s/ = \frac{400}{n_0\ /\mathrm{mm}^{-3}/}. \qquad (7)$$

Large air ions are scattered much more slowly.

In the case of electroaerosols it is sometimes n[illegible] consider a fourth mechanism [illegible]ional sedimentation. The speed o[illegible]ng of a droplet of water with a [illegible] 1 to 30 µm is expressed by an a[illegible] formula:

$$v\ /\mathrm{mm\ s^{-1}}/ = 0.12\ (r\ /\mu\mathrm{m}/)^2. \qquad (8)$$

Unipolar air ions can decay only by settling on the walls of a room. The loss of mobility due to settling on aerosol particles is also possible. In the case of high ionizatin the latter phenomenon is of secondary importance as there are not enough aerosol particles for all small air ions. A decrease in the concentration is exclusively determined by electrostatic scattering.

In the case of bipolar ionization air ions decay by recombination. In low levels of ionization the calculation of recombination is complicated since it is necessary to consider the presence of aerosols (Israel, 1957; Siksna, 1961). In high ionization only the recombination of small air ions with other small air ions is essential. In this case the formula reads as follows:

$$\frac{dn}{dt}\ /\mathrm{mm^{-3}\ s^{-1}}/ = q\ /\mathrm{mm^{-3}\ c^{-1}}/ - 0.0016 \times \times (n/\mathrm{mm^{-3}}/)^2. \qquad (9)$$

The time of the decay of the concentration by a half of the original one on condition that $q = 0$ will be the following:

$$\tau\ /\mathrm{s}/ = \frac{600}{n_0\ /\mathrm{mm^{-3}}/}. \qquad (10)$$

It is interesting to compare the formulas (7) and (10). The stability of unipolar and bipolar ionization proves to be one and the same.

Details of the theory of recombination may be found in the reports of Natanson (1959) and Siksna (1964, 1965).

A basic problem in the theory of air ionization is the balance of the rise and decay of air ions. The simplest part of it is the case of the homogeneous generation of air ions This ideal situation is close to the condition created by considerable mixing of the air in a closed room. It is sufficient to characterize the ionizing power of the ion generator by the intensity of the current of air ions according to $I = qVe$, where V stands for the volume of the room. From the condition of the balance follows:

$$I\ /\mathrm{pA}/ = 0.25\ V\ /\mathrm{m^3}/ \times (n\ /\mathrm{mm^{-3}}/)^2 \qquad (11)$$

(small air ions, bipolar ionization),

$$I\ /\mathrm{pA}/ = 0.35\ V\ /\mathrm{m^3}/ \times (n\ /\mathrm{mm^{-3}}/)^2 \qquad (12)$$

(small air ions, unipolar ionization). Despite the larger coefficient of formula (12) it is easier to carry out unipolar ionization since, in this case, electrostatic scattering promotes the travel of air ions. In the case of bipolar ionization it is necessary to remove and mix air ions with the sole help of air flow.

In a highly ionized air the average lifetime of an air ion coincides with the time t which is defined by formulas (7) and (10). Under normal atmospheric conditions the average lifetime of a small air ions is about one minute and due to the small concentration, formula (10) is invalid.

Information regarding ionization of the outdoor atmosphere was compiled by Israel (1957), while data on ionization of the air in closed rooms may be obtained from a paper by Siksna and Eichmeier (1966).

Removal of unipolar air ions in the immobile air from a source with an unlimited ability of generating air ions (strong α-preparation, corona air ionizer) was discussed by Wagner (1955), Whitby and Mc Farland (1961) and Tammet (1963 b).

The concentration of air ions at the distance r from a small-sized air ionizer placed at the distance R from the walls of the room and maintained at the voltage U will be calculated irrespectively of mobility as follows:

$$n\ /\mathrm{mm^{-3}}/ = \frac{40\ U\ /\mathrm{kV}/}{\sqrt{R\ /\mathrm{m}/ \times (r\ /\mathrm{m}/)^3}}. \qquad (13)$$

The theory of the dispersion of air ions from a generator by the air-flow was considered in the paper by Tammet (1963 b), detailed experimental data on radium air ionizers were presented by Martin (1954).