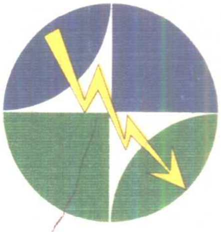
FIFTH INTERNATIONAL CONFERENCE ON ATMOSPHERIC ELECTRICITY

Garmisch-Partenkirchen 2 · · · · 7 September 1974



SUMMARIES

OF

CONTRIBUTED

PAPERS

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SESSION 1

Chairman: G.A. Dawson

Ions, Basic Research

1. V.A. Mohnen:

   Formation, Nature and Mobility of Ions of Atmospheric Importance

   (invited)

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Thomson, B. A. & J. V. Iribarne

Positive and Negative Ion Mobility Spectra of Spray-Produced Ions

B. A. Thomson and J. V. Iribarne

The production of ions by evaporation of charged aqueous droplets may shed light on the properties of atmospheric ions and has importance as an atmospheric process.

The positive and negative mobility spectra of ions remaining after atomized water or solution droplets have evaporated were measured by a time-of-flight method at atmospheric pressure and under a variety of conditions including different humidities, solution conductivities and ionic ages. The striking feature in the results is the difference between the positive spectrum (with two broad peaks at a reduced mobility of 1.13 and 0.95 $\mathrm{x}10^{-4}\ \mathrm{m}^2/\mathrm{V.s}$) and the negative spectrum (with a very narrow peak at $1.77\mathrm{x}10^{-4}\mathrm{m}^2/\mathrm{V.s}$), implying large mass differences (approximately 300 and 450 amu for the positive peaks against 96 amu for the negative peak). The addition of NaCl to the sprayed solution produces a new positive ion of mobility 0.76 $\mathrm{x}10^{-4}\mathrm{m}^2/\mathrm{V.s}$ for weak solutions, and largely depletes the small ions of both signs for concentrations greater than 10^{-3}M. Neither increasing the relative humidity of the air in the drift tube (to 80%) nor increasing the aging time of the ions (from greater than 45ms to greater than 400ms) had a significant effect on the mobility of the fastest ions.

Comparative measurements of the number of condensation nuclei left by the evaporated spray with a General Electric counter showed a gradual increase with the concentration of NaCl. Increasing the net charge carried by the spray produces an increase in ions but not in condensation nuclei.

3 Castleman, Jr.A.W. & I.N. Tang

ON THE MOLECULAR PROPERTIES OF ATMOSPHERIC ION CLUSTERS AND THEIR RELATIONSHIP TO NUCLEATION*

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Abstract

Atmospheric ions exist as clusters of polar molecules surrounding a central charge, and an understanding of their molecular properties such as bonding and structure is imperative in order to further our basic knowledge concerning their role in atmospheric processes.

Extensive systematic studies of the bond energies and entropy changes resulting from successive molecular additions to ion clusters are being carried out in our Laboratory. Recent results were obtained for the clustering of water vapor about Na^+ and the radon progeny ions Pb^+ and Bi^+, NH_3 about NH_4^+, Bi^+, Na^+, K^+, and Rb^+, and water vapor and SO_2 about NO^+, H_3O^+, and Na^+. The thermodynamic data show that SO_2 and H_2O are largely electrostatically bonded to the electronically closed-shell alkali metal ions. The results also provide evidence that hydrogen bonding is not a prerequisite to the formation of relatively stable ion clusters.

Of particular significance was the finding that the bond energies for polar molecules clustered about ions of open electronic structure are far greater than that expected for a simple ion-dipole interaction. The results clearly establish the fact that chemical bonding is quite important in effecting the formation of atmospheric ions.

The present work has shown the importance of the chemical nature of the central ion, in addition to electrical charge, in establishing the stability of atmospheric ion clusters. Furthermore, these studies have led to a clarification of the role of small clusters in ion induced nucleation phenomena, a topic which will also be addressed in the paper.

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* This research was performed under the auspices of the U. S. Atomic Energy Commission and partially supported by the National Science Foundation (AG423).

4 Cabane, M., Madelaine,G., Bricard, J. + Krien,P..

"MOBILITY SPECTRUM OF IONS CREATED IN CASES OF ATMOSPHERIC PRESSURE"

by

M.Cabane[+] G. Madelaine[++] J. Bricard[+] et P.Krien[++]

The study in the atmospheric air of charged particles due to the action of ionizing radiations (cosmic rays, natural radioactivity) as well as the ions created artificially in pure gases, have stimulated numerous works. A parameter often utilized is mobility, in spite of the fact that it is rather difficult to connect it to physico-chemical properties of ions (mass, structure).

In a preceding work (Thesis of the 3rd cycle), we had undertaken to artificially create ions in the atmospheric air by means of the Corona effect and we had obtained a certain number of new results (discrete or continuous change of the mobility in terms of evolution time, influence of the hygrometric degree of the air).

We have had for our goal here to develop the method used previously with success, while applying it to the atmospheric air as well as to the gases of controlled composition in such a way to study the behaviour of the ions in terms of their evolution time and to the hygrometric degree of the gas. The ions are no longer created by the Corona effect, but by ionization α so as to have a production of ions more stable in time. The measurements are carried out at atmospheric pressure. The method used consists of allowing the ions to drift over a length x, under the effect of a field $\vec{E}$, which permits them to have contact with the gas during a time in terms of x and of E. Next, with the help of a repetitive cross field applied between two wire systems of a grid square to the beam, one obtains some bundles of ions to which the drift time ΔT over a length l and under the effect of a field $\vec{E}_m$ is

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connected with the mobility k by : $k = 1 . E_m^{-1} . \Delta t^{-1}$. From the measurement of Δt,worked out with the oscilloscope, one deduces the value of k.

The study undertaken in this work has permitted us to state precisely the mobility change of the ions in terms of the evolution time τ in the atmospheric air: existence of a mobility limit for the discrete spectrum in the period of time studied, diminution, as τ increases, of the mobility of the ions of the continuous spectrum following an experimental law which can permit us to define the changes of the probability of fixation of a neutral molecule of these ions. The fact that one observes a discrete spectrum and a continuous spectrum, satisfies the theory of nucleation on charged particles : presence of stable agglomerates of fixed mobilities and of instable agglomerates of which the dimensions increase with the time and whose mobility diminishes. However, the nucleation being observed for the water vapour content well inferior to saturation, thus making it necessary that an impurity of very weak vapour pressure presents itself in the air, which favors the formation of nuclei.

In the case of measurements carried out on the mixtures, pure gas-water vapour, by comparing our results to the values of the mobility of ions of identified mass, we have found that for the weak values of evolution time τ and of the hygrometry p, the ions of the discrete spectrum were the atomic or molecular ions of the carrier gas, whereas when τ or p increase, these ions are replaced by hydrates, certain of which are particularly stable. As for that which concerns the ions of continuous spectrum, one has observed in terms of the hygrometry and of the ageing parameter, a change in agreement with our observation on the atmospheric air and which follows the same experimental law; it is equally necessary to call attention to the presence of a gaseous impurity other than the water vapour, in order to explain the development of these ions.

5 Kojima, H. & T. Sekikawa

H.Kojima and T.Sekikawa (Japan.)

An Experimental Method for Determining the Charged Fraction on Aerosols.

The purpose of the present investigation is to determine experimentally the charged fraction of submicron aerosols. Experimental arrangement consists of an ion denuder (I.D.) and an ion mobility analyzer of cylindrical type which are connected in series. The air is irradiated by ionization sources (^{210}Po 100 μCi) for bringing aerosols into a charge equilibrium before introducing into both tubes. The irradiated air is introduced to the I.D. and all the charged particles are removed. The uncharged particles which are not removed in the I.D. are irradiated by ^{210}Po again. And then, ion-mobility distribution of the particles which are charged is obtained by the ion analyzer. The ion-mobility distribution is transformed to the ion-size distribution by using the formula of Fuchs (1962).

In front of the I.D., the charged fraction of particles with radius r, a_r is Nr/Zr. Nr is the concentration of the charged particles and Zr is that of total particles containing the neutral particles. After the I.D., the charged fraction, a_r becomes $Nr' / Zr - Nr$. From both relations, the following equation for the a_r can be obtained,

$$a_r = \frac{Nr - Nr'}{Nr} .$$

When a high voltage is supplied to the I.D., Nr' is obtained by the ion analyzer, and when not, Nr is obtained. Thus the value of a_r can be determined experimentally.

EVOLUTION OF TROPSPHERIC IONS

M.L. Huertas and J. Fontan

The purpose of this work is to clarify the agglomeration phenomena around the small positive and negative ions of tropospheric air.

Evolution of tropospheric ions is not well known. Polluting vapors act upon this evolution, according to chemical reactions which are not well understood.

The apparatus used enables us to measure simultaneously the mobility and the mass of ions created in a mixture of atmospheric air and various polluting vapors, at a pressure up to 40 Torr.

The experimental results have shown the importance of protonation in the positive ion formation and the importance of deprotonation in the negative ion formation.

Finally a mathematical model has allowed a qualitative approach to the sequence of ion-molecule reactions in the lower troposphere.

7 McKnight, Lee G. & Eoin W. Gray

IDENTITY AND INTERACTIONS OF ATMOSPHERIC IONS WITH ORGANIC CONTAMINANTS,

Lee G. McKnight, Bell Laboratories, Murray Hill, New Jersey, 07974 U.S.A. and Eoin W. Gray, Bell Laboratories, Columbus, Ohio, 43213 U.S.A.

Interactions of ions with trace impurities in the atmosphere can lead to dramatic changes in the ion species even though the reactants are present in only trace amounts. The processes of charge exchange, ion clustering and proton transfer are found to convert ions of primary air species into those characteristic of trace constituents in the mixture. For these measurements we have used a drift cell-mass spectrometer combination to mass analyze ions produced from arc and glow discharge sources in air and in air-like mixtures at pressures up to 5 Torr. The interactions of the ions with trace impurities present in the drift cell completely dominate the ion chemistry, with the result that ions extracted from the gas after reaction are completely different from those produced by the primary ionization process. The rapidity of these reactions indicates that ions formed in the atmosphere will have their chemistry and identity dominated by trace species present in the atmosphere. These results have been applied to the problem of relay contact activation in which deposition of organic material on low current relay contacts results in an increase in relay arc duration and a consequent increase in relay contact erosion. We will show specific application to the case of ions interacting with organic materials present in the environment surrounding telephone relays.

8 Wilkening, Marvin H.

Marvin H. Wilkening -- USA

Influence of the Electric Fields of Thunderstorms on ^{222}Rn Daughter Ion Concentrations

Radon 222 and its short-lived daughter products are important to the study of atmospheric electricity generally not only because of their significant role in production of ion pairs near the earth's surface, but also for their use as tracers in the study of certain aspects of charge transport in the vicinity of thunderstorms. Some of the ^{222}Rn daughters present in the atmosphere at a given time are known to exist as positive ions having mobilities in the range of ordinary atmospheric small ions. Previous work has shown that the concentration of these ions near the ground decreases markedly under the influence of electric fields associated with thunderstorms although the concentration of the parent ^{222}Rn remains essentially unchanged.

It is the purpose of this paper to describe the nature of this effect based upon observations of more than 50 thunderstorms during which all or most of the following variables were recorded: magnitude and sign of the electric field, total small ion concentration, atmospheric electric polar conductivity, condensation nucleus concentration, total radon daughter radioactivity, corona current, wind speed and direction, humidity, and temperature. These data show that the decrease in ^{222}Rn daughter ions is due primarily to upward migration from ground level under the influence of the storm-produced electric fields and not to attachment or recombination effects.

A one-dimensional time-dependent numerical model has been developed by Roffman in our laboratory which includes terms for ion attachment and recombination, electric field, and vertical wind in addition to the usual terms for radioactive decay and eddy diffusion. Agreement with the experimental data on the electric field effect is good; hence, the use of ^{222}Rn daughter ions in the study of certain features of the thunderstorm electrical environment is indicated.

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Hoppel, J. A.

Ion-Aerosol Attachment Coefficients and the Diffusional Charging of Aerosols

W. A. Hoppel
Naval Research Laboratory, USA

ABSTRACT

The attachment of ions to charged and uncharged aerosols of radii much larger than the ionic mean free path is satisfactorily treated by diffusion theory. For aerosols with radii the same order or smaller than the ionic mean free path, theoretical treatments have been less satisfactory and the common practice is to define a "limiting sphere" with a radius about a mean free path greater than the aerosol radius. More rigorous treatments must take into account both three-body trapping and image-force trapping. Three-body trapping is the dominate factor in ion-ion recombination and occurs when an ion in the vicinity of an aerosol loses enough energy upon collision with a neutral molecule to assure trapping by the electrostatic forces. Since image forces increase faster than r^{-2} there exists a critical apsoidal distance (the image trapping distance) which divides those ionic orbits which terminate on the aerosol particle from those which escape. The relative importance of the image capture distance and the three-body trapping distance has been evaluated for various size aerosols with different net charge. The results show that for uncharged nuclei the image capture sphere is always larger than the trapping distance and therefore the trapping distance plays no role in the attachment of ions to uncharged particles. However, for singly charged particles with radii below about 2×10^{-6} cm the trapping distance is larger than the image capture distance, and therefore must be included in ion-aerosol attachment theories. Calculations of the combination coefficients using these results will be presented. From the attachment coefficients between differently charged species the equilibrium charge distribution on small aerosols can be determined.

10 Krasnogorskaya, N.V. Neizvestniy, A.J.

ON THE VELOCITY OF COAGULATION GROWTH OF CHARGED CLOUD DROPLETS

N.V.Krasnogorskaya, A.J.Neizvestniy
(Institute of Applied Goephysics and Central Aerological
Observatory, Hydrometeorological Service of the USSR).

The experimental results to determine collision efficiency of freely falling neutral and charged ($q < 1.10^{-5}$esu) droplets of comparable and equal sizes in the radius range $5 \leq r_{1,2} \leq 30$ mkm are given. The obtained experimental values of collision efficiency of neutral droplets are approximately twice as large as the calculated values of Davis-Sator (Nature, 215, 1371-1372, 1967), Hocking-Jonas (Q.J. Roy.Met.Soc.,96,410,1970) and agree with values calculated by Davis (J.Atm.Sci.29,5, 1972) and Jonas (Q.J.Roy.Met. Soc., 98, 417, 1972). There was found the value of dimensionless parameter $E=9.10^{-3}$, when Hocking-Jonas results will be in good agreement with our experimental data (Krasnogorskaya N.V.,Neizvestnij A.J., Meteorologija i gydrologija, N 12, 1973).

The solution of coagulation equation where the experimental values of the efficiency are applied causes the twofold increase of the velocity of coagulation growth of neutral particles. Rather high values of particles growth velocity in the investigated coagulation mechanisms, providing remarkably larger values of collision efficiency. The experiments showed that gravitational electric coagulation can be considered as such a mechanism. When $r_2/r_1 > 0{,}4$ the collision efficiency of the opposite charged or charged droplets with neutral ones increases compared with neutral from 2 to 50 times. It is shown that there exist a rather wide range of the like-charged droplets where collision efficiency is higher than neutral one or neutral with charged droplets of the same sizes. The coalescence of the like-charged droplets leads to the accumulation growth velocity enough to form precipitation in warm clouds. (Krasnogorskaya N.V., Elektrichestvo Hujnih sloev atmosphery i metody ego izmerenija, Hydrometizdat, L. 1972).

Concept for a Paper for the Fifth ICAE (no title)

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Division of Rad. Protection, Air Monitoring Section
Bhabha Atomic Research Center, Bombay

(a) The contribution of ionizing radiations from natural sources in the formation of nuclei in the troposphere, stratosphere and mesosphere will be treated, based on laboratory experiments. The formation of nuclei in the upper troposphere and lower stratosphere by effects induced by radiation chemistry and photochemistry of gases will be considered in particular. In these regions of the atmosphere, the ionizing energy is mainly supplied by cosmic rays. The presence of singlet molecular oxygen and certain free radicals, particularly HO_2, seems to aid the nucleation of small particles by the ionizing radiations.

(b) The problems is urgent because these studies provide some insight into the formation mechanism of Aitken nuclei in the stratosphere, for which sufficient indirect eveidence has become available in the recent years. These nuclei are likely precursers of the aerosols in the stratosphere whcih have a role in controlling the solar energy input of the lower atmosphere. The problem assumes great significance in view of the likely increase in the aerosol content of the stratosphere triggered by the influx of pollution gases from man-made sources.

These studies are also important in understanding the mechanisms by which certain solar events can cause perturbations in the stratosphere and the troposphere. Possible auroral-cirrus relationships reported in the literature could be explained on the basis of ion-induced nucleation, because the auroral events are accompanied by an influx of ionizing radiations.

(c) The effect of ionizing radiations in the nucleation of particles has been studied in laboratory reaction vessels. A source a gamma rays has been used to simulate the dose from natural sources of ionizing radiations. Photolysed oxygen has been used to simulate the solar UV effect in the stratosphere.

The nucleation of particles by ionizing radiations has been studied in the presence of trace levels of SO_2.

(d) Mixtures of pure nitrogen, photolysed oxygen and trace quantities of SO_2 have shown very pronounced ion-induced nucleation effects.

(e) The broader scope of these studies has been discussed uncer (b). The problem is of fundamental interest in the field of atmospheric electricity.

12 **Wiendl, E.**

FIFTH INTERNATIONAL CONFERENCE ON ATMOSPHERIC ELECTRICITY, 9/2-7/74

Contributed paper for session 1: Ions, basic research

STRUCTURE OF LIQUID H_2SO_4 - H_2O CLUSTERS AROUND IONS: THERMODYNAMIC THEORY

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Abstract. It was calculated by how many water molecules and sulfuric acid molecules a singly charged ion is surrounded at 25 C and at relative humidities of 7,35%, 20%, 50%, 100%. Their size and composition is given by the minimum of the droplet free energy of formation. The assumptions follow the heteromolecular nucleation theory and are expressed in the following equation (Kiang & Stauffer, 1973):

$$\frac{\Delta G}{kT} = -n_A \ln(P_A/P_{A\infty}) - n_B \ln(P_B/P_{B\infty}) + 4\pi R^2 \gamma/kT + q^2/2RkT$$

with ΔG = formation free energy; n_A, n_B = number of H_2O and H_2SO_4 molecules; P_A, P_B = actual gas partial pressures; $P_{A\infty}$, $P_{B\infty}$ = vapor pressure in equilibrium for the mixture; $P_A/P_{A\infty}^{pure}$ = R.H.= relative humidity; $P_B/P_{B\infty}^{pure}$ = a = activityof H_2SO_4; R = Cluster radius; γ = surface tension; q = unit charge (=$4{,}8\cdot10^{-10}$ e.s.u.). Typical results for the cluster distribution ($\propto \exp(-G/kT)$) are shown in the figure(R= 4...8Å). At least the cluster distribution for pure water was compared with the experiment (Castleman & Tang, 1972) and showed good agreement. The results for binary mixtures could not yet be tested. With increased activity or increased relative humidity the cluster grows.

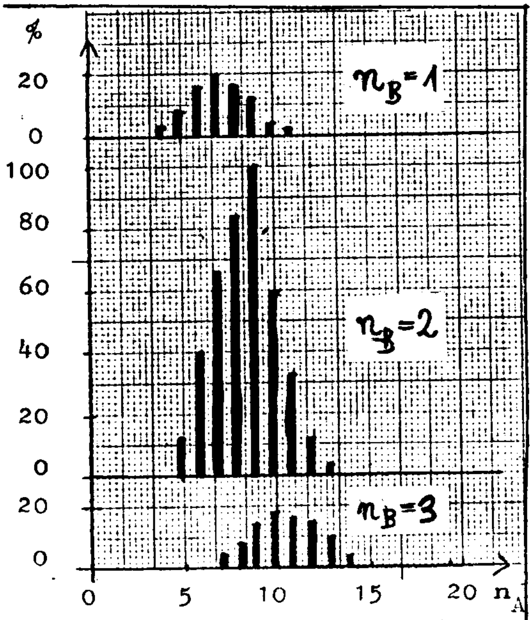

Fig1: Cluster distributions calculated as function of n_A, for various n_B; R.H. = 50%, a= 10^{-5}