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# IONS IN GASES[1]

By Professor JOHN ZELENY

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WHAT I propose to do in this paper is to outline briefly some of the difficulties which have been met in our attempts to get a better understanding of gaseous ions, and to indicate the present state of our knowledge about these ions. And then lastly, I shall go somewhat afield to say something about the theories that have been proposed to account for lightning.

To begin, then, what is there that we should like to know about ions in gases? We should like to know their mass, size, composition and structure. We should like to know the amount of charge that each carries. And we should like to know how they differ and what part each plays in the various electrical discharges. For obvious reasons, I shall not attempt to discuss all these various aspects of the subject.

The problem of size and that of mass, which is usually connected with it, has been one of great perplexity. This problem presented itself at the very outset of the study of these ions, and has remained with us ever since.

Forty-four years have passed since Thomson and Rutherford[2] adopted the ionization theory to explain the conductivity imparted to gases by x-rays. At the time, the electron had not been isolated, and the process of ionization of a diatomic molecule was regarded as consisting in the pulling apart of its two atoms.

However, when Thomson and Rutherford obtained a rough estimate of the speeds with which the ions migrate in an electric field, they found that the mobility was much smaller than an ion of atomic size should have according to the kinetic theory of gases.

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[1] Address of the retiring president of the American Physical Society given in Philadelphia, December 27, 1940.

[2] J. J. Thomson and E. Rutherford, *Phil. Mag.*, 42: 392, 1896.

To account for this discrepancy, these investigators proposed the explanation that, because of its charge, each ion attracts to itself a considerable number of molecules which retard its migratory motion. This idea of ion clusters did not appeal to a number of physicists.

It was soon discovered,[3] too, that in gases like air and hydrogen the mobility of the negative ions is considerably greater than that of the positive ions. A disparity between the two kinds exists in all gases, although not always in the same sense.

A new factor was thus introduced into the problem that also called for explanation.

To be sure, the usual process of the ionization of a molecule is now universally considered to consist in the ejection of one or more electrons from the molecule. Thus initially, the positive ion is a charged molecule, while the negative ion is the detached electron itself. In a few gases like nitrogen and the inert gases, the electron remains free and is highly mobile. In most gases, however, electrons of low speed readily attach themselves to molecules, and hence in these gases the negative ions, at least in their early life, also are of molecular size. The question now is, after this stage of equality has been reached, whether either or both of the ions resist further change, and, in case they do change, what is the nature of this change? The answer depends on the kind and purity of the gas used, and on other factors as well, some of which will be considered presently.

It soon became apparent that the kinetic theory of gases, as developed for uncharged molecules, is not applicable to ions without modification.[4] Owing to its charge, an ion polarizes a near-by neutral molecule, making of it a dipole. Because the field about an ion is divergent, a resultant attraction comes into play between it and such a polarized molecule, which at larger distances exceeds the other forces operative between them. Moreover, the molecules of some gases, like water vapor, for example, are normally polar, and the attraction between these molecules and ions is still greater than it is between ions and molecules, the polarity in which is produced by induction alone.

The diminution in the free paths of the ions arising from this attraction is so large that when correction for its action was taken into account in the formula for mobility, the theoretical values found for the mobility of the ions in a number of simple gases,[5] on the assumption that the ions are monomolecular, were not far from the values obtained by experiment.

Notwithstanding the disagreement in other cases, it almost seemed as if the theory of ion clusters had been dealt a knock-out blow.

However, this proved not to be the case. The number of experimental findings, which could not be explained on the hypothesis of an unchanging ion, only increased as more data were accumulated. And the argument was advanced that since the attractive forces between ions and molecules, owing to the polarization of the latter, are strong enough to deflect ions out of their paths so much as theory showed, they must also be large enough to cause permanent attachment between an ion and a molecule on close approach. It was argued that the two effects go together, that you can not have large decreases in the free paths of ions without at the same time having a high probability of attachment between ions and molecules.

Today, no one, as far as I know, contends that ions always continue in their original state. Some will only go so far as to concede a grouping of two or three molecules. Others present evidence of ions composed of as many as seven molecules. I think no one now believes that in the common gases there are any ion clusters in which the layer of molecules about the ion is more than one molecule deep.

There are some who believe that neutral molecules never adhere to ions in the sense that the molecules retain their identity but rather that such molecules as do become attached to an ion always merge with it to form a single more complex chemical molecule. I dare say at times it may be difficult to tell, without further evidence, just what the state of an aggregate is. However, it is a well-established fact that in some gases a part of the molecules are segregated into clusters even at room temperatures. Hence, it is not unreasonable to suppose that the additional attraction, arising from the charge on an ion, may enable clusters to form in some other gases.

In low pressure glow discharges accurate measurements of the masses of the ions there present can be made directly by means of mass spectrographs. These energetic discharges are a favorable seat for chemical reactions, and the measurements in a gas like air[6] actually show the presence, in greatly different amounts, of a number of different kinds of positive ions, some of which are interpreted as being compounds of the elements present.

Negative ions are found but rarely in these discharges, because the fields in them are too strong to permit the attachment of electrons to molecules. This raises the question whether clusters, which would form around positive ions in low fields, may be unable here to withstand the more energetic collisions with the molecules of the gas. However, the age of the ions in these discharges at the time of measurement, is at

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[3] J. Zeleny, *Phil. Mag.*, 46: 120, 1898.

[4] P. Langevin, *Ann. de Chim. et Phys.*, (7) 28: 316, 1903; (8) 5: 245, 1905.

[5] E. M. Wellisch, *Phil. Trans.*, A 209: 249, 1909. W. Sutherland, *Phil. Mag.*, 18: 341, 1909.

[6] O. Luhr, *Phys. Rev.*, 38: 1730, 1931; 44: 459, 1933.

most but a few millionths of a second, whereas in weak fields at higher pressures large changes in mobility are at times observed to take place very much later.

There is every reason to suppose that in still more energetic discharges, like sparks, for example, the ions are all simple. The electrons are not able to attach themselves to molecules, and clusters can not form around the positive ions.

At the time of the earlier experiments on ionic mobilities in gases at normal pressures, the state of our knowledge on these matters was such that no significance was placed on the presence of small amounts of foreign molecules in the gas used. To-day, the presence of extremely minute quantities of impurities, even beyond the possibility of detection by chemical or spectroscopic means, has assumed paramount importance.

There are two principal ways in which an impurity may affect the mobilities of ions. In the first place, a foreign molecule may have a lower ionizing potential than that of the surrounding molecules. Under these conditions, the energy relations permit the transfer of the charge from the ion to the foreign molecule at close approach, provided some way is open for the removal of the excess energy which is liberated. Such collisions, though comparatively rare when the amount of impurity is small, would nevertheless in a short time transform the ions of the main gas into ions of the impurity. So what we would be measuring is the mobility of the ions of this impurity when we thought we were measuring that of the ions in the main gas.

An impurity in a gas may influence mobility measurements in a second way, provided its molecules are more polar or more easily polarizable than the molecules of the main body of gas. The possession of a high polarity might cause these molecules to adhere to ions when the surrounding molecules could not do so, and might even gradually displace less polar molecules which may have become attached to the ions previously.

The formation of ion aggregates, whether the adhering molecules are those of the main gas or those of an abundant impurity, may easily at times be completed in less than a thousandth of a second. This interval is about the shortest that can be used in mobility measurements.

Naturally, the smaller the amount of impurity present the longer will it take for the process to be completed, and this time might even run into seconds. As a matter of fact the largest variations between different observations by the same experimenter, and among those of different experimenters, are often found when extreme precautions have been taken to secure great purity in the gas used. A very slight but variable residue of some impurity might well be the cause of such disagreements.

It is easy to imagine the confusion that would result if, for example, a gas contained a very small amount of one polar impurity and a still smaller amount of a second more polar impurity. The monomolecular ions might first quickly form aggregates composed of molecules of the main gas, which would gradually be transformed into clusters composed chiefly of the less polar and more abundant impurity, only to be changed finally into clusters of the more scarce and more polar contamination.

The mobility observed may thus depend not only upon the kind and amount of the impurity present but also upon the time after the formation of the ions that the measurements are made.

When the method used had a high resolving power the mobility spectrum has shown two distinct mobility peaks[7] in a given gas under some conditions and only one under others. Can this be explained otherwise than on the assumption of a change in ion aggregates?

Older ions are often found to be present in an unresolved group,[8] the mobility of the fastest of which may be 25 per cent. or more higher than the mobility of the slowest ones. For this reason disagreement between different observers has at times arisen, since some of the methods used measure the mobility of the slowest ions present, others that of the fastest ions, and still others the mobility of the most numerous type.

The presence of a small amount of water vapor in air reduces the mobility of its negative ions[9] and at the same time increases that of the positive ions. Molecular aggregates about the ions are again indicated.

When ions produced in one gas are passed through a different gas their mobility is usually found to depend only on the gas through which they are passing[10] and is independent of the gas in which they originated. Since an exchange of charge from the ion to a molecule of the second gas is ruled out in a special experiment with radioactive ions, we must again seek an explanation in some kind of cluster formation.

Enough has been said to show the unsatisfactory condition that existed a few years ago, where so much depended on conjecture and where suspicion was thrown on the credentials of every ion that had thus far been investigated. Something drastic needed to be done if experiment was to be a true guide to theory

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[7] H. A. Erikson, *Phys. Rev.*, 17: 421, 1921; 26: 465, 1925.

[8] M. LaPorte, *Ann. de Phys.*, 8: 466, 710, 1927; J. Zeleny, *Phys. Rev.*, 34: 310, 1929; J. L. Hampshere, *Proc. Roy. Soc.*, 127: 298, 1930.

[9] J. Zeleny, *Phil. Trans.*, A195: 193, 1900; *Phys. Rev.*, 36: 35, 1930.

[10] E. Rutherford, *Phil. Mag.*, 5: 95, 1903; A. Blanc, *Jour. de Phys.*, (4) 7: 825, 1908; E. M. Wellisch, *Proc. Roy. Soc.*, 82: 500, 1909.

and in turn theory be a guide to further experiment. It seemed manadatory, if ions of assured identity were ever to be made available, that the most unusual care must be taken both in the purification of the gas used and in the outgassing of all parts of the measuring apparatus.[11]

Experiments under such conditions have been carried out in recent years with interesting results. To begin with, the mobility of the positive ions in helium was now found to be about four times as large as that reported previously.[12] Especially significant are the measurements made of the mobilities of the positive ions of the five alkali metals when moving through the five inert gases.[13] The reason for the choice of these substances was that the ionizing potentials of the alkali metals are in all cases lower than those of the gases used, so that the metal ions are not able to transfer their charges to the molecules of the gas through which they are passing. Contrary to previous results, the mobilities of the different ions now differed widely among themselves when passing through the same gas. The mobilities diminished in a regular manner with increase in the atomic weight of the ions used, decreasing for example in the gas krypton from 4.03 cm/sec in a unit field for the lithium ion of atomic weight 7, down to 1.44 for the caesium ion of atomic weight 133.

The above values are in fairly satisfactory agreement with those computed by Langevin's formula[14] for mobility, which was derived on the simple assumption that molecules are spherical, elastic and polarizable. The largest disagreement is for helium where the observed values are about 20 per cent. higher than the theoretical ones.

These results are encouraging because, from the regularity of the relations, there is a very high degree of probability that the ions here in question are in reality all monatomic.

A number of other revealing experiments were done with these alkali ions in the inert gases. For example, when lithium ions were passed through these gases at room temperatures, and *low fields were used* in making the mobility measurements, another set of ions appeared in addition to the ones noted above.[15] The mobility of these in xenon, for instance, was but little more than a quarter of that of the faster ions. When the temperature was now reduced to a very low value, the faster group disappeared altogether and the slow ions alone were detected in all the gases, except helium. Hence, these slow ions must result from the attachment of molecules, of the inert gases themselves, to the lithium ions. Now this is very interesting. The noble gases are called inert gases because they are chemically inert. Yet here they are adhering to the alkali ions. The union is not likely to be a chemical one.

Taking one more example; a small amount of water vapor added to any one of the inert gases, reduced the mobility of all the alkali ions through it.[16] The lighter ions lost most, so that now the mobilities of all of the ions were roughly equal. It is natural to suppose that the decrease of mobility was due to the attachment of water molecules to the ions, and an estimate of the upper limit of the number of molecules so attached to any ion can be made on the supposition that the change of mass alone affects the mobility, although actually the size of the ion is also a factor. A clustered lithium ion in argon had almost the same mobility as a caesium unclustered ion, and, on the supposition made, it must therefore have a mass of 133 units, the same as that of caesium. If the increase of 126 units in the mass of the lithium is due to water molecules then a simple division shows that there must be seven of them clustered about the ion.

When the strength of the field used in these measurements which were done in the presence of water vapor was gradually increased, the mobility rose to that of the unclustered ion. The aggregates could no longer withstand the more energetic collisions with the molecules of the gas, and so the ions remained monomolecular.

However, the information furnished by the use of this improved technique, valuable as it is, is mainly qualitative. We must remember that it is not possible to determine the exact masses of ions from their mobilities alone, because the size of the ion is always involved as well. Unfortunately, too, theory shows that mobility values respond less and less to changes in the ion's mass as this mass gets larger and larger.

Furthermore, energy relations permit a molecular ion, on close approach to an uncharged molecule of the same kind, to give up its charge to the uncharged molecule. This exchange would reduce the mobility of the ion. However, the probability of such an exchange in any gas is still unknown. Much remains unknown, too, about some of the energy states in molecules and about the forces arising from them. Until more exact knowledge on some of these points is obtained we must not expect further refinements in the mobility formula as it applies even to monomolecular ions.

Still less can theory give us an answer as to the kind of ion cluster, if any, that can form in any gas under given circumstances, nor as to the connected problem of accounting for the differences between the

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[11] L. B. Loeb, *Phys. Rev.*, 36: 152, 1930.

[12] A. M. Tyndall and C. F. Powell, *Proc. Roy. Soc.*, 134: 125, 1931.

[13] A. M. Tyndall and C. F. Powell, *Proc. Roy. Soc.*, 136: 145, 1932; C. F. Powell and L. Brata, *Proc. Roy. Soc.*, 138: 117, 1932.

[14] Reference 4.

[15] R. J. Munson and K. Hoselitz, *Proc. Roy. Soc.*, 172: 43, 1939.

[16] R. J. Munson and A. M. Tyndall, *Proc. Roy. Soc.*, 172: 28, 1939.

positive and the negative ions. A goodly array of precise experimental data obtained under simple but definitely known conditions may, on the other hand, help lead the theorists to a more exact formulation of the laws of intermolecular action.

Our atmosphere is slightly conducting owing to the incessant ionizing action of cosmic rays and the radiations from radioactive substances, to which at high altitudes must be added the radiation from our sun.

Many of the ions thus produced become attached to certain large nuclei which are always present in the air, and predominantly so in the neighborhood of cities. The small ions are thus changed into so called large ions and some of these have diameters a hundred times that of a nitrogen molecule.

Since these ions do not recombine readily, owing to their slow thermal motion, there may be as many as 50,000 or more of them in a cubic centimeter in some places, which is greatly in excess of the number of small ions present.

The nuclei to which the small ions become attached appear to be invisible droplets of water, which have formed around some hygroscopic substance that is in all probability a product of combustion.

The positive ions always predominate in the atmosphere, and for this reason there is a vertical electric field near the earth's surface which in clear weather amounts to about 100 volts per meter. The atmospheric ions moving in this field constitute a downward current of over 1,000 amperes taken over the whole of the earth's surface. This current must somehow be neutralized. The most common belief is that this is accomplished mainly by lightning and by point discharges from objects on the earth.

The question arises by what process the two electricities are separated to produce the large differences of potential necessary for both of these kinds of discharge, potentials which may reach a billion volts.

It is generally agreed that the work of separation is done mainly by the wind and by gravity acting on charged rain drops as they fall. There is much dispute however as to how the drops get charged in the first place.

Several processes have been proposed to account for the charges on these drops, none of which has received general support.

I want lastly to consider the central ideas of some of these theories, leaving aside all details of application.

Gunn[17] has recently suggested that the small ions in the air are the source of these charges, these ions behaving like water molecules because they have water molecules attached to them. As I understand the argument, in the upper portion of a cloud to which ascending winds have brought moisture laden air, water vapor is condensing onto the rain drops and the flow of the vapor is naturally toward the drops, and so there the ions must also diffuse in the same direction. As the negative ions diffuse the faster, the drops will here become charged negatively. On the other hand, drops falling in the unsaturated air near the bottom of a cloud are evaporating and so the flow of vapor is here away from the drops, and as the diffusion of the ions again partakes of this flow, so the argument states, the drops will now become charged positively. In both cases each drop is surrounded by a volume of gas having a charge opposite in sign to its own. As the drops fall and air currents carry away the charged gas, large differences of potential may in this way be developed between the two portions of the cloud, and between the cloud and earth as well.

What I can not follow in the argument and this may not be decisive against the theory, is the idea that the diffusion of ions must follow the concentration gradient of the water vapor. The ions will establish their own concentration gradient, which in both cases will be toward the rain drops where alone they are being absorbed. There is never any force driving a molecule with or against a concentration gradient. Every molecule and so also every ion, in its wanderings, is a law unto itself, and moves about independently of what neighboring molecules may be doing. Changes in concentration that may take place with time are determined solely by statistical considerations.

I feel that the experimental data by which Gunn supports his theory, and which he states were obtained under not well-controlled conditions, need verification as regards the positive charge he found was acquired by a water drop, when placed in an unsaturated atmosphere of ionized air.

C. T. R. Wilson[18] has postulated a different process by which rain drops get charged, this time from the large ions in the atmosphere. Rain drops are normally charged by induction in the earth's field, positively on the lower side and negatively on the upper side. The terminal velocity of fall of the drops is greater than the downward speed of the large positive ions moving in the earth's field. These positive ions therefore can not overtake the drops from the rear and such of them as a drop overtakes are pushed aside by the positive charge on the bottom of the drop.

The upward moving negative ions, however, are attracted by the positive charge on the lower side of the drop which thus acquires a negative charge. The fall of these negatively charged drops from the upper to the lower part of a cloud gives this part a negative charge and leaves the upper portion charged positively by the ions which were left behind. After the

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[17] R. Gunn, *Terr. Mag.*, 40: 79, 1935.

[18] C. T. R. Wilson, *Jour. Frank. Inst.*, 208: 1, 1929.

drops have fallen far enough, the field between the earth and the bottom of the cloud is thus reversed, in confirmation of what experiment shows. The polar character of the cloud's charges is also in agreement with experiment. An objection that I have to this theory, to which its advocates have not given a satisfactory answer, is that it completely ignores the great air disturbances which accompany all thunderstorms, and which, it would seem, must in some way be one of the essential conditions for lightning production. According to the process postulated, lightning should be as likely to occur during a gentle shower as during a turbulent storm; in cold weather as in hot; near the Pacific coast as often as near the Atlantic. But such is not the case.

Another theory that has attracted much attention is that of Simpson.[19] This theory does not make use primarily of either the small or the large ions already present in the atmosphere. It postulates that the storm manufactures its own ions. It is well known that when a water drop is disrupted by an air blast, for example, the droplets which result from the disruption are found to be positively charged while an equal negative charge appears on ions in the air. Simpson seized upon this process as the one active in a thunderstorm. Swiftly ascending currents of air in the front part of the storm meeting falling rain drops tear them asunder with the resulting separation of electricities that has been described. The positively charged droplets may in time grow by coalescence, only to be disrupted again on reaching a certain size. Eventually, the drops fall away from the turbulent region of the cloud, the negative ions are carried upward by the air currents, and the high potential differences requisite for lightning are gradually built up.

This theory has a strong appeal because it makes use of the high vertical winds characteristic of thunderstorms to generate the large charges found in them. The comparative lack of lightning during cold weather and its entire absence in the Arctic regions may have a possible explanation on this theory. The argument is like this. After the wind has pulled a part of a drop into a film, the film breaks and snaps back into a number of droplets. These are charged positively because, in jerking back, the film loses some of the negative charge from a double layer supposed to exist on its surface. The faster the film contracts the greater its loss of charge. The speed of contraction depends largely on the viscosity of the liquid, and this decreases rapidly with rise of temperature, so that a warm film will contract faster than a cold one. Experiment has confirmed this reasoning,[20] for it was found that the charges obtained by disruption of drops falling through an air blast increase rapidly as the temperature of the drops is raised.

Hence we should expect potentials sufficient for the production of lightning to be reached with less violent air currents when the drops are warm than when they are cold. The only question that remains open is whether at the altitudes where the drops are being disrupted, the temperature is really different when it is undergoing large changes at the earth's surface.

The main argument directed against Simpson's theory is that the charges predicted by it in the clouds are more often than not of the wrong sign. Simpson[21] has countered these objections, but the arguments on both sides are too involved to be considered here.

The conditions in a storm are complicated and seem to vary with time and place, and the information about the actual distribution of the charges in a thunderstorm is still meager indeed. A more accurate knowledge of the location of these charges would be helpful in reaching a decision between the various theories, although in the end it may turn out that more than one of the processes which have been described, play some part in the phenomenon of lightning production.

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# BOTANICAL RESEARCH BY UNFASHIONABLE TECHNICS[1]

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NEARLY two years ago in suggesting that among certain crops in the United States there was a relation between disease damage and pollination behavior, I ventured to use volume of publication on the diseases of these crops in relation to their farm value as a measure of the commercial importance of diseases in their culture.[2]

The main thesis that, at least among the crops classed as "grains," disease losses are much more important in those groups which are wholly or largely self-pollinated than in those which are largely cross-

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[19] G. C. Simpson, *Phil. Trans.*, A 209: 379, 1909.

[20] J. Zeleny, *Phys. Rev.*, 44: 837, 1933.

[21] G. C. Simpson, *Proc. Roy. Soc.*, 114: 376, 1927.

[1] Address of the vice-president and chairman of the Section for the Botanical Sciences of the American Association for the Advancement of Science, Philadelphia, December 29, 1940.

[2] SCIENCE, 89: 339–340, 1939.