CHAPTER 3

CHARGING MECHANISMS

3.1 SUMMARY

There are several basic charging processes proposed which in one way or another might contribute to atmospheric electric phenomena. Some of the more important are contact electrification, electrochemical charging, influence charging, diffusion charging and mechanisms involving freezing and splinting of ice particles. Most of the above charging mechanisms were devised to explain the charging of thunder clouds. Some theories, such as those involving influence charging for example, will not operate in the earlier stages of cloud growth, and others, which involve freezing and ice, cannot be considered dominating since warm tropical thunderstorms exist which do not contain ice. There are numerous other theories which will not be mentioned here and there are even theories which argue that a combination of all charging mechanisms might be at play at one and the same time. The situation is very challenging. The latest theory to be proposed is that of the electrochemical process put forward by the author. The electrochemical charging mechanism has the advantage of being able to explain both thunderstorm charging and fairweather electricity. So far it is the only charging mechanism that can be readily demonstrated by working laboratory models. Contact electrification involves mechanical contact between solids where electrons from a lower work function material spill over to a higher work function material. Contact potentials are of the order of a few tenths of a volt and might occur in the atmosphere when solid precipitation particles of different temperatures collide or when solid precipitation particles bounce off material surfaces either on the ground or in the atmosphere.

Any process in which charge is captured or transferred by ions is by definition an electrochemical process. Charge transfer by ions can be referred to as oxidation-reduction reactions. An ion which gains an electron is reduced and an ion that loses an electron is oxidized. Electrochemical potentials are encountered in everyday life and can be found in batteries and dry cells for example, and has been known to chemists and included in their text books for centuries. One problem, however, is that the language and conventions used by chemists are not exactly tailor-made for physicists who therefore, in the author's opinion, seem to shun the electrochemical effect and often confuse it with contact electrification. An attempt will be made later to explain the difference between contact potentials and electrochemical potentials as seen by a non-chemist.

Influence charging deals with charges that appear on material surfaces which are exposed to an electric field. For example, dust resting on the earth's surface will be negatively charged during normal fairweather conditions since the electric field lines from the positive space charge in the atmosphere above must terminate on the negatively charged earth's surface (the surface in this example being covered with dust). During strong winds the negative charged dust particles can become airborne and form highly electrified dust clouds. Dust and sandstorms are most often found to be negatively charged. The same explanation can be applied to waterfall electricity where the negative charge, induced by the fairweather field on a surface of water, is being carried over the edge of a waterfall. As the electrified water falls over the edge it breaks up into small drops and forms a mist of negative space charge, referred to as the Lenard effect or waterfall electricity, first discovered by Tralles of Bern in 1786. Induction charging in thunder clouds has been considered by several investigators and is based on the idea that cloud drops, which are polarized while subject to the electric fairweather field, preferentially capture negative charge from smaller drops. As large drops fall and collide with smaller drops a transfer of charge is believed to occur where the upper half or negative pole of a smaller drop gives up its charge during the encounter. Negative charge collected in this manner would descend and occupy the lower portion of a cloud while the smaller drops with excess positive charge would remain behind to form an upper positive region.

3.2 CONTACT CHARGING

There are many excellent books and papers on contact potentials or Volta potentials, such as Loeb (1958) and Lord Kelvin's famous paper presented at the Bakerian lecture to the Royal Society (1898). But ever since Voltas original observations there has been confusion between contact potentials and electrochemical potentials, a situation which persists even today. For example, Lord Kelvin became very upset when Professor Lodge presented his paper "On the Seat of the Electromotive Force in a Voltaic Cell" (1885) and later in a private letter to Lord Kelvin he expressed his belief that contact potentials are related to the difference in oxidation energies of different materials. Loeb in his book warns, "Volta potentials must never be confused with electrolytic potentials". With due respect to both Kelvin and Loeb (the latter was a colleague of the author's) the author believes that Professor Lodge was also right.

Kelvin's condenser system which is shown in Fig. 19 demonstrates how volta or contact potentials are measured. It consists of two large capacitor plates made of dissimilar metals (copper and zinc) which are separated by an adjustable air gap. A switch and an electrometer are connected in parallel with the capacitor plates. The plates are connected to an electrometer. At first the switch k is momentarily closed which will allow electrons to flow from the zinc plate to the copper plate because zinc has a lower work function than copper. An electric field with a total potential of V_c, which is the difference in work function between the two metals, will appear between the two surfaces. When the spacing between the plates is increased from a to b the field lines will extend and the potential across the electrometer will increase to $V = V_c(a+b)/a$. In the above example the effects of fringing fields and stray capacitance were neglected. The diagram in Fig. 20 illustrates the relationship between work functions and contact potentials. Fig. 20a shows a typical potential well diagram for a metal

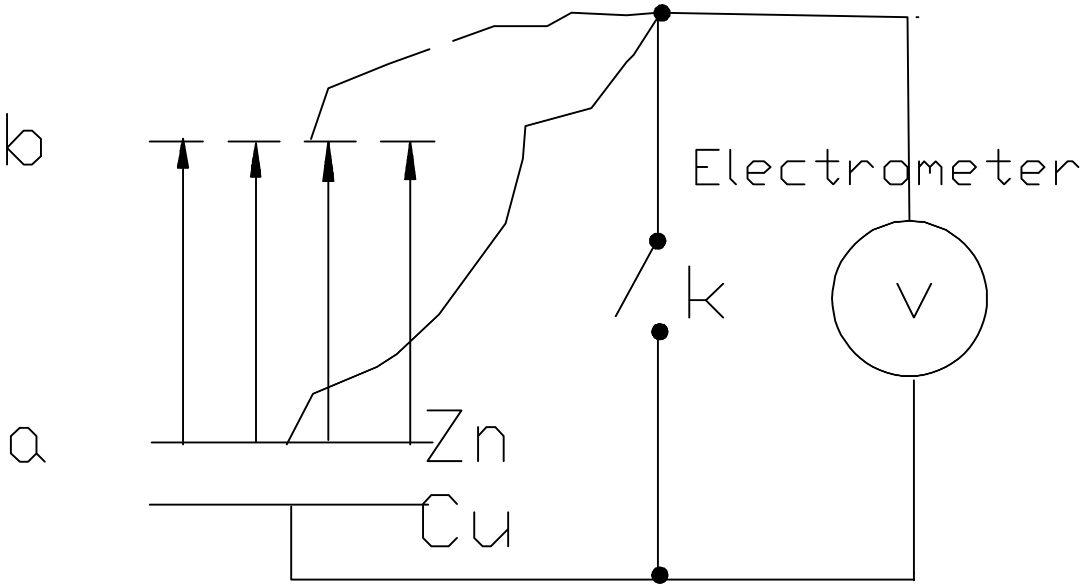

Fig. 19 Lord Kelvin's condenser system.

surface where the conduction and valence electrons are trapped at an energy level which is equal to the work function of the material in question. The potential barrier set up by the work function is represented in Figs. 20b and 20c by small electric cells between the conduction band of the material and its outermost surface. At first, before the switch k has been closed, there is no field between the zinc and copper surfaces. On closing the switch electrons will spill over from the zinc, having the lower workfunction to the

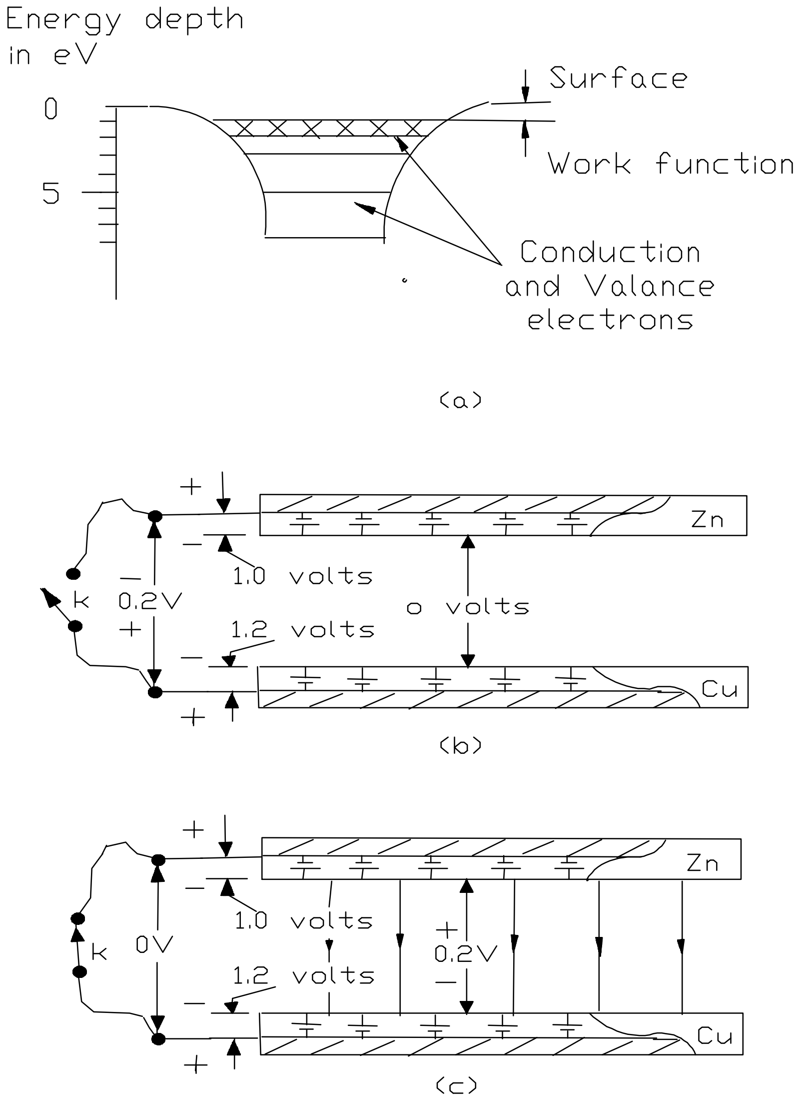

Fig. 20 Contact potential between zinc and copper. (a) Potential well diagram of a metal surface. (b) Electric field before contact is made. (c) Electric field after contact is made.

higher or deeper potential well of the copper. Bringing the conduction bands of both materials in electric contact will cause the difference in work function potential to appear across the gap of the plates. The amount of charge transferred is V_cC, where C is the capacitance of the plates. One characteristic feature of contact charging is that the current ceases as soon as the capacitance C is fully charged; i.e. contact potentials are not current driving sources such as galvanic cells, for example. The total amount of energy dissipated in the contact charging process is

$$W = \tfrac{1}{2} V^2 C \tag{3}$$

It is interesting to note that in his lecture to the Royal Society, Kelvin mentioned one experiment in which he placed a drop of cold water between the plates in his condenser apparatus and found the electrometer swing toward the opposite direction to that of the contact potential, but with the same magnitude. He attributed this effect to electrolytical conduction and not to contact potential charging. Experiments by Maclean and Goto in Glasgow in 1890 proved that zinc and copper, with fumes from flames passing up between them, gave, when connected to an electrometer, deviations in the same direction, as if cold water had been in place of the flame. Kelvin also mentioned that beside the wonderful agency in fumes from flames, there were reports by other investigators that ultraviolet light and x-rays traversing the gap between the plates caused the same effect as that of cold water. These effects, Kelvin thought, would to some degree fulfill Professor Lodge's idea of some potentially oxidizing process, but, "each one fails wholly or partially to maintain electric force or voltaic potential difference in the space between them". Further communication between Kelvin and Professor Lodge broke down when Lodge, in a letter, said that Kelvin was unrepentant.

Are contact potentials related to the chemical properties of the materials in question or are they purely a physical phenomenon? To clarify this problem one first needs to ask; where does the energy come from that causes contact potentials to build up? The contact potential which equals the difference in work function between two materials is also equal to the binding energy difference between the electrons in the materials. For example, the electrons in copper are more tightly bound to the atoms in the surface lattice than the electrons in zinc. Therefore, it will require more work to remove an electron from the copper surface than from the zinc surface, thus the name "work function". The chemical binding forces between the metal atoms can be pictured as hooks bonding the atoms together in all directions. However, at the surface there will be dangling bonds because the outermost atoms will have nothing to attach to outside the surface boundary. These dangling bonds make up for the surface energy or work function potentials which are simulated by the electric cells in Fig. 20 b and c. Since the energy of dangling bonds are chemical in nature then any transfer of charge, due to this energy, could technically be classified as an electrochemical process.

What will happen if the space between the plates in Fig 20c is filled with an equal amount of positive and negative ions either in form of a liquid or an ionized gas such as air? Will the negative ions go to the positive plate and the positive ions to the negative plate of the condenser and will there be a continuous current flowing in the circuit as long as the ion supply lasts? The answer is yes. But does the energy that drives the current in the circuit come from the contact potential (potential difference in work function between the materials)? The answer is no. First, the energy available from the contact potential is too minute (see Equation (3)) and cannot sustain a current for very long. It is therefore very clear that the energy driving the current must come from the ions themselves as they interact and recombine with the surfaces. Recombination here means the neutralization of an ion as it loses its charge to a material surface. The electric field between the plates, set up by the contact potential, see Fig. 21a, will draw negative ions to the zinc and positive ions to the copper. Once negative ions enter the zinc, charge is brought to the surface in the form of electrons.

These new electrons will immediately spill over from the zinc to the deeper potential well of the copper work function. However, no constant current can flow unless other electrons are allowed to leave the copper electrode at the same rate new electrons spill over from the zinc; i.e. the rate of negative charge brought to the zinc by negative ions must equal the rate of negative charge leaving the copper to combine with the positive ions drawn to the copper plate.

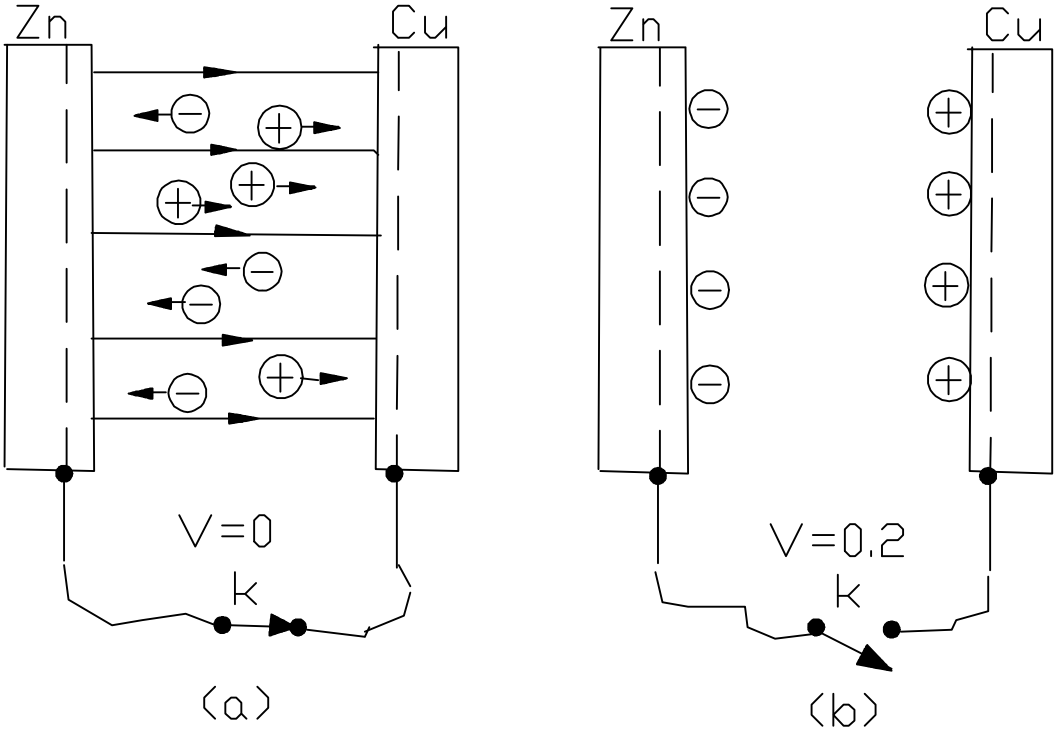

Fig. 21 Contact potentials in an ionized environment. (a) Ion current with switch k closed. (b) Potential build-up with switch k open.

What is the source of energy that is capable of lifting the electrons back out of the potential well of the copper work function? It is obviously not the work function or contact potential itself because that would be analogous to lifting oneself by the hair. The energy supplied must come from the ions residing in the spacing between the plates. The ionization or recombination energies of the ions will provide the necessary energy and a current will flow as long as the supply of ions lasts unless switch k in Fig. 21a is opened. If the current is interrupted by the switch, ions will continue to flow and charge the electrodes until a back-emf is built up that cancels the original field of the contact potential across the plates, at which point the flow of ions ceases. A potential equal to the contact potential will now appear across the switch and a situation such as shown in Fig. 21b will be reached.

The presence of ions between two electrodes of dissimilar materials and their ability to generate a steady current is nothing less than a galvanic cell. The primary source of energy is the ionization agency which might be radioactivity or cosmic rays as in the case of our ionized atmosphere. Ions are also produced in liquids where one or both electrode materials might slowly go into solution in the form of ions. The dissolved ions supply the energy that drives galvanic currents through circuits and usually at the cost of the lower work function material itself. A typical example is the flashlight battery or dry cell. Most charging processes involving ions are electrochemical processes.

3.3 ELECTROCHEMICAL CHARGING

Electrochemistry has played a major part in both industry and science for the last two hundred years. It might come as a surprise, however, to discover that the function of the familiar dry cell, such as used in portable radios, is not yet perfectly understood. The chemical reactions taking place are believed to be as follows: zinc metal from the outside casing is dissolved by the acidic electrolyte and leaves the container wall as positive metal ions. The charge removed by the positive ions going into the solution will cause a back- emf to build up between the zinc and electrolyte. When the back-emf has reached the same value as the solvation energy, the process stops because the electric field of the back-emf will prevent more ions from going into the solution. The result is an electric half cell with the positive metal ions in the solution forming a tightly bound electric double layer with the negative charged zinc. The other half of the cell is the carbon rod which has the function of supplying electrons to the electrolyte during operation but, the exact chemical reaction involved is not known. The voltage of the cell is determined by the difference in potential between the two half cells. The absolute energy or voltage of each half reaction is not known and no method has yet been devised to measure half cell potentials separately. The problem is how to electrically connect a voltmeter across the double layer without introducing another half cell reaction. Chemists have therefore settled for a compromise method whereby all types of half cells are compared to the voltage produced by a standard cell, the hydrogen half cell. This arbitrary method considers the potential of the hydrogen half cell as equal to zero and the difference in potential between the hydrogen half cell and any other half cell can be found in tables under the heading of Electromotive Force Series. One difficulty is that the potentials listed in the Electromotive Force Series refer to electrodes which are immersed in their own individual solutions containing their own ions, whereas in the dry cell both electrodes are in the same solution; i.e. a solution which contains zinc ions but no carbon ions. Another important question is what part does contact potential play in the electrochemical cell? The contact potential is often equal to or very near the potential of the cell itself and contact potentials are hardly ever mentioned in electrochemistry. Are electrochemical and contact potentials so closely related that when Professor Lodge argued with Lord Kelvin 100 years ago, he was right stating that they are of the same nature? It is now known for certain that the valence electrons, which determine the magnitude of contact potentials in metals, also determine the energy involved in electrochemical reactions.

In order to understand the electrochemical charging mechanism, especially as applied to atmospheric electricity, it might be helpful to describe a few laboratory and field experiments which were carried out in an attempt to clarify some of the above problems. Consider the following tests, which can readily be performed in the laboratory, and which are shown in Figs 22 a and 22 b:

1. Lower into an empty glass beaker two electrodes of differing materials (e.g. gold and magnesium) and connect an electrometer across the two electrodes. When a suitable radio-active source (e.g. Po 210, 500$_m$Cu) is placed at the bottom of the beaker, a potential of 1.2 volts will be registered between the electrodes, magnesium being negative with respect to gold.

2. Remove the radioactive source and fill the beaker with sufficient water to partially immerse both electrodes. The electrometer will again register a potential of 1.2 volts and the same polarity.

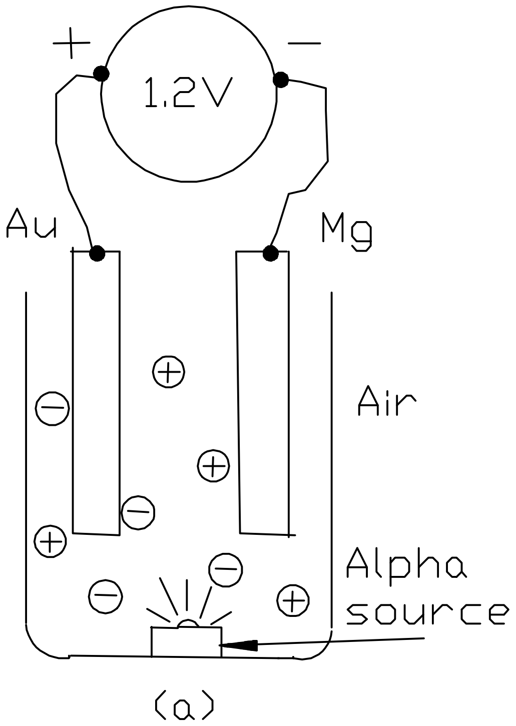

Fig. 22 Experiment demonstrating electrochemical charging. (a) Galvanic cell with ionized air as electrolyte. (b) Galvanic cell with water as electrolyte.

Both experiments deal with an electrochemical cell, using water for electrolyte in one case and air in the other. The fact that water contains ion pairs makes it an electrically conducting electrolyte which is vital for an electrochemical cell. In the first case, Fig. 22a, the beaker contains air instead of water, but the air is slightly ionized by the radioactive source, and although the number of ion pairs is relatively low, the ionized air is electrically conducting and exhibits the same properties characteristic of an electrolyte.

The average number of ions in the atmosphere is of the order of one billion pairs per cubic metre. The atmosphere is thus very much like an electrolyte. Its ion pairs are produced mainly by the constant bombardment of cosmic rays that reach our atmosphere from solar and stellar sources. Other ions are produced by radiation from radioactive materials in the atmosphere and in the earth's crust (see section 2.1.).

That material surfaces in contact with the ionized atmosphere are subject to electrochemical charging can also be shown by simply probing the atmosphere with electrodes and it can be easily demonstrated that in the absence of external electric fields negative ions rather than positive ions have a tendency to adhere to material surfaces. It can also be observed that when the probes are ventilated by strong winds, more ions are supplied and the negative ion current to the probes increases accordingly. At first, when such measurements were performed it was not at all clear what caused this type of charging although it was believed at the time that work function potentials might play an important part in the charging process. Experiments were therefore set up in the laboratory in an attempt to duplicate the field measurements described. Surfaces of diverse materials were ventilated by artificially ionized air. The results revealed a marked difference in activity among various materials in contact with the ionized air. For example, a small sheet of magnesium metal will absorb negative ions and continue to charge until it reaches a potential of -1.6 volts with respect to its surroundings. Each material tested was found to reach its own characteristic potential. An abridged list of these materials with their potentials appears in Table 1. The potentials in Table 1 agree with the potentials measured by the Gerdien cylinder shown in Fig. 11 section 2.1.

Material	Work function	Equilibrium Potential Volts
Magnesium	3.66	-1.6
Wet Filter Paper	-	-1.05
Aluminium	4.24	-1.0
Cadmium	4.22	-1.0
Tantalum	4.25	-0.65
Molybdenum	4.50	-0.6
Copper	4.65	-0.45
Stainless Steel	4.75	-0.4
Ice	-	-0.4
Gold	5.35	-0.22

Table 1. Work function and electrochemical equilibrium potentials for different materials.

At first it was disappointing to discover that the potentials in Table 1 were not at all proportional but rather inversely proportional to the work function potentials of the different materials in question. However, Table 1 has a very familiar appearance to the chemist; it resembles a chemical activity series in which the electrical potentials are values related to the oxidation energies of the materials in question. To further prove the electrochemical effect, the same materials were immersed in distilled water, two at a time. Differences of potential between the two materials were then measured and found to be directly proportional to the respective differences between their values in Table 1. From the experiments and the results of Table 1 it became clear that we were dealing with an electrochemical effect and the following conclusions were drawn: negative ions in air are formed from acidic molecules such as O_2 and NO_2. These molecules are electrophilic (electron seekers) and capture free electrons produced in air by the various ionization processes. The molecular ion, with its valence slightly reduced by a captured electron, still remains acidic and very active as an oxidizer. When the molecular ion with its piggy back electron oxidizes a surface material, negative charge is transferred by the captured electron to the surface. As more ions reach the surface, a negative back-emf will build up, eventually repelling any incoming ions until no more can reach the surface. Just as in the case of the dry cell an electrical equilibrium potential is achieved. The electrochemical reaction halts when the back-emf has reached a value equal to the oxidation potential, or the energy of the chemical oxidation-reduction reaction involved. Oxidation- reduction reactions can be described as follows: if two elements combine where one wants to share one or more of its electrons with another element which is an electron acceptor, then an oxidation-reduction reaction has taken place. The electron donor is said to be oxidized and the electron acceptor is reduced. It is interesting to note that in Table 1 the elements on top of the activity list are the elements with the lowest work functions. These elements freely share their valence electrons and become easily oxidized because of their lower electron binding energies or lower work functions. Electronegative elements or compounds are the electron seeking oxidizers that want to react with and oxidize material surfaces. The oxidizers or electron seekers appear most commonly as negative ions in the atmosphere and solutions because of their tendency to pick up free electrons in the surrounding environment. When the oxidizer reacts with a material surface it brings a captured electron along. The electron will charge the surface and the chemical reaction can therefore be classified as an electrochemical reaction.

The fact that oxidizers in general appear as negative ions forms the basis for electrochemistry in the atmosphere and in solutions. It is very important to remember, especially in the case of atmospheric electrochemistry, that the process which brings the negative ion to a material surface is the chemical reaction and not the electric field of the ionic charge itself. In an electrochemical reaction the electron simply enjoys a piggy-back ride to the surface and the image force produced by its charge is too feeble and short in range to compete with chemical processes. Also, the strength of the image forces are equal for both positive and negative ions so that no preferential charging of either sign can be expected. Nevertheless, a theory put forward by Phillips and Gunn (1954) considers the difference in mobility between negative and positive ions as possible mechanism for preferential charging. This theory will be discussed in section 3.4.

Numerous experiments in ionized air revealed that all metals and conductors tested proved to be oxidized by negative ions and achieved negative equilibrium potentials. No positive equilibrium potentials were ever encountered. In cases where two electrodes are immersed in an ionized medium, both electrodes become negatively charged relative to the electrolyte, the lower work function material being more negative. The potential between the electrodes equals the difference in oxidation potentials between the materials which also seems to equal their difference in work function except for the reversal of sign. The results were the same for electrodes immersed in ionic solutions where the electrodes did not go into solution. No tests were performed involving solvation energies.

One striking feature of the electrochemical charging process is the formation of the electric double layer. The oxidiation potential and the thickness of the double layer determines the charge density on the oxidized surface. In normally ionized air the double layer thickness is about 1 mm which means that a surface of water, for example, which has an oxidation potential of -0.25 volts, will charge to

$$Q / \mathrm{m}^2 = V_0 e_0 / d \tag{4}$$

where d is the double layer thickness and V_0 the oxidation potential. The value of d was derived from laboratory experiments which proved that the average thickness of the double-layer in air, to the accuracy of the measurements, is equal to the average distance between the ions. It appears that each time a negative ion reaches the surface, it leaves behind a positive ion at a distance equalling the average ion spacing. This distance for normally ionized atmosphere is about one millimetre. In an experiment that followed, isolated spheres (to simulate cloud drops) were ventilated by ionized air for the purpose of studying the charge collection on their surfaces. Negative ions reacting with the surface of a drop or a sphere leave behind positive ions in the surrounding air, thus building up a diffuse space-charge cloud around the sphere. This cloud of positive ions forms an electric double-layer with the charged surface of the sphere. The double-layer, formed by the charged surface of a sphere surrounded by its diffusion cloud of opposite charge, constitutes a spherical capacitor with a capacitance of

$$C = 4pe_0 R(1 + R / d) \tag{5}$$

R is the radius of the sphere, and d is the mean thickness of the double-layer. The charge on the sphere can then be calculated from the electrostatic expression

$$Q = V_0 C = V_0 4pe_0 R(1 + R / d) \tag{6}$$

where the double-layer voltage, V_0, is also the oxidation- reduction potential of the reaction between the ions and material in question. The sphere with its attached double- layer is, of course, electrically neutral with regard to its surroundings. No drastic charge separation has yet occurred.

The fact that the sphere or drop is ventilated (by falling through the atmosphere for example) is of the utmost importance because the flow of air will partially strip away and remove the outer positive layer of the double-layer, a process that not only increases the potential of the sphere but also makes it appear to be negatively charged relative to its general surroundings. For example, removing the outer-charged layer to infinity will increase the potential on the sphere to

$$V = \frac{Q}{C} = V_0(1 + R / d) \tag{7}$$

Common experimental values for charged water drops are shown in Figure 23. These values were obtained from actual measurements in

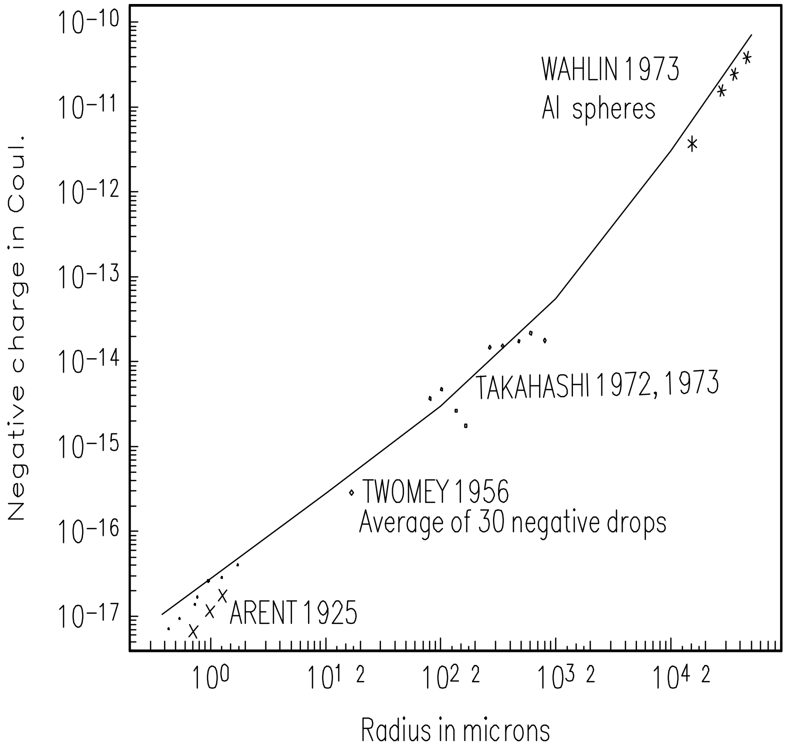

Fig. 23 Charge-size measurements of rain drops compared to values predicted by the electrochemical charging process.

the atmosphere by several investigators and are compared here to the predicted values represented by the solid curve. The curve is constructed from Equation (6), using a double-layer thickness of one millimetre, a distance that equals average ion spacing in the normally ionized atmosphere. An oxidation potential of $V_0 = -0.26$ volts for water was chosen from the experimental results of Chalmers and Pasquill (1937) who, in their laboratory, measured the equilibrium potentials on water drops. The oxidation potential for water in Table 1 is -0.4 volts which is the value obtained for water when ventilated by an equal amount of positive and negative ions. In the normally ionized atmosphere there are more positive than negative ions. A typical ratio is $N^+ / N^- = 1.2$ which will lower the equilibrium potential to about one third (see the results in Fig. 11) and which agrees with Chalmers and Pasquill's results.

3.4.1 OTHER CHARGING PROCESSES

Except for the well established effects of contact and electrochemical potentials there have been several other charging mechanisms proposed in order to explain atmospheric electric phenomena. Some involve influence charging in combination with colliding drops such as the Elster-Geitel theory, or influence charging and the capture of ions as proposed by Wilson. There are charging mechanisms which consider ice splintering and freezing of water drops to be important in producing charge on precipitation in clouds. The process of evaporation and recondensation of water has intrigued many investigators, including Volta, as a possible source of positive and negative charge in clouds. Takahashi (1973) has recently carried out work along these lines. The validity of the above charging mechanisms are difficult to verify since they lack rigid experimental proof. Recent years have seen many sophisticated computer models which will work if the right parameters are plugged in. This is especially true for influence charging mechanisms involving collision between polarized drops in strong vertical electric fields. Some mathematical computer models are often conceptually difficult. Since mathematics is only a tool of science it is more desirable to have a conceptual theory that is mathematical sound than a mathematical theory that is not conceptually sensible.

3.4.2 THE ELSTER-GEITEL PROCESS

The Elster-Geitel (1885) process deals only with the charging of precipitation particles such as drops in clouds. It is based on the assumption that cloud drops, which are polarized in the electric fairweather field, collide with each other and exchange surface charges in a manner that will enhance the fairweather field to a magnitude found in thunderstorms. The proposed charging mechanism is shown in Fig. 24 where a smaller drop which is still light enough to be swept upwards by the updraft winds in the cloud, collides with a much larger and heavier drop falling down through the cloud. Since the large drop is polarized in the electric fairweather field its upper surfaces will attain a small excess of negative charge while the same amount of positive charge will appear on the lower surface. A small drop bouncing off the lower surface will pick up some of the positive charge at the moment of contact, and bring it along to the top of the cloud while the heavier and larger drop, now negative from the loss of positive charge, will continue to fall and bring negative charge to the lower region of the cloud. It can easily be seen that as

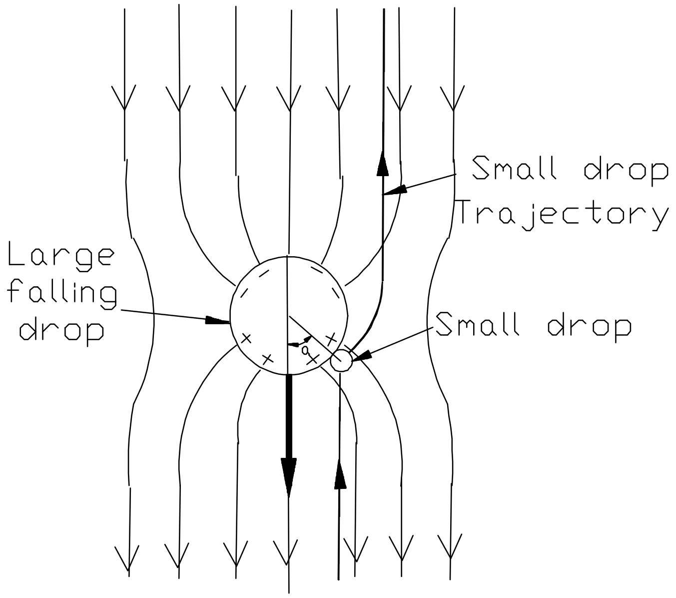

Fig. 24 The Elster-Geitel charging process of cloud drops.

charge is being separated the electric field strength will increase which in turn intensifies the charging process.

Although sophisticated computer models of the Elster-Geitel theory have been studied (Sartor (1954), Levin (1975) and (1983)) the general feeling is that the charging mechanism is too weak. The theory might possibly work if the initial electric field strength was equal to that found in thunderstorms in which case some other process must prevail (Pathak 1980). Unfortunately there is no laboratory support for the Elster-Geitel theory and some of the unanswered questions are: do small drops really bounce off larger drops at a reasonable rate or do they simply coalesce? How important is the grazing angle of the impact?

3.4.3 THE WILSON EFFECT

The Wilson (1929) effect is similar to the Elster-Geitel process with the exception that instead of small drops colliding with larger polarized drops negative ions are believed to be swept up by the larger drops as they fall through the normally ionized air. The positive charge induced on the bottom half of a large drop is believed to preferentially collect negative ions as the drop falls down to lower altitudes thus leaving an excess positive charge behind at higher levels. One serious objection to the Wilson theory is that there are not enough ions produced inside a thunder cloud to account for the amount of charge separated.

3.4.4 DIFFUSION CHARGING

Gunn (1957) considered a charging mechanism which is based on the difference in mobility between positive and negative ions. He assumed that since negative ions display a higher mobility in an electric field than do positive ions they must be less massive and therefore also have a greater diffusion coefficient in the absence of electric fields.

The expected result is that negative ions will diffuse on to cloud drops at a higher rate than positive ions can. Cloud drops will therefore become more negatively charged and as they fall down to the lower region of the cloud they leave an excess of positive charge behind in the upper region. Experiments with metal spheres ventilated by ionized air were carried out by Phillips and Gunn (1954), see Fig. 25. They confirmed that chrome plated metal spheres exposed to ionized air indeed charged negatively and reach certain equilibrium potentials.

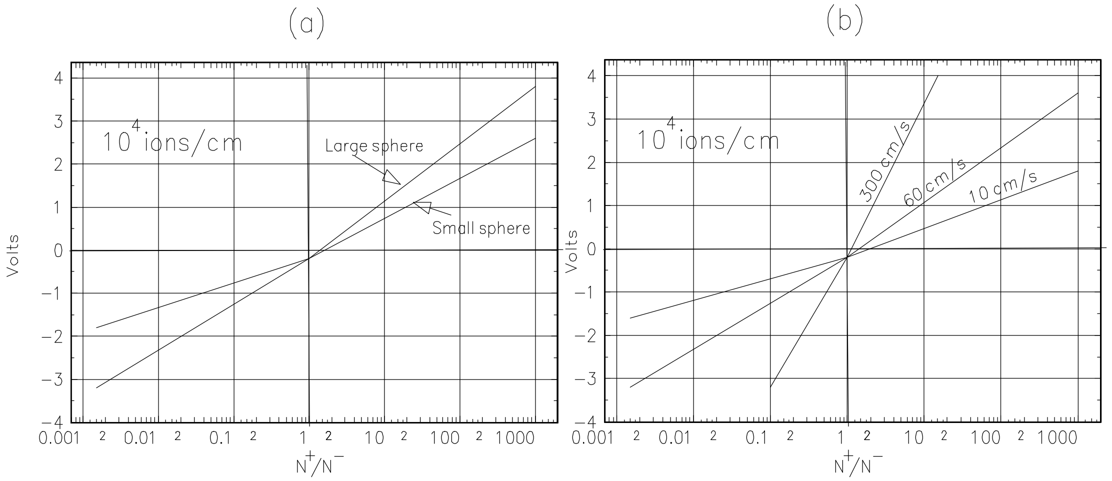

Fig. 25 Phillip's and Gunn's Experiment with metal spheres. (a) Equilibrium potentials for different dia. spheres. (b) Equilibrium potentials for different air velocities.

What is interesting about Phillips' and Gunn's experiment is its similarity to the experiments which demonstrate the electrochemical charging mechanism by the use of Gerdien cylinders, see Figs. 10 and 11. In fact, some investigators argue that the equilibrium potentials in Table 1 and the results shown in Figs. 10 and 11 can be explained by the diffusion theory. But this is hard to believe since the diffusion theory does not predict that different materials charge to different equilibrium potentials as shown in Table 1. Also, the energy of the diffusion process relates to the thermal agitation of the ions in their atmospheric environment and is determined by the air temperature. This means that the equilibrium potential, using Boltzmann's constant k and a maximum air temperature of $T = 20$ C, cannot exceed

$\frac{3}{2}kT \times 0.25$ or 0.008 volts where 0.25 represents the 25 percent higher mobility of negative ions over positive ions. This is only 3% of the values shown in Table 1 and the graphs of Phillips and Gunn (Fig. 25).

3.4.5 FREEZING POTENTIALS

Although it is known that warm clouds (clouds that do not contain ice or frozen precipitation) can charge to considerable potentials and occasionally produce lightning, there is still a great deal of attention devoted to charging processes that might involve icing. One reason for this is the observation by Simpson and Scrase (1937) who noticed that separation of charge in thunderclouds seems to occur in regions where the temperature is below freezing. They thought that colliding ice particles might charge negatively and leave positive charge behind in the air in the form of positive ions. The idea was further developed by Reynolds (1954). Workman and Reynolds (1950, 1953) have also discussed a theory in which glazing processes were assumed to produce charge. Many theories have been put forward which involve freezing of water, but again there are, unfortunately, no convincing laboratory experiments.