The structure and stability of ball lightning

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Contents

The main characteristics of ball lightning are well established. They include its general appearance (shape, size range, brightness, etc.), its peculiar motion and, less satisfactorily, its energy content. A remarkably consistent picture emerges from the thousands of detailed descriptions which are now available. There is, however, no such consistency in the various hypotheses that have been put forward to explain ball lightning. The only thing most of them share is an ability to explain a few aspects of the phenomenon at the expense of physically impossible requirements in other areas.

If one is to accept that a single phenomenon is being described in all these observations, it seems clear that ball lightning is, at the very least, an electrical and chemical phenomenon; and several branches of both disciplines seem to be involved.

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High humidities are nearly always implied and it is known that the behaviour of strong electrolytes in saturated water vapour cannot be properly modelled thermodynamically. An approximate way of circumventing this problem is developed. It allows a thorough, if only approximate, thermodynamic analysis to be undertaken.

From this, phenomena that explain the structure and stability of ball lightning are predictable. They arise quite naturally by considering the nature, energetics and fate of ions escaping from a hot air plasma into the cool, high humidity environment of electrically charged air.

The model resulting is as follows. A central plasma core is surrounded by a cooler, intermediate zone, in which recombination of most or all of the high-energy ions takes place. Further out is a zone in which temperatures are low enough for any ions present to become extensively hydrated. Hydrated ions can also form spontaneously in the inner, hotter, parts of this hydration zone. Near the surface of the ball is a region, quite essential to the model, in which thermochemical refrigeration can take place.

In an established ball, energy is supplied not only by electric fields and, possibly, electromagnetic fields, but also by the production of nitric acid from nitrogen and oxygen and by the hydration of the ions. It is shown that, if NO_2^- and H_3O^+ ions become hydrated by more than about five water molecules before they can combine at the edge of the ball, the reaction will be endothermic and can refrigerate its surface.

The ball can thus be considered as a thermochemical heat pump powered by the electric field of a thunder storm. The surface refrigeration allows the condensation of water in quantities sufficient to counteract the buoyancy of the hot plasma. The in-flow of N_2 and O_2 produces both nitrous and nitric acids, the latter being dissolved in the water droplets. The flow of gas inwards past these droplets (and past those condensed around an excess of H_3O^+ ions) provides an effective surface tension for the ball which appears sufficient to explain its shape and mechanical stability.

Clearly explanations for the surface coolness and frequently reported cloudiness are provided at the same time. All the well documented properties (amounting to over 20 distinct properties in total) can be explained in a consistent manner within the framework of the model.

1. Introduction

Over the past 200 years, roughly 2000 observations of ball lightning have been reported in sufficient detail for scientists to take them seriously. Yet there are still scientists who cannot accept that they exist. Lord Kelvin believed they were all optical illusions while Faraday, for good reason, was sure that they were not electrical phenomena. Many models for the phenomenon now exist but none can satisfactorily explain all the characteristic properties.

If they are not electrical phenomena, it is difficult to explain why they are almost invariably associated with stormy weather, why they have occasionally been seen to form from normal electric discharges and why they so frequently behave as if they were charged spheres. Because they can be hot enough to melt holes in glass, it is not easy to see why they so rarely rise as a result of the inevitable buoyancy forces. Sometimes they just disappear, so they must be gaseous. But it is not obvious how

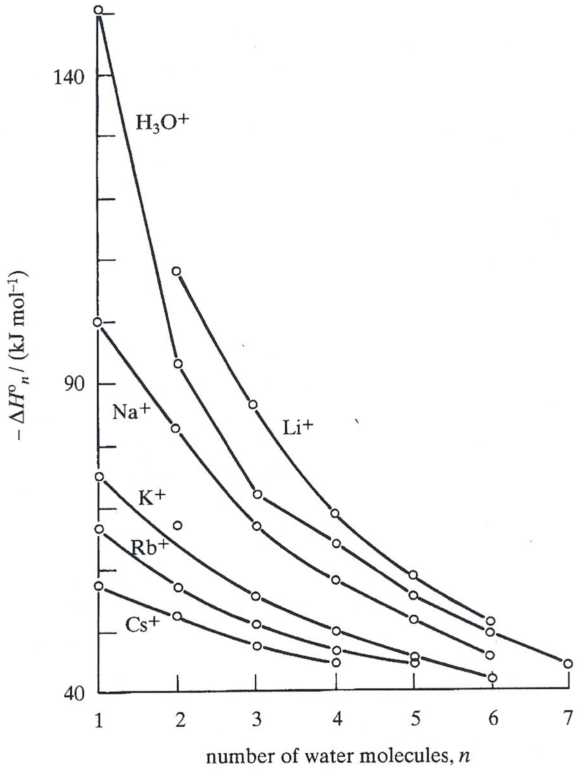

Figure 1. Enthalpies of hydration of cations as measured by Kebarle and co-workers. For the large cations, the enthalpies do not differ much from the enthalpy of condensation of pure water, -44 kJ mol^{-1}.

there can be a surface between two gases that is sufficiently stable to allow the balls to bounce or to squeeze through small holes.

A reconciliation of these apparent contradictions is provided by an approximate thermodynamic analysis of the processes which must be occurring as ions escape from a hot air plasma into moist, electrically charged, air.

The most serious limitation to this approach is the absence of data on the hydration of ions at high relative humidities. In fact it was the extremely poor understanding of the thermodynamics of electrolytes in saturated steam (Turner 1989), which first led to the thought that the two areas of ignorance might be connected. Concerning the behaviour of ions in saturated steam, we really only know that Dalton's Law of partial pressures cannot possibly hold and this has far reaching consequences. There are, however, good data on ionic hydration at rather low water vapour pressures. It therefore seemed worth trying to develop an estimation procedure which was applicable much nearer to saturation.

After addressing this problem in §2, the matter of the chemical species released from an air plasma is considered in §3. The observed properties of ball lightning and existing models are then described in §4 and the earlier thermodynamic conclusions, together with associated kinetic considerations, are used to explain the structure and stability of ball lightning in §5.

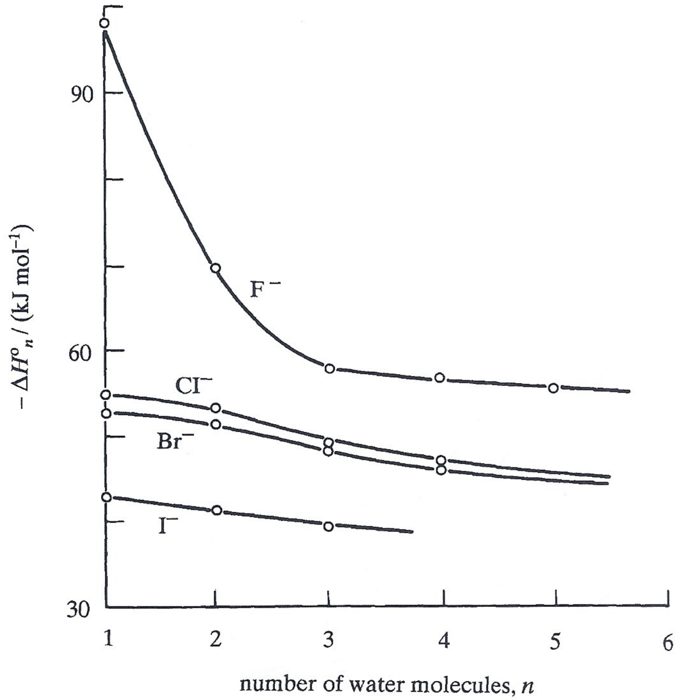

Figure 2. Enthalpies of hydration of anions as measured by Kebarle and co-workers. Larger anions have enthalpies which differ still less from the enthalpy of condensation of water.

2. Thermodynamics of gas phase ion hydration

(a) *Available data on simple ions*

Because the hydration of ions is basically an electrostatic phenomenon, it is reasonable to expect a degree of order in the gas phase thermodynamics and this has been shown to be so (Dzidic & Kebarle 1970; Arshadi *et al.* 1970).

These authors measured the equilibrium constants, K, of the gas phase formation reactions for cations, $M^+.nH_2O$ and anions, $X^-.nH_2O$,

$$M^+(n-1)H_2O+H_2O = M^+.nH_2O \tag{1}$$

and

$$X(n-1)H_2O+H_2O = X^-.nH_2O \tag{2}$$

using specially designed high pressure mass spectrometry equipment. From the temperature dependence of K, the standard heats and entropies of the reaction were obtained via the relations

$$\Delta G^0 = -RT\ln K = \Delta H^0 - T\Delta S^0 \tag{3}$$

from the usual plot of $\ln K$ and $1/T$. The linearity of these plots suggested that ΔH^0 is essentially independent of temperature, so that the standard heat capacities of the reaction, ΔC^0_p, could all be taken as zero. This assumption has been made for all the equilibria considered in this paper.

Figures 1 and 2 display the standard enthalpies for simple cations and anions as obtained by Kebarle and co-workers (Arshadi *et al.* 1970, for the halides; Dzidic & Kebarle 1970, for alkali metal ions; Kebarle *et al.* 1967, for the H_3O^+ ion).

A clear dependence on ionic size is apparent. For the anions, the smaller magnitude

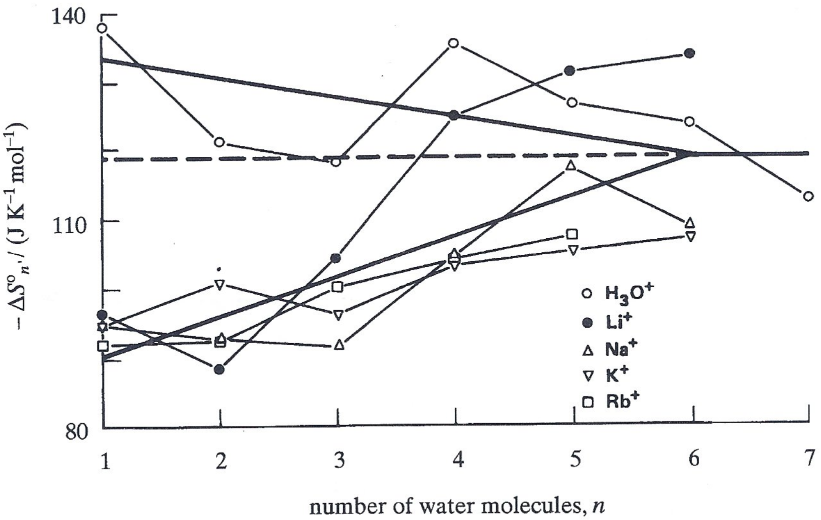

Figure 3. Entropies of hydration of various cations. The larger cations (i.e. those other than H_3O^+ and Li^+) have rather similar entropies of hydration but all are tending towards the entropy of condensation of water as n increases. ---, standard entropy of condensation; ——, smoothed entropies.

of the heats is as expected (although the similarity of Cl^- and Br^- is not) because they are much larger.

The situation seems much less tidy with the entropies. Figures 3 and 4 display nearly all the relevant values from the studies under consideration. There is no obvious reason to expect the values of ΔS^0 to vary smoothly with increasing n. However, it is arguable that much of the irregularity in the behaviour (perhaps not the value for the formation of $F^-.4H_2O$) is a consequence of experimental error. A comparison of the discrepancies in ΔS^0 values for many hydration equilibria (see Keesee & Castleman 1986) supports this contention. It should be appreciated that, while the slope (which gives the enthalpy change) of a van't Hoff plot is well defined, the intercept of the graph, which yields the entropy change, represents a long extrapolation.

The two solid straight lines shown in figure 3 represent smoothed values of the standard entropies for H_3O^+ and for the other cations. A similar straight line in figure 4 yields smoothed entropies for the anions.

(*b*) *Estimation procedure*

The horizontal line at -119 J K^{-1} mol^{-1} in figure 3 represents the standard entropy of condensation of water at 25 °C. For very large clusters, ΔS^0 would inevitably tend towards this value since one would be considering condensation onto a decreasingly impure droplet of water. The ΔS^0 values appear to be converging on this value fairly rapidly, which suggests that the molar entropies of water in complexes containing six or seven water molecules do not differ greatly from the entropies of similarly sized clusters of water molecules. Clearly, from figures 3 and 4, the smoothing straight lines could almost equally satisfactorily have been chosen to intersect the condensation line at $n = 5$ or $n = 7$. In all the larger hydrates, of course, the major contribution to ΔS^0 is the loss of translational freedom of the gaseous H_2O molecule.

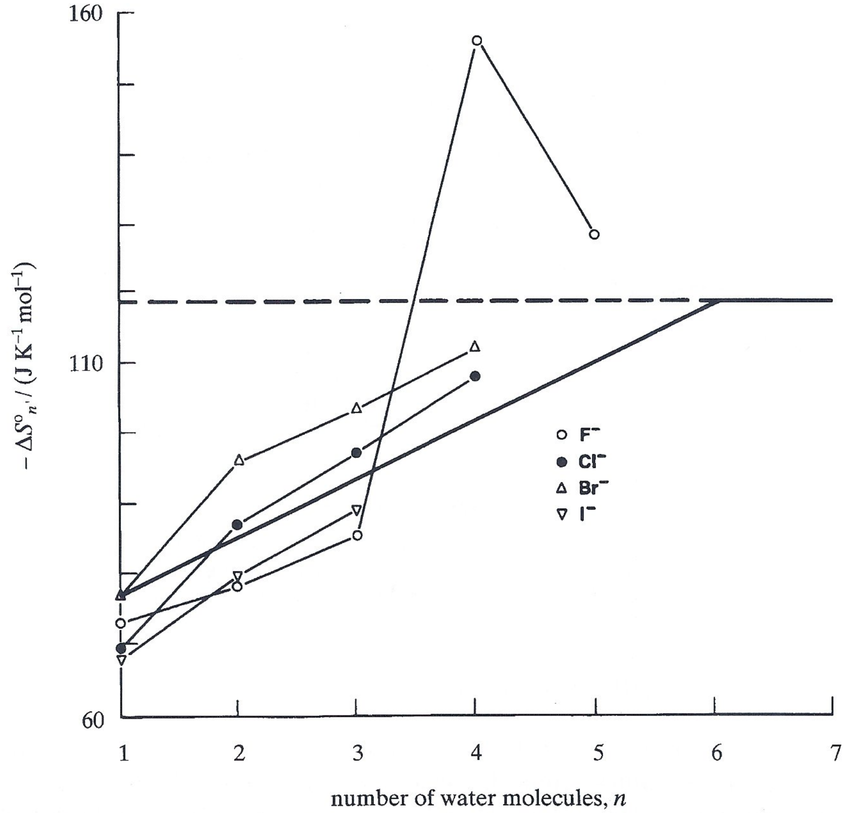

Figure 4. Entropies of hydration of various anions. Apart from F^-, the behaviour is similar to that of the larger alkali metal cations. ---, standard entropy of condensation; ——, smoothed entropies.

If the addition of water molecules to the larger clusters is thermodynamically similar to the condensation of pure water, then the enthalpies should show the same tendency. It can be seen from figures 1 and 2 that this is so since the molar enthalpy of condensation for water is -44 kJ mol^{-1}.

The use of these smoothed enthalpy and entropy values enables one to estimate the relative stabilities of hydrate clusters at different temperatures not only for stable states at higher water fugacity but also into the metastable range. By using the smoothed enthalpies and entropies, the measured equilibrium constants could be recovered satisfactorily.

Hydration enthalpies and entropies are also available for a wide range of polyatomic ions (Keesee & Castleman 1986) but such measurements do not extend to the higher hydrates ($n \geqslant 3$). For all such species, we assumed, both with ΔH^0 and ΔS^0, that the values converge linearly towards the values for pure water at $n = 4$. Again, for higher values of n, we assign water condensation values.

Because molecular ions can undergo chemical reactions which most monatomic ions cannot, a completely independent check of the estimation procedure is, in principle, available. We shall see (§3*b*) that such a test is possible on a directly relevant system and that it confirms the predictions of the estimation procedure.

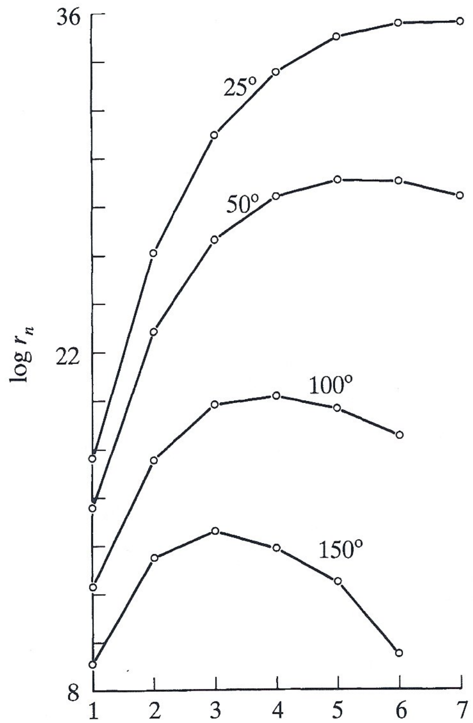

Figure 5. Relative concentrations, r_n, of H_3O^+ hydrates at temperatures of 150 °C and below. The predominant species contains increasing numbers of water molecules as temperatures are reduced. Free H_3O^+ would be undetectable even at 150 °C.

(*c*) *Chemical speciation*

From the estimated equilibrium constants and the partial pressure of water, relative concentrations of the various hydrate species can be obtained. We take the fugacity of each component to be given by its partial pressure. For water, the vapour pressure is taken to be that appropriate to saturation at 25 °C (0.0342 bar). The results of such calculations, for seven hydration reactions of the ion H_3O^+, are illustrated in figure 5.

Here, for a species $H_3O^+.nH_2O$, the concentration, r_n, relative to that of the unhydrated ion is plotted against the hydration number, n. A similar plot for K^+ is shown in figure 6. It shows the same general features but the predominance of hydrates over the bare ion is much less marked. Anions are still less strongly hydrated, but even here, for Br^- say, equilibrium r_n values rise to 10^{11}.

It is clear that free ions would be virtually undetectable at equilibrium for low temperatures. Furthermore, the hydration reaction is known to proceed very rapidly (Kebarle *et al.* 1967; Young *et al.* 1970). Thus, as a first approximation, local equilibrium between ions and water can reasonably be assumed and significant hydration must be expected at even quite low relative humidities. It will be seen (§4*d*) that these conclusions force crucial modifications to an otherwise excellent ball lightning model (Powell & Finkelstein 1969).

It can also be seen that for all the ions, larger complexes predominate the lower the temperature. At 25 °C (where saturation of the vapour has been assumed) the species

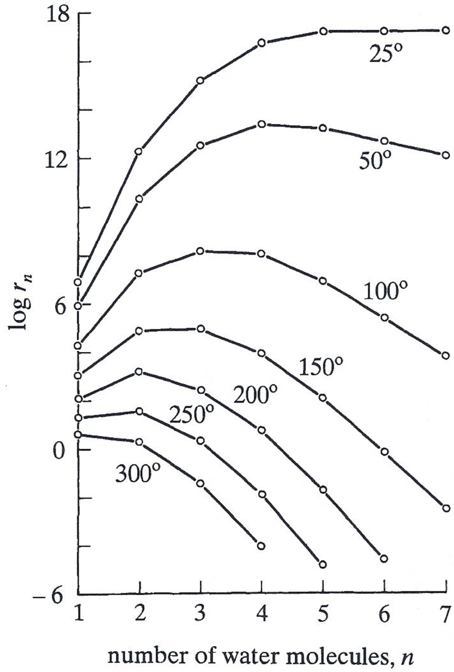

Figure 6. Relative concentrations, r_n, of the hydrates of K^+. The behaviour is qualitatively similar to that of H_3O^+ but the much lower values of r_n result from weaker hydration.

distributions are levelling off and, however large n became, the complexes would be predicted to be equally stable. This is, of course, to be expected, because we are effectively considering condensation onto small water droplets while the effects of surface tension and metastable states have not been considered. In practice, as pointed out by Dzidic & Kebarle (1970), metastable states should be formed up to $n \approx 20$ and only at higher n values than this would spontaneous condensation occur.

At first sight one would not think that these considerations would have any relevance to ball lightning, as the plasma must be releasing heat and there is no way in which high humidities could be maintained near to a globe of ball lightning. It will be seen later that this simple picture is incorrect.

3. Chemical species released from an air plasma

It is necessary to consider next the nature of any ions that may be able to escape from an air plasma into humid air. For the present purposes we only need to consider the chemistry of nitrogen, oxygen and hydrogen (from water vapour). Carbon dioxide may also play a part but it does not seem necessary to invoke any major contribution from carbon (except, possibly as a metastable intermediate).

Around an open air plasma at atmospheric pressure, there will be a boundary, of unspecified and variable thickness, over which the temperature drops from that at the edge of the plasma to that of the ambient air. Somewhere between these two temperatures there will be one at which the hydration reactions of the type considered in §2 will begin to occur. We refer to the region below this temperature as the hydration zone, with the region between it and the plasma referred to as the intermediate zone.

(*a*) *Reactions in the intermediate zone*

The JANAF thermochemical tables (Chase *et al.* 1985) which contain only well-characterized species, list 50 gaseous chemical species containing only combinations of N, O and H. Unless otherwise stated all thermodynamic arguments that follow are based on the JANAF data. These 50 species vary widely in stability and several are of such high energy that they are unlikely to be formed in a plasma at 2500 K. We have neglected contributions from all species that are significantly less stable than those which Powell & Finkelstein (1969) considered could be involved in air plasma processes at 2000–2500 K.

At this temperature, the plasma is not likely to be in thermodynamic equilibrium, its chemical state being largely determined by kinetic processes. Because we are principally concerned with phenomena at even lower temperatures, the main role of thermodynamics here is to distinguish between processes which could occur and those which could not. In this way it is possible to simplify the overall picture of the processes occurring as one moves away from the plasma.

Ideally, of course, we require a complete analysis involving the rates of mass and heat transfer, as well as the rates of all relevant chemical reactions. Rate constants are available for many of the reactions that occur just outside the plasma (Baulch *et al.* 1984; Steinfeld *et al.* 1987). However, there are so many reactions that can occur at lower temperatures, whose rates and thermochemistry are not known, that modelling on this basis would be unconvincingly speculative. The best we can do at present is to note that there are plenty of third bodies, especially in the hydration zone, that can remove the reaction heat. Thus, except for species known or plausibly arguable to have a long lifetime, only thermodynamically stable species are expected to escape very far.

The high-energy species considered by Powell & Finkelstein (1969) as likely components of an air plasma near 2500 K are the following N_2^*, O_2^* (where * indicates an excited state), NO, NO_2, O, H, OH, N_2^+, O^+, O_2^+, NO^+, N^-, O_2^-, NO^-, H_2O^-, H^-, OH^-. We have also considered the species H^+, NO_2^+, O_3, HNO_2, HNO_3, N_2O_3, N_2O_4, N_2O_5, NO_3, NO_2 and NO_3^- (which are all more stable than the earlier mentioned species).

We are principally concerned with the question of which ions are likely to last long enough to become extensively hydrated at the outer perimeter of the hydration zone. To assess which are thermodynamically the stablest it is necessary to consider the free energies of all feasible reactions with those stable neutral molecules that are likely to be present in significant quantity, i.e. interconversions involving N_2, O_2, H_2O, NO, NO_2, HNO_2, etc. In this way it is easily shown that such reactions as

$$2O_2^+ + N_2 = 2NO^+ + O_2, \tag{4}$$

$$2H^+ + N_2 + \tfrac{3}{2}O_2 = 2NO^+ + HO_2, \tag{5}$$

$$2NO_2^+ = 2NO^+ + O_2, \tag{6}$$

$$O_2^- + NO_2 = NO_2^- + O_2, \tag{7}$$

$$OH^- + HNO_2 = NO_2^- + H_2O, \tag{8}$$

could only proceed to the right over the temperature range of interest. Thus, so long as an appropriate kinetic pathway is available, we would expect the predominant

Table 1. *Thermodynamics of hydration of* NO^+

n	1	2	3	4	>4
$-\Delta H^0/(\text{kJ mol}^{-1})$	79.5	67.8	55.7	43.9	43.9
$-\Delta S^0/(\text{J mol}^{-1}\text{ K}^{-1})$	98	105	112	119	119

ions entering the hydration zone (at about 500 °C) to be NO^+, NO_2^- and NO_3^- (reliable thermochemical data are lacking in gaseous NO_3^- but the conclusion seems firm).

A rather delicate balance applies between the cations NO^+ and H_3O^+ (which becomes increasingly important at lower temperatures). The transformation can, in principle, occur by such reactions as the following:

$$2NO^+ + 3H_2O = 2H_3O^+ + 2NO + \tfrac{1}{2}O_2 \tag{9}$$

or

$$2NO^+ + 3H_2O + \tfrac{1}{2}O_2 = 2H_3O^+ + 2NO_2. \tag{10}$$

However, the standard enthalpy and entropy of reaction (9) are both unfavourable so that, if it were the only possible reaction, the formation of H_3O^+ would not be favoured at any temperature. Reaction (10) does have a negative enthalpy though its negative entropy makes the standard free energy, ΔG^0, positive, ΔG^0 values at 25, 100, 200 and 300 °C are 33.5, 48.6, 68.7 and 88.8 kJ mol^{-1} respectively. These are relatively small values. Thus, the possibility exists that hydration might tip the balance in favour of H_3O^+.

(*b*) *Reactions in the hydration zone*

To illustrate the expected influence of hydration we assume that reaction (10), as well as the various hydration processes for NO^+ and H_3O^+, are at equilibrium. We again take the partial pressure of water to be 0.0324 bar (saturation at 25 °C) and arbitrarily take the NO_2 pressure to be 0.01 bar (because its presence in low concentration is sometimes inferred in air plasmas and ball lightning). The standard enthalpies and entropies of hydration for NO^+ were taken from the compilation of Keesee & Castleman (1986) and, where necessary, estimated in the manner described in §2. The resulting data, which refer to the reaction

$$NO^+(n-1)H_2O + H_2O = NO^+nH_2O \tag{11}$$

are as given in table 1.

Using this information and analogous data on H_3O^+ from Kebarle *et al.* (1967) all needed equilibrium constants were calculated. These were used to calculate the equilibrium speciation of all important cations over the temperature range 25–500 °C. Most of the results are plotted in figure 7 as concentrations relative to the concentration of free NO^+. Although (for clarity) not all relevant species are plotted, the trends are clearly indicated.

It is apparent that above about 350 °C, unhydrated NO^+ predominates with higher and higher hydrates of H_3O^+ becoming predominant as temperatures drop below 300 °C. At the lower temperatures (below about 150 °C) the curve for the ion $NO^+.3H_2O$ (not illustrated) lies very close to that for $H_3O^+.H_2O$. Thus, in this temperature range, total NO^+ levels are negligible compared with the total of hydrated H_3O^+ species.

The molecularity of reaction (10) requires two NO^+ ions to come together before either is destroyed by reaction with an anion. Thus it is unlikely that this particular

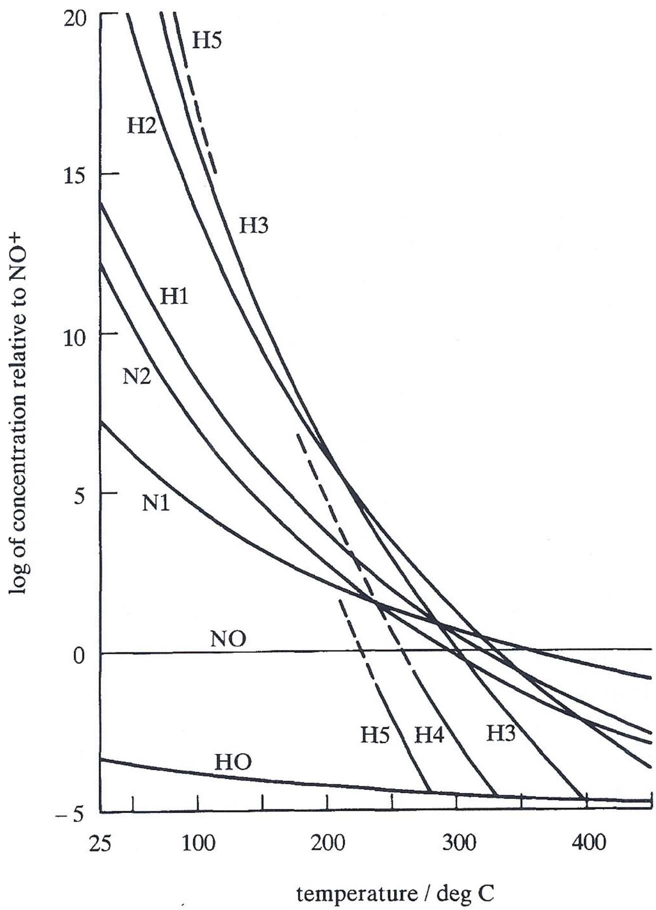

Figure 7. Cation speciation in the hydration zone. Above about 350 °C, NO^+ is the predominant cation in either its free or mono-hydrated form. Under all conditions it is more important than the bare H_3O^+ ion, but the hydrates of H_3O^+ begin to predominate over NO^+ hydrates below about 310 °C. Below 200 °C, NO^+ and its hydrates would be undetectable. NO = NO^+, Nx = $NO^+ xH_2O$, HO = H_3O^+, Hx = $H_3O^+ xH_2O$.

reaction would be on the kinetic pathway for the conversion of NO^+ to H_3O^+. Figure 7, in principle, only indicates the states towards which the actual reactions would be tending. Clearly, however, the final products will be the various higher hydrates of H_3O^+.

In practice the actual transformation is more likely to go via reactions that have a more favourable molecularity and which include the step

$$NO^+ . nH_2O = H_3O^+(n-2)H_2O + HNO_2. \tag{12}$$

If we use the smoothed NO^+ hydration data from table 1 and the smoothed H_3O^+ hydration data considered in §2*b*, the standard free energies of table 2 are obtained for reaction (12). Thus this reaction could only proceed with $n > 4$. That is, the hydrate $NO^+ . 3H_2O$ would not be expected to decompose but $NO^+ . 4H_2O$ would.

It happens that the kinetics of hydration and subsequent transformation of NO^+ have been studied at 23 °C by Puckett & Teague (1971). They show that reaction (12) proceeds spontaneously for $n = 4$ but not at lower values. This finding provides

Table 2. *Standard free energies for reaction* (12)

n	2	3	4	5	6
$\Delta G^0_{298K}/(\mathrm{kJ\ mol^{-1}})$	506	136	-47	-142	-210
$\Delta G^0_{373K}/(\mathrm{kJ\ mol^{-1}})$	482	119	-58	-147	-211

support for the estimation procedures of §2. Also the study shows that all the rates are fast. All should be complete in at most milliseconds even at 23 °C so one would expect H_3O^+ to be the only important cation to emerge from the hydration zone.

For the anions, there are more uncertainties. The main reason is that two anions (NO_2^- and NO_3^-) can be formed whose thermodynamic stabilities do not differ sufficiently to ensure the rapid transformation of one into the other. Unfortunately, relevant information on their kinetics of conversion in the gas phase are lacking as are reliable data on the thermodynamics of formation of gaseous NO_3^-.

The non-appearance of this anion in either the JANAF (Chase *et al.* 1985) or NBS (Wagman *et al.* 1982) tables presumably reflects the great uncertainty over the heat of formation. Values of -255.12 and -372.4 kJ mol^{-1} have been tabulated elsewhere (Karapet'yants & Karapet'yants 1970). If this range can be assumed to include the true value, NO_3^- is undoubtedly the more stable at low temperatures. However, at least in aqueous solution at 25 °C, the oxidation of NO_2^- by O_2 is slow. It seems reasonable, therefore, to conclude that both anions are potentially capable of surviving the hydration zone to near ambient temperatures.

Further evidence for this can be claimed if one accepts the later conclusions of this paper that all these processes occur inside a ball of lightning. A smell resembling NO_2 is frequently reported as accompanying such globes and on one occasion was visually and chemically identified issuing from one (Dmitriev 1967). This implies that oxidation to the $+5$ state has not gone to completion inside the ball itself.

If NO^+ cannot penetrate the hydration zone, it seems unlikely that any less stable ion could. The condensation of water molecules around any metastable ion that entered the hydration zone would probably stabilize the transition state of any process which might otherwise have led to slow reaction. It is therefore concluded that only the four ions considered above are important in the hydration zone.

(c) *Fate of neutral molecules*

Such arguments do not apply to metastable (uncharged) molecules however. Certainly there is indirect evidence that NO_2 and O_3 can escape as their characteristic smells are often associated with electrical discharges in air as well as with ball lightning. There may be many other metastable species which could be relevant to the stability of ball lightning. Two obvious ones are molecular nitrogen and oxygen in their excited states.

Powell & Finkelstein (1969) briefly discuss three metastable states of nitrogen in considering the species which could be responsible for the emission of light from a free floating air plasma that they suggested was basically ball lightning. These were the $A^3\Sigma_u^+$, $^3\Delta_u$ and $\omega'\Delta_u$ states whose energies they give as 6.17, 7.35 and 8.89 eV respectively. They discounted the 6.17 eV state because of its very short collisional lifetime in air but could not be so definite about the higher energy states. As they noted, Kenty (1964) had observed afterglows in N_2-rare gas mixtures which persisted for 10 s and which he attributed to the presence of either the 7.35 eV or 8.89 eV state of nitrogen. In the absence of direct evidence for the rapid deactivation of the 7.35 eV and 8.89 eV states in air, it seems worth considering the possibility that a significant number of metastable nitrogen molecules do survive for a significant time in ball lightning.

If they do, then the available energy is sufficient (for either state) to make the following reaction a spontaneous process over the whole temperature range of interest:

$$N_2^* + O_3 = NO^+ + NO_2^-. \tag{13}$$

Thus, if these processes could occur in an established lightning ball, no external electric field would be required to produce ions within it. If this or similar reactions, such as

$$N_2^* + N_2O_4 = NO^+ + NO_3^- + N_2 \tag{14}$$

were to occur near the edge of the ball, the ions produced would, if they were cool enough, be rapidly hydrated. No claim is made that either of the above reactions is necessarily important to the stability of ball lightning but some high energy metastable species could play this sort of role.

A possibly more important type of reaction is one that could only occur in the hydration zone. An example is a reaction involving one of the metastable oxygen species, O_2^*, which Powell & Finkelstein (1969) suggested might have a reasonably long lifetime. This is the $b'\Sigma_g^+$ state, to which they assign an energy of 1.63 eV.

On this basis, the reaction

$$N_2O_3 + O_2^* = NO^+ + NO_2^- + O_2 \tag{15}$$

would (at 25 °C) have the very unfavourable standard free energy of $+510$ kJ mol^{-1}. However, if we allow for the favourable hydration energetics of the ions, we can use the thermochemical data discussed earlier to show that the reaction

$$O_2^* + N_2O_3 + 2nH_2O = H_3O^+.(n-2)H_2O + NO_2^-.nH_2O + HNO_2 + O_2 \tag{16}$$

would have a favourable free energy for $n > 6$. If such processes can occur, there need be no free ions in the cooler parts of the intermediate zone for ions to be present in the hydration zone. Presumably, in a fairly modest electric field, the reaction could proceed for lower values of n. As we shall see, such processes probably play a crucial part in explaining some of the properties of ball lightning.

(*d*) *Other processes*

The reactions leading to the destruction of the more energetic species from the plasma would presumably begin close to it and the large amounts of heat liberated by the ionic recombination reactions would help reduce heat losses from it. Such reactions anywhere in the intermediate zone would have a similar influence as would the hydration reactions which are all exothermic.

It is convenient to consider here a reaction that would be able to proceed if there were liquid water present. It is a reaction which is known to occur during thunder storms: the production of nitric acid from nitrogen and oxygen. The relevant 25 °C thermochemical parameters for the reaction

$$N_2 + \tfrac{5}{2}O_2 + H_2O(l) = 2\ HNO_3(aq) \tag{17}$$

are standard free energy, $\Delta G^0 = +14.63$ kJ mol^{-1},

standard enthalpy, $\Delta H^0 = -128.89$ kJ mol^{-1},

standard entropy, $\Delta S^0 = -481.57$ J mol^{-1} K^{-1}.

(All data are from the 1982 NBS tables of Wagman *et al.*).

The standard free energy is positive but not to be a large extent. In practice, the free energy is not directly relevant here because the parameters listed refer to the overall process and this clearly is not at equilibrium at 25 °C. The forward reaction would certainly be able to occur in the intermediate zone because the species escaping the plasma are much more energetic than nitrogen, oxygen, and liquid water. However, the reverse reaction does not proceed under normal ambient conditions. Thus 128.89 kJ mol^{-1} of nitrogen would be deposited either in the plasma or the intermediate zone. Where this heat is liberated (i.e. at what temperature) would depend on the detailed mechanism and this is not known.

4. Evidence and speculations concerning ball lightning

(a) *Observational facts*

The books of Singer (1971), Stakhanov (1979) and Barry (1980) provide convincing evidence for the existence of ball lightning as a real phenomenon. All three refer to individual accounts and statistical analyses of large numbers of observations. A more recent survey by Smirnov (1987) contains an even larger collection of statistical information. There is remarkable unanimity about the main characteristics gleaned from the over 2000 observations.

Ball lightning is almost invariably observed during thundery weather, though not necessarily during a storm. It appears to be a free floating globe of glowing gas, usually spherical, which can enter buildings, sometimes apparently squeezing through fairly small spaces. It frequently moves horizontally (at speeds between 0.1 and 10 m s^{-1}) a metre or so above the ground. Very little heat appears to be emitted. Colours and brightness vary, as do sizes which usually fall in the range 5–30 cm diameter. Mostly the lightning lasts (or is observed) for less than 50 s, although of roughly 1000 observations in the Russian survey 70 apparently lasted over 100 s (Stakhanov 1979). During its lifetime it rarely changes significantly in either size or colour but its life can end in two quite distinct ways: explosively or by simply disappearing.

The birth of ball lightning is seldom seen, although it has occasionally been observed forming from linear lightning in the sky and growing out of and detaching itself from electrical discharges on the ground. It has also been observed to fall from the cloud base. More rarely it, or something very like it, has been reported as appearing out of the air: for example, between a woman's downward pointing finger and the ground. Rarely also, though on several occasions, it has been reported rolling on or bouncing off, usually wet, surfaces.

Clearly, the credibility of the witnesses is an important consideration when it comes to the rarer observations. From what has been said, however, it is apparent, on the basis of thousands of observations that the objects have considerable stability. Because they are gaseous, this represents one of their most surprising features and it is one which, in my opinion, has received no really satisfactory explanation to date.

There is general qualitative agreement by experts about most of the following characteristics of a lightning ball:

(i) its emission of light and sometimes cloudy appearance;
(ii) its near spherical shape;
(iii) its colour, size and smell;

(iv) its sound and the radio-interference it produces;
(v) its apparent surface coolness;
(vi) its considerable stability as an entity;
(vii) its lack of buoyancy;
(viii) its association with stormy weather;
(ix) its frequent horizontal but occasional erratic motion;
(x) its tendency to be drawn into buildings;
(xi) its prolonged existence even inside buildings and aircraft;
(xii) its estimated energy content;
(xiii) its estimated temperature;
(xiv) its formation and lifetime;
(xv) its two modes of demise.

(b) *Estimated properties and models*

Although few of the qualitative facts are in dispute, some of the estimated ranges for the quantitative properties differ. Not surprisingly, in view of the nature of the evidence, this can reflect the preference of an author for some particular model.

Some of the many hypotheses can be easily dismissed but even then Singer (1971), Stakhanov (1979) and Barry (1980), after detailed consideration, appeared to prefer different models and different ranges of properties. I am heavily indebted to the assessments of existing data and models given in the books of these authors. The incompatibility of existing models with all the agreed properties of ball lightning has led one authority to propose a recent alternative (Smirnov 1987) which I do not accept as it requires the rejection of many reliable qualitative observations.

This section briefly discusses how well some of the quantitative properties of ball lightning are explained by the best existing hypotheses. As may already be apparent, it is accepted here that ball lightning is of one basic type. Stakhanov (1979) and Barry (1980) quote contrary evidence but both seem, on balance, to favour this conclusion.

Several of the physical and chemical influences previously used in attempts to explain it certainly have a part to play but it is assumed here that there is only one phenomenon. To accept this, however, it may be necessary (as Stakhanov has suggested) to discount one frequently quoted estimate of the energy content of ball lightning which was based on the quantity of water reportedly lost from a barrel when a fireball entered it (Goodlet 1937). The energy density implied was roughly 10 kJ cm^{-3} which is three to four orders of magnitude greater than the range of 1–10 J cm^{-3} considered normal by Stakhanov (1979). Barry (1980) provides fairly convincing evidence for a much wider range of energy density but still considers that values above 0.2 kJ cm^{-3} are of dubious validity. This conclusion is based on the assumption that the balls are energy sufficient. It becomes less secure if the balls are being powered by external sources.

(c) *Energy supply and lifetime*

Hypotheses concerning the energy source are generally divided into two basic groups. One assumes that the ball is continuously fed by an outside source, most realistically either the electric field imposed by the clouds or a radio frequency field transmitted from partial discharges in the clouds. The second group assumes that no such external source is needed, the ball being created with sufficient energy in it to fuel it for its full lifetime. Organic materials, unstable molecules produced in the thundercloud (e.g. O_3) and plasma from a lightning stroke have been suggested as the internal source.

The main strength of the first group is that it is relatively easy to explain the long life (greater than 100 s) of some ball lightning. The main advantage of the latter group (at least in Stakhanov's view) is that it provides a better explanation of the frequently observed mobility of the globe and its occasional appearance inside enclosed and electrically shielded areas. Singer (1971) tended to favour an external supply of energy preferably by radio-frequency (RF) excitation, whereas Stakhanov prefers an energy self-sufficient ball whose energy originated from the plasma of a lighting stroke or a point discharge (Stakhanov 1979, 1984).

In his view the ball lightning plasma is of rather low temperature (500–700 K) under which conditions ions would be extensively hydrated. He considers that his model can adequately explain the energy content of the ball without the need to call on external energy sources. However, using arguments based on the evidence of the charge density in more normal (higher temperature) plasmas, this has been shown to be unrealistic (Vorob'ev 1983).

There seems no reason why both internal and external energy sources should not contribute. The plasma globe could store the electrical energy it received from local dielectric breakdown and use it either to supplement or replace the external source if this becomes unavailable (e.g. from a loss or reduction of the electric or electromagnetic field). Several species potentially capable of storing such energy have been identified in §3*c*.

Singer (1971) has discussed in some detail the possibility that ball lightning is powered by natural electromagnetic radiation. Many relevant experiments are described and it is clear that there is a large discrepancy between the power levels found necessary to produce a plasma in the laboratory and those that seem to be available in nature even in a violent thunderstorm. Despite this, Singer appears to consider electromagnetic radiation as one of the most probable power sources for ball lightning. There certainly are examples, such as the observation of balls inside aircraft, where such radiation appears to be the only likely source of external power. Also, there is good evidence of radio-frequency interference being associated with the presence of ball lightning (Dmitriev 1967; Singer 1971).

The point of view adopted in this paper is that, under most circumstances, the DC field of a thunderstorm provides most of the required external power, at least during the formation of the ball. Electrical breakdown is an electrically noisy process and, because of the inverse square law, it seems to the author that any RF effects in ball lightning processes are more likely to result from internally generated radiation than from the clouds or from the stepped leaders of lightning strokes. A role for external radio-frequency power is not, however, discounted especially if some means of concentrating the power is available.

(*d*) *Further considerations of existing models*

A number of weaknesses in the best existing models have already been referred to. Before proposing a new model for the structure and stability of ball lightning, it is necessary to raise a number of other points.

Neither Singer (1971) nor Stakhanov (1979) favoured theories that involve a freakish accumulation of a chemical fuel. The clear association with electrical phenomena is one reason. In addition, one of the (less extensive) American surveys (Rayle 1966) suggested that 44 % as many people had seen ball lightning as had seen lightning impact points at close range. Powell & Finkelstein (1969) have pointed out that, bearing in mind the great difference in brightness, ball lightning might be almost as common as normal lightning and should not be regarded as particularly rare. It does, therefore, seem reasonable to assume that no freakish concentration of fuel is involved. This view is not universally accepted, however. Smirnov (1987) disagrees and Barry (1980) seems to have doubts.

The much discussed RF excitation theory (Kapitza 1955) involved focused radio waves but, as pointed out by Powell & Finkelstein (1969), among others, Kapitza's model implies coupling from a narrow frequency band and very much greater power levels are needed than are conceivable in nature. Stakhanov (1979) was mainly criticising Kapitza's model when he pointed out that the motion of ball lightning is also difficult to explain by a standing wave or focused excitation mechanism. But he was also criticising the nonlinear DC discharge model of Powell & Finkelstein (1969).

This seems a much more reasonable model in many respects and I accept that these authors have correctly identified many of the processes that lead to the emission of light. The differing colours probably are (as their experiments imply) largely a result of impurities. Clearly, in stormy weather the air can be close to its breakdown potential and it might only require a single insect or the local stopping of a secondary cosmic ray to start an avalanche process in the air. If an insect, for example, were to initiate the process in nature then its composition could be reflected in the colour. In this case that would be more or less orange, which is the most common ball lightning colour.

Powell & Finkelstein (1969) assume that, in nature, ball lightning is powered by the DC field which exists between the earth and cloud base. They suggest that, for balls of typical diameter and a temperature of 2000–2500 K, the multiplication of electrons by atomic collisions (Townsend multiplication) should be sufficient to maintain the plasma at realistic electric fields. Their model assumes that the necessary current is carried by a widely spreading channel in the air above and below the ball; also that the buoyancy of the hot plasma is counteracted by electrostatic forces which result from the faster transport of electrons and anions than of cations.

The main problem with the Powell & Finkelstein model is that it ignores the extensive hydration of ions (including anions formed by electron capture) which, as we have seen, must occur in high humidity air. There is other evidence also. Townsend's (1915) discussion of early experimental work suggests that there can be a factor of well over 100 between the diffusion rates of bare and heavily hydrated ions in air. With little difference in ion mobility, the model provides nothing to counter the buoyancy.

The required exact balancing of forces in any case seems inconsistent with the frequent reports of prolonged movement in a horizontal plane a metre or so above the ground. Furthermore, the explanation is rendered unnecessary if one accepts that heavily hydrated ions should (as Stakhanov suggests) be helping to counteract the buoyancy of the low density hot gas.

If the ions are sufficiently hydrated to contribute significantly to the mass of the ball and hence hold it down, and if it has some (as yet unspecified) mechanical stability, an additional means of feeding energy to an established ball becomes available: an alternating field component on top of the DC field resulting from inter-cloud discharges.

Presumably, cations and anions would be drifting out of the ball in opposite directions as a consequence of the DC field. They would be increasingly hydrated and slowed down as they reach cooler regions. However, a reasonable number of ions could be maintained in the ball's centre by this AC field and the RF field generated locally in the breakdown process. As may already have been implied, the model developed later does not assume that all the energy required comes either directly or indirectly from the electric field.

(e) *Plasma temperature*

There is an important difference between the plasma temperature range required by Stakhanov's analysis (1979) and that implied in most other studies (Singer 1967; Barry 1980). One of the highest estimates of a ball's temperature was that of Dmitriev (1967, 1969) who suggested a value of approximately 14000 °C based mainly on his experience with plasmas. Powell & Finkelstein (1969) measured the temperature of the kind of light emitting plasma they produced by radio-frequency excitation and which was capable of a brief existence with no external energy supply. The result, which is assumed in their model, was 2000–2500 K.

Stakhanov (1979) puts the temperature in the range 500–700 K, based mostly on buoyancy considerations, on heat loss calculations and on convincing evidence for the low temperature surface of some ball lightning. Among the lines of evidence on the last point were several cases where ball lightning had come into contact with people's skin (in one case rolling down their calf) without producing any sensation of pain. People who have been in close range of ball lightning frequently comment on its unexpected coolness (Singer 1971) and of people questioned who have been closer than one metre, only 10% said they sensed any heat at all (Stakhanov 1979). Both analyses agree with the non-thermal source of the light, but the two temperature ranges are irreconcilable.

In fact, the centres of the globes can almost certainly differ in temperature and there is other evidence that this is so. Singer (1971) mentions several cases where ball lightning bored circular holes in glass window panes and Powell & Finkelstein (1969) refer to another example. They also refer to a case (apparently much more rare) where a ball was reported to have passed through a window pane without doing any damage to it. As soda glass cannot be melted below 1300 K it is clear that some (and possibly most) ball lightning has a much higher temperature than is implied by Stakhanov's analysis.

It seems extremely unlikely that the mechanism by which light is produced could be the same at more than 2000 K, where free electrons are involved, and at more than 700 K, where extensive hydration of all charged species is expected. Thus, if even a few fireballs really do have maximum temperatures below 700 K, some very unusual physics and chemistry must be going on in them. In view of our very limited knowledge concerning the behaviour of electrolytes in high humidity air (§1), this is by no means impossible, and, if one of the rarer observations reported in Singer's book (1971) is accepted, it must be possible. The incident referred to (on page 45) is one in which a German engineer and his wife became surrounded by an exceptionally large (4 m diameter) globe which caused them no harm.

We shall, however, concentrate only on much better supported evidence and will accept that there can be a central plasma zone having a temperature of at least 2000 K. The approach will be to see how far we can get without making any *ad hoc* assumptions.

5. A new model for ball lightning

In this section most attention is initially directed towards the stability of the globe, this being the aspect of the phenomenon which has been treated least satisfactorily in the past. In describing the processes that must be occurring, explanations for several other characteristics occur naturally.

(a) *Assumptions and early stages of formation*

The model accepts the considerable evidence for an association of ball lightning with conditions of high humidity. It is assumed that, at least during the formation stage, very high humidity is needed so that the ion clusters can form. Probably, fairly high humidity is also necessary for ball lightning to have a significantly long lifetime. However, once it has formed, it could re-cycle the water vapour locally and be largely self-sufficient in water.

We start from the conclusions of §§2 and 3 and with an acceptance that it is possible to produce some kind of free floating air plasma, like that produced by Powell & Finkelstein (1969). The model also assumes that thundery conditions are necessary and that they leave a positive space charge in the vicinity of the plasma. Where this is produced from a corona discharge the excess charge would, under normal thunder storm conditions, be positive (Schonland 1964). Where the plasma is, for example, at a sharp bend in a lightning channel (i.e. perhaps a precursor to bead lightning) it would arise as a consequence of the rapid conduction away of electrons in the channel. Mainly for these reasons, but partly also because of the exceptionally favourable hydration thermodynamics of the proton (§2) we consider only the case of an excess of positive charge.

One could think of the plasma blob at this stage as a region where, because of the higher temperature and rapid ion motion, there is a gap in the space charge. All the lower temperature ions would be rapidly solvated and the coolest (i.e. those at the edge) would be most heavily hydrated. So the excess of ions will reside somewhere in the vicinity of the edge of the plasma and move at a comparatively slow speed under the influence of a sea of other ions of positive charge. At this stage of the description there is nothing in particular to distinguish the excess charges near the plasma from their neighbours except that the hotter ones will be lighter and move faster. If a cool region could be established at the edge of the plasma, the ions would move quite slowly and could be considered as a part of the blob itself.

(b) *Thermochemical refrigeration*

We have seen that ions escaping from a plasma will be increasingly hydrated and slowed down as they diffuse away. For now we simply assume that some ions of both charges are able, either by their own diffusion or with the help of metastable intermediaries (§3*c*), to reach the cooler regions of the hydration zone before their charges are neutralized. What happens on neutralization will depend on their identity and on the extent to which they have been hydrated.

As shown in §2*a*, the hydration process is strongly exothermic whatever the ions involved. Thus, as the ions are diffusing out and becoming hydrated, the hydration reaction is adding heat to the system. This process, therefore, keeps the hydration zone fairly hot. (Should nitric acid formation be possible as a consequence of the proximity of liquid water, it would also add to this process of thermochemical

Table 3. *Standard state thermodynamics of reactions* (18)

n	0	1	3	5	7	10	15
$\Delta H^0/(\mathrm{kJ\ mol^{-1}})$	−700	−487	−217	−11	169	433	872
$\Delta S^0/(\mathrm{J\ mol^{-1}\ K^{-1}})$	14	241	687	1174	1640	2332	3521
$\Delta G^0/(\mathrm{kJ\ mol^{-1}})$	−704	−559	−422	−361	−320	−262	−177

lagging.) If, however, the ions can avoid neutralization until they become heavily hydrated, a very different situation arises.

It is informative to compare (in table 3) the 25 °C standard enthalpies, ΔH^0, entropies, ΔS^0, and free energies, ΔG^0, of a related group of reactions,

$$H_3O^+ . nH_2O + NO_2^- . nH_2O = HNO_2 + (2n+1)H_2O. \tag{18}$$

These will represent one of the two possible classes of charge neutralization reaction which are possible towards the outside of the hydration zone. The others, of course, involve the formation of nitric acid.

These properties are related by the thermodynamic identity $\Delta G^0 = \Delta H^0 - T\Delta S^0$. It is clear that, while the charge neutralization reaction of unhydrated ions is strongly exothermic, that of the most heavily hydrated ions is endothermic to a comparable extent. All the reactions are strongly favoured (negative free energy) but for low values of n this results from a favourable enthalpy while the heavily hydrated ions react because of the entropy production. The latter can be considered as a process that leads to the evaporation of water. The necessary heat must be found from the surroundings.

Thus, if the ions can survive long enough to become hydrated by more than about five water molecules, their subsequent neutralization should significantly cool the air locally. I believe that this chemically induced refrigeration process does occur, that it provides the explanation for the relative harmlessness of light contact with the outside of the plasma ball and part of the explanation for the cloudiness often reported or implied as a characteristic of ball lightning. Condensation nuclei are also likely to be required for the mist to form and the surplus of positive charges could provide some. Nitric acid could well provide others. Ball lightning can, then, be thought of as a kind of thermochemical heat pump.

(c) *Charge neutralization and ion pairing*

The existence of a refrigeration zone at the surface of the ball is an essential part of the present model. Because its formation requires the oppositely charged ions to become heavily hydrated before they annihilate each other, it is desirable to consider whether there are any other phenomena that could delay charge neutralization once the ion clusters collide.

The charge annihilation process certainly is favoured thermodynamically for all the gas phase recombination reactions. For reactions like (18) to proceed the ion clusters would first have to come into contact. This intermediate state has close similarities with the sort of solvent separated ion pairs with which solution chemists are familiar. Frequently, because of the very favourable hydration energy (of at least the cation), solvent separated pairs predominate over contact ion pairs (see, for example, Conway 1981).

Of course, a pair of hydrated ions in air is unlikely to behave exactly as it would in a liquid solvent. One significant difference is the compressibility of the two fluids, as it is known that solutions of electrolytes in water near to its critical point exhibit very anomalous thermodynamic properties as a direct consequence of the compressibility (Turner 1983, 1988).

In this connection, a variety of calculations were made of the radial charge distribution of a dilute, strong electrolyte in a moderately compressible solvent (S. J. Peters, unpublished results). An analytical approach and Monte Carlo simulations were found to make the same qualitative prediction. The results have been taken as evidence that contact ion pairs are relatively less important in a compressible than in an otherwise identical, incompressible, solvent (Turner 1989).

Another, more purely chemical, way of looking at the problem can be illustrated by using some of the data presented in table 3. For example, the values of ΔH^0, ΔS^0 and ΔG^0 for the reaction

$$H_3O^+.15H_2O+NO_2^-.15H_2O = H_3O^+.10H_2O+NO_2^-.10H_2O+10H_2O \tag{19}$$

are given by the differences of the relevant data in table 3 for $n = 15$ and $n = 10$. These suggest $\Delta H^0 = +439\ \mathrm{kJ\ mol^{-1}}$; $\Delta S^0 = +1189\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $\Delta G^0 = +85\ \mathrm{kJ\ mol^{-1}}$. This reaction formally represents all the species in their hypothetical standard states where interionic effects are absent. For obvious electrostatic reasons the analogous reaction when the ions are close enough to be considered paired will be different: presumably it will have a more negative free energy and probably one which is negative in an absolute sense. However, ΔH^0 is likely still to be positive (unfavourable), the standard entropy only being favourable.

It does, therefore, seem reasonable to think that a heavily hydrated ion pair in air sits in a free energy well which is deep enough to inhibit charge neutralization. If we consider this metastable solvent separated ion pair, there would be no net enthalpy advantage to a slightly closer approach of the ions (because of the very favourable enthalpy of solvation). The available entropy advantage could be gained only by the peripheral water molecules of the complex. This would extract heat and make it more difficult for the water molecules separating the ions to obtain enough energy to be displaced. There is no reason, therefore, to expect particularly rapid charge neutralization.

If we accept that some of the more important ions can reach the refrigeration zone unreacted, then one would expect significantly different behaviour for the two possible charge neutralization products: nitric and nitrous acid. This can be seen by comparing the free energies of the following reactions:

$$HNO_3(g) = HNO_3(aq), \tag{20}$$

$$HNO_2(g) = HNO_2(aq). \tag{21}$$

(The designation (aq) does not distinguish between ionized and unionized solute.) From the NBS tables (Wagman *et al.* 1982) it is seen that the respective standard free energies at 25 °C are $\Delta G^0 = -36.5\ \mathrm{kJ\ mol^{-1}}$ and $\Delta G^0 = -4.6\ \mathrm{kJ\ mol^{-1}}$. This is equivalent to the prediction of partial pressures of 4×10^{-7} and 0.16 bar for the respective gases in equilibrium with acid of unit activity. Below these pressures the gas would tend to evaporate from the solution, whereas above them it would tend to condense. It seems reasonable to assume that the standing partial pressure of both gases (HNO_3 and HNO_2) will lie between these two limits. The reasons for believing this are that the higher limit represents an incredibly high conversion of oxygen while the lower limit would imply virtually undetectable levels of acid. Using the

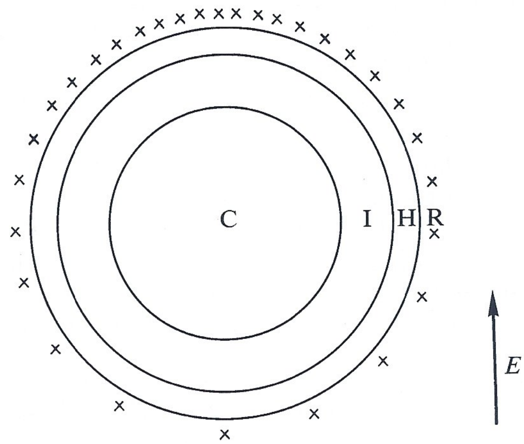

Figure 8. The structure of ball lightning according to the new model. C represents the plasma core, I the intermediate zone where high energy species are being destroyed, H the hydration zone and R the refrigeration zone. The crosses represent positively charged ion clusters.

NBS thermochemical data (Wagman *et al.* 1982) the standard free energy of the gas phase reaction

$$2NO_2 + H_2O = HNO_3 + HNO_2 \tag{22}$$

is calculated to be $+5.23$ kJ mol^{-1}. Such a small value implies that the reaction lies only slightly to the left at equilibrium so that the partial pressures of the acids should not be orders of magnitude lower than that of NO_2 which is known, at least sometimes, to be detectable in the vicinity of ball lightning (Dmitriev 1967, 1969).

These arguments support the earlier suggestion that nitric acid production has different consequences from that of nitrous acid: droplets would remain and provide condensation nuclei additional to those provided by the excess of (H_3O^+) ions.

(*d*) *Mechanical stability*

From now on we shall accept that, for ball lightning to have a significant lifetime, it must be surrounded by water droplets which have condensed onto ions and onto nitric acid.

For each two moles of aqueous nitric acid produced, 2.5 moles of O_2 and 1 mole of N_2 would be consumed. The inward flow of these gases past the droplets would provide a force (additional to that produced by the space charge) tending to give the ball spherical symmetry. The resulting model of ball lightning has, then, the basic shell structure of figure 8.

In principle, if we knew sufficient about the ball's temperature profile and about the mechanism and kinetics of the formation of nitric and nitrous acids, we could calculate what the flow rate would be. In view of the various phenomena that currently cannot be quantified, such an approach is impractical. Fortunately, the question of the air flow rate into the ball can be considered in a much simpler manner on the basis of other, quite different, properties of the phenomenon.

Ball lightning is more often than not reported to move freely in a horizontal plane, typically a metre or so above the ground. The model of Powell & Finkelstein (1969) attempts to explain this by an exact balancing of the upward buoyancy force by electrical forces that are assumed to operate when the normal field direction has been reversed. As pointed out in §4*d*, a frequent exact balancing of this sort seems highly improbable and these forces would lift the ball when the more normal field direction applies.

It seems more reasonable to assume that the only downward force normally acting (usual storm field direction) arises from the weight of the ion clusters and water droplets. If this force slightly exceeds the buoyancy force, the difference would be made up by electrostatic repulsion between the ball and earth. A number of early models treated ball lightning as a phenomenon of electrostatics but none offered a realistic explanation of how charge neutralization could be avoided (Singer 1971). The tendency of balls to move into buildings or down chimneys is fairly simply explained if the electrical potentials operating at the time favour it. Their occasional tendency to move parallel with the walls of a room (which are presumably at a somewhat similar potential to the floor) is also partially explained as an electrostatic repulsion.

Furthermore, it is known that, after a lightning discharge, the vertical direction of the electric field can change its sign (Powell & Finkelstein 1969). A lightning ball in the vicinity would then be attracted to earthed objects rather than being repelled and this could provide one explanation for the more violent of the two ways in which ball lightning is extinguished. Presumably the more usual quiet extinguishing occurs when the applied field (either DC or RF) or the humidity becomes too low. Some explosive destructions of ball lightning probably result from the rapid oxidation of organic materials like pine needles or a swarm of insects. The occasionally reported 'shaggy' form of ball lightning may result from a less extreme form of the same phenomenon.

We therefore assume that the buoyancy of the hot plasma can be more than balanced by the weight of the ion clusters and acidified water droplets. As the balls do sometimes rise, we assume, for the purposes of the following calculations, that the droplet weight and buoyancy forces are of similar magnitude while the contribution by the electrostatic repulsion force is negligible.

Descriptions of ball lightning often refer to the balls being hazy, misty, having a clearly defined edge or sometimes not having a clearly defined edge (Singer 1971). Occasionally it is stated that they appear transparent. If cloudiness is to be observable the particle diameters must exceed about 0.2 μm.

It can readily be shown that at a realistic ion concentration, the weight of the ion cluster (even containing 20 water molecules) would not be anything like sufficient to hold down a central plasma at 2000 K. This was one of the reasons which led Stakhanov to put a 700 K upper temperature limit on his cluster plasma. Thus the buoyancy force of hot plasma can be equated simply to the total weight of the droplets, $\frac{4}{3}\pi r_\mathrm{d}^3 . n_\mathrm{d} \rho_\mathrm{w}$ (r_d being their radius, n_d their number and ρ_w the density of water). The two forces will be equal if

$$n_\mathrm{d} r_\mathrm{d} \rho_\mathrm{w} = r_\mathrm{p}^3(\rho_\mathrm{a} - \rho_\mathrm{p}), \tag{23}$$

where ρ_a and ρ_p are respectively the densities of ambient temperature air and the plasma. The latter can be calculated on the assumption that it is a perfect gas having a temperature of 2000 K.

If these particles are to be held in position at an average distance r_b from the centre of the ball, they will be subject to a force given by Stokes' law. The total excess inward pressure ΔP can thus be calculated and expressed in terms of an effective surface tension, σ, via the standard relationship for the excess pressure inside a drop (Lewis & Randall 1961)

$$\Delta P = \frac{2\sigma}{r_b} = \frac{6\pi\eta r_d u n_d}{4\pi r_b^2}, \tag{24}$$

where η is the viscosity of air and u is its inward radial velocity.

Stakhanov (1979) has, in fact, estimated an effective surface tension for ball lightning on the basis of its usual slight departure from spherical symmetry using the relation for the capillary constant, α (Landau & Lifshitz 1953).

$$\alpha = \sqrt{\left[\frac{2\sigma}{(\rho_p - \rho_a)\, g}\right]}. \tag{25}$$

The gravitational distortion of a droplet from spherical symmetry leads to a pear shaped mass when α is comparable in magnitude with its radius, r_p. Stakhanov concludes that σ lies between 1 and 10 dyn cm^{-1}.

We first assume a value of 5 dyn cm^{-1} for σ, a plasma radius, r_p, of 5 cm, an outer ball radius, r_b, of 7.5 cm and a droplet radius, r_d, of 0.2 μm. If we take the viscosity of air to be 185×10^{-6} poise (dyn cm s^{-2}) we obtain 1.6×10^{13} for n_d, the number of droplets and 8.7×10^{-4} cm s^{-1} for the air velocity, u.

Since such a low velocity is required to give $\sigma = 5$ dyn cm^{-1} there would appear to be no difficulty in explaining the stability of the ball in this way. However, the velocity is very much lower than one would intuitively have expected and it represents an extremely small rate of nitric acid production. If we assume the droplets to have a radius of 1 μm, this gives $n_d = 1.25 \times 10^{11}$ and $u = 2.2 \times 10^{-2}$ cm s^{-1}, which still seems very low.

In my opinion, the weakest link in the arguments just presented is Stakhanov's estimate of the effective surface tension. Most important is the likelihood that in many cases the oval shape is not due to a weight effect (via the parameter α) but to the presence of the strong DC field elongating the ball in the field direction. The best photograph given in Singer's book (1971) is clearly oval; it does not show the pear shape which Stakhanov's explanation requires.

If one attributes the oval shape to this effect and assumes that the mean droplet size is not effected by a slight wind, it is possible to obtain a more realistic effective surface tension estimate than Stakhanov's. It is clear that the frequently reported reluctance of ball lightning to be swept along in a light breeze would imply a much larger relative velocity than the 2.2×10^{-2} cm s^{-1} calculated above. For a wind speed of 1 m s^{-1}, the surface tension of the ball would have to be raised to 227 dyn cm^{-1} to make the two velocities comparable. For the smaller droplet size, the equivalent surface tension would have to be 5.7×10^3 dyn cm^{-1}. These figures seem reasonable on the grounds that a 20 cm diameter balloon, inflated to 0.1 bar above atmospheric pressure would have an effective surface tension of 5×10^5 dyn cm^{-1}. Several observers have likened the motion of some ball lightning to that of a child's balloon.

It therefore appears that the production of nitric acid in the ball leads to an inflow of air which gives it great mechanical stability. The fact that on several occasions ball lightning has been observed to bounce off wet surfaces (Singer 1971) requires it to have considerable stability as does its ability to squeeze through small openings.

The model described also suggests a contribution to the required restoring force during bouncing from evaporation of the surface water that is forced into the hotter regions of the ball. It would appear that the large, stabilizing ion clusters can re-form on a timescale which is rapid compared with the (presumably rather slow) process of bouncing.

If one accepts that a large DC field is crucial to the existence of high-energy ball lightning, one would actually expect the balls to be oval. That they are frequently so close being spherical also supports the argument for a rather large effective surface tension.

(*e*) *Size*

If the model outlined is correct, it seems clear that the size of a typical lightning ball depends on too many unknown quantities to allow a realistic prediction of its size at present. The last section has, however, shown that a ball of typical size shows a stability which is consistent with the model.

The normal size range is not the only aspect of the size of ball lightning which needs explaining, however. Another characteristic that is almost always noted is that the size of the globe hardly changes during its lifetime. A good model should be able to provide at least a qualitative explanation of this fact. It seems, then, that the size of the ball is determined at its creation. Presumably this depends mainly on the electric field, perhaps the RF power available, the humidity and the temperature which apply at the time. When formed from a point discharge it could depend on the local density of the positive space charge and hence, presumably, on the electric field applied for some time before its formation. Chemical compounds present at the discharge point could either catalize or inhibit the processes occurring inside the ball and thus influence its size. Other factors may also be involved if it can develop from the channel of ordinary lightning.

Starting with an established ball we consider what would be expected to happen to it if more energy were suddenly applied by increasing the electric field. Clearly there would be an increased rate of production of ions and also (in the plasma) an increase in temperature. The latter factor might be expected to lead to an increase in size. But there would also be an increased rate of production of nitric acid which would require a faster inflow of air. Also, the increased ion production would lead to an increased ion concentration in the lower temperature regions and to an increased demand for water which could presumably be satisfied as long as a sufficient quantity of water was available in the form of droplets on the periphery of the ball. The evaporation of these droplets would tend to impede the advance of the hotter regions and the higher concentration of heavily hydrated ions in this region would tend to increase the refrigeration rate. In other words, the temperature gradient would increase but not necessarily the ball's size.

It would clearly be desirable to quantify these arguments but at least the model does provide a mechanism for resisting expansion of the ball when the power supplied to it increases. On reduction of the field, and after any stored fuel capable of producing ions had been used, the processes would all be slowed down. The reverse of the above arguments would again presumably tend to keep the ball's size constant. However, as the temperature and species concentration gradients decrease, the boundary between the heating and refrigeration zones will become poorly defined. At some stage the lack of a well-defined refrigeration zone will produce a loss of mechanical stability and the ball would have expired by its quiet method.

(f) Spontaneous ionization

In the few sketchily reported cases of a lightning ball's passage inside an aircraft fuselage, the ball appears to have either formed in or originally drifted into the pilot's cabin before proceeding down the passenger aisle. Its formation, for example on a radio antenna, might therefore involve a large DC field in a region not surrounded by metal. It is almost inconceivable, however, that a DC field could contribute directly either to the ball's energy supply or stability once it was passing down the metal tube of the fuselage. If these balls are receiving an external supply of energy, the most likely candidate would appear to be radio-frequency excitation. The principal cause of interference with VHF communication systems on aircraft in a thunderstorm is believed to be sparking that occurs when different parts of the fuselage are electrostatically charged to different potentials (Borek 1981).

Stability presents an equally interesting problem. In the absence of a large DC field, we cannot assume any contribution to the prolonged avoidance of mutual charge annihilation by the drift of charges in opposite directions. The ball's stability would almost certainly depend on RF fields and the spontaneous ion forming reactions of §3*c* combined with the kinetic stability of the solvent separated ion pairs described in §5*c*.

Thus, as long as the ball has a sufficient supply of energy (either stored internally in high energy molecules, or via radio frequency excitation) the continuous presence of a large DC field would not appear to be necessary. It may, however, be needed in the formation of a ball.

It is probably necessary to invoke the same chemical mechanism of low temperature ion production to explain the fact that ball lightning can squeeze itself through quite small openings; presumably under electrostatic influences. Balls have several times been described as flowing through holes down to 1 cm in diameter. This has been seen with balls up to 10–20 cm in diameter (Stakhanov 1979). Charring of wood (which led to a fire) was reported on one occasion, but damage does not usually seem to have occurred.

During passage through a hole, the stability of the ends of the elongated regions would still seem to require that they be fed with ions produced somewhere in the ball. One would not expect the normal plasma processes to proceed very satisfactorily once it had lost its spherical symmetry. Nor is it easy to see how sufficient ions could travel to the end of the constricted region without re-combining. The low temperature production of ions within the hydration zone seems a more attractive hypothesis. It probably plays an important part in giving all lightning balls their mechanical stability.

(g) Other relevant observations

The model proposed has qualitatively explained nearly all the most characteristic properties of ball lightning and it has done so, with two exceptions, by arguing only from well established knowledge. The first exception is the assumption (shown to be reasonable on the basis that solvent separated ion pairs probably have significant kinetic stability) that ions can become hydrated by more than five molecules of water before they annihilate each other's charge. The other assumption is that some unspecified metastable species is produced in the plasma that can lead to spontaneous ion formation at fairly low temperatures. The properties of ball lightning are most economically explained if this is the $b'\Sigma_g^+$ state of oxygen.

Fifteen general properties of ball lightning were originally listed (in §4). Some of these cover several specific aspects and the total number is actually over twenty. Of these, a number have not been directly referred to although they have obvious explanations consistent with the model. For example, because we accept the phenomenon as a consequence of the electrical breakdown of air, its occasionally reported sound (hissing and crackling akin to the sound of a corona discharge) is explicable to the extent that there are explanations for the similar but better known electrical phenomena. The same applies to the radio interference with which ball lightning appears to be associated.

The erratic motion of the balls and their reported reluctance to be simply swept along in the direction of the prevailing wind (Singer 1971) appear to be explicable as consequences of the processes which give them mechanical stability. Presumably, any departures from spherical symmetry in the surrounding temperature or relative humidity could result in water droplets of a different size locally and hence a force on the ball whose origin is not obvious to the observer. Changes in the electric field would clearly have a similar influence.

A few of the less commonly reported aspects of ball lightning behaviour remain to be explained. These are of two types which are sometimes, but by no means always, made on ordinary, free floating lightning balls. The first concerns the occasional description of structure within the ball. One of the clearest was given by Dmitriev (1967) and described in some detail by Singer (1971). This was the uniquely well monitored ball from which Dmitriev was able to measure significant concentrations of ozone and nitrogen dioxide. It had also been associated with considerable radio interference and evidence for (presumably electrostatic) guidance over a string of large rafts which extended most of the way across a river.

The ball contained a bright yellow–white centre 6–8 cm in diameter which was surrounded by two outer zones. Next to the core was a dark violet shell between 1 and 2 cm thick and on the outside, a bright blue shell roughly 2 cm thick. These observations seem to be consistent with the model presented since, in fact, it predicts three regions where light might be emitted. Not far from the plasma should be a normal continuum emission due to ion–ion recombination. But one might also expect a continuum emission where the hydrated ions are recombining in the refrigeration zone.

The ball appears to have been one of the brighter ones and it was observed for over a minute. It was somewhat oval with its long dimension vertical. The oval shape is most naturally interpreted as resulting from the large DC field which was evidently present. A number of other uniquely valuable observations were made (Dmitriev 1979) and they all appear to be consistent with the present qualitative model.

No mention of rotation of the ball is made, at least in Singer's (1971) summary, and there may have been none. According to Stakhanov (1979), however, in 30% of observations, a slow rotation of the ball was observed. An explanation for such rotation also results naturally from the proposed model. Both methods of production (via ordinary lightning or corona discharge) suggest an excess of positive charge and, for a floating ball, this implies a positive charge on the earth if the balls are to float electrostatically. Positive ions would be tending to diffuse upwards and negative ones downwards where they would be neutralized. Thus the ball would have an excess of charge (positive) on top (see figure 8).

The droplets condensing around ions would be expected to be larger than those around paired ions (because the field extends further), so we should expect that the ball would be top heavy and susceptible to slow rotation. Such rotation might not be noticeable if it is sufficiently slow compared with charge neutralization at the bottom and uncompensated charge production at the top.

From the foregoing it seems that all the most characteristic features of ball lightning and most of its less frequently observed characteristics can be explained on the basis of the model.

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