Chemical Energy from the Air.

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Abstract

The air contains chemical energy which natural air plasmas occasionally extract. Two simulations of the simplest of form of air plasma (which is ball lightning) were made accidentally in the mid eighteenth century - but they could not be repeated. A precise balancing of electrical and chemical effects, during the charging process, can explain all the observations. Had the air's energy been harnessed long ago, man-made global warming need never have become a problem.

The preparations were made successively in two very large Leyden jars while each jar was being charged. No subsequent claimed simulation of ball lightning has ever proved successful. The question addressed here is why we still cannot simulate ball lightning or its relatives in the laboratory while Nature continues to succeed - but only very occasionally.

Diverse clues from many observations of ball lightning and its more complex relatives (such as earth-lights and Unpredictable Flying Objects, UFOs) are used. The interpretational problems all reflect an undeveloped area of chemical thermodynamics and our consequent ignorance concerning how moist atmospheric ions close to an air plasma will behave. Despite these limitations, even the strangest characteristics of all long-lived air plasmas can now be explained - though at best semi-quantitatively.

1. Introduction.

Since at least the mid nineteenth century (1), it has been considered impossible to reconcile all the seemingly anomalous characteristics of ball lightning unless most of the reliable witnesses of the balls were mistaken or unless more than a single phenomenon was being described. Since then, multiple attempts to explain the observations have been made and extensively discussed (2-8).

Two decades ago, Singer (9) noted that a total of 10,000 credible accounts had by then been provided to interested physicists but, although he accepted the plentiful statistical evidence showing that a single phenomenon seemed to be involved, he still considered that the nature of ball lightning was a mystery. Unfortunately, Singer made no reference to the electrochemical model of Stakhanov (10) and its later modifications and extensions (11-13).

Stakhanov (10) concluded that *nearly all* the strangest characteristics of ball lightning could be explained on the basis of a simple electrochemical model. His most important conclusions were that ball lightning possesses an *effective surface tension* and that its magnitude is reasonable. He used this and other plausible assumptions, to explain the phenomenon. The characteristics he could explain included a ball's ability to bounce and to squeeze through holes of smaller diameter than its own. Stakhanov employed thermodynamic data, which had recently been obtained, on the hydration of ions in low pressure air. He found that the hydrated ions (he called them clusters) were heavy enough to explain why ball lightning plasmas rarely ever rise because of their expected buoyancy.

He had assumed that all the ions inside ball lightning plasmas are hydrated and that their total weight explains why these moist air plasmas usually hug the ground. However, the ions he considered were insufficiently heavy to explain the lack of buoyancy of the most energetic (the hottest) plasmas whose temperatures had been estimated by suitably qualified witnesses. In 1994 (11), *the origin* of Stakhanov's "effective surface tension" was explained and his temperature limitation was also shown to have a simple explanation based on the electrostriction of ions in any moist gas. This allows extremely heavy ions to form close to the plasmas - not, as Stakhanov had assumed, *inside* it. Interpolations of the standard state thermodynamic properties of *the only two ions* likely to be present in low temperature plasmas, were used. The interpolations were between the properties of the ions in an aqueous solution (14) and those obtained in gas phase studies (15).

In an appendix to a very early treatise on the air (16), Priestley described and discussed two very unusual observations. They had been made during successive experiments several years before his book was published. Two 3/4 inch (19 mm) diameter "balls of fire" formed, apparently out of thin air, while two very large Leyden jars were being charged. The original experiments had been performed by a physics lecturer and his patron (J. Arden and W. Constable, FRS). Production of the balls was of obvious interest because, as Priestley realized, several aspects of their behaviour simulated those of ball lightning. A few years later it was noted that the balls also resembled other, larger, kinds of air plasma (17).

Despite all we have learned in the last 250 years, the *chemistry* of atmospheric *ions* is still very poorly understood (18) as are several of the details of how charges become separated inside thunderclouds (19). This lack of progress and our failure to produce plasmas resembling those made in 1757 seem related (12,13,18,20). It is obviously desirable to understand, as precisely as possible, why these plasma balls are all so rare in Nature - but very much more so in the laboratory.

2. The Experiments of Arden and Constable.

The better observed of the two balls produced by Arden and Constable in the eighteenth century took a slow path from inside the Leyden jar through its open top and back again. This probably made it visible for most of its life. No lifetimes for the balls were reported but it has been estimated (13), based on the duration of the conversation that took place during the first of the two events. The ball must have taken roughly 4 seconds to reach its maximum height above the jar. Its total lifetime was probably at least double this and it could presumably have been longer still had not the balls both ended their lives when they contacted and penetrated the jar walls.

Specific clues suggesting similarities to lightning balls include the following: near neutral buoyancy, a spherical shape, attraction to metals, the fact that colour and size remained constant, a spinning motion and a lifetime fairly typical of ball lightning. After each ball exploded, a pungent gas filled most of the (large) room used for the experiments. Most of these characteristics have been repeatedly reported for ball lightning. Even more significant was the way in which both balls ended their lives by destructively penetrating the sides of the jar in which they had formed (13). In each case, the well defined circular hole in the glass was observed to be the same size as the better observed ball - the one that escaped the Leyden jar.

Priestley probably did not realize just how characteristic of some lightning balls the observations were, but he was clear that they had formed directly from the air and that their characteristics simulated several characteristics of natural lightning balls. Unfortunately, Priestly lived just too early to understand anything at all about air chemistry; in fact, he still believed in the phlogiston theory of burning.

Nevertheless, he stressed the importance of the findings and closed his discussion with the following comment “Could we repeat this experiment, there would not, I think, be any natural phenomenon in which the electric fluid is concerned, that we could not imitate at pleasure. This circumstance alone makes it a very interesting object of investigation.” (16, p 383).

Inside the Leyden jars, a brass chain conducted the charges formed by an “electrical machine” to the inner surface of the jar. It now seems (13) that, in both cases where a plasma ball was created, at least one small gap between the links of the chain must have been present. A brief spark between such a link must have produced UV radiation of sufficient energy to ionize the air (18). Since the formation of neither O and OH requires very high energy UV, the air in the jar will certainly have absorbed some of the UV and strongly oxidizing conditions (ultimately yielding nitric acid) would have prevailed throughout most of the interiors of the jars. At the same time, very close to the spark, electrons would have provided chemically reducing conditions. These are thought to be the electrochemical conditions under which a lightning ball can be created (21).

It seems likely that the unusually long lives of both balls observed was mainly a result of the fact that favourable electrochemical conditions were maintained for several seconds during both the experiments. This might imply that such oxidizing conditions are essential for an air plasma to have a long life. Either a spark or the presence of a *locally* reducing environment can, in principle and as far as we know, allow a plasma ball to *form in the first place* (21). It is important to realize that the conditions required for a plasma ball to form are probably not identical to those needed for it to have a long life (18). This is certainly true of normal gas flames.

Many chemical impurities in the air can act both as oxidizing and reducing agents (depending on the specific reactions involved). Mixtures of chemicals can produce similar effects. Since impurities in the air vary widely and since their concentrations *always* greatly exceed those of ions, this fact probably helps account for the rarity of all air plasmas. In the Leyden jar experiments, electrons from the postulated spark will have provided the necessary reducing agents - but only locally.

In fact, the system is probably more complicated than this because of the near certainty that population inversions (of atomic or molecular energy levels) can *also be essential* (22). We obviously have no idea what combination of frequencies accompanied the air breakdown process or how much electrical power was delivered in the Leyden jar experiments. In addition, we know little about the detailed geometry of the experimental setup - except that it is likely to have followed standard practices of the time. Fortunately, this potential problem does not seem to be serious.

Surprisingly, most of the equipment used in the experiments *still exists* - and I have seen it. It now seems likely that the heavy brass chain conducting the current to the jar’s interior was *undisturbed* while the first jar was being replaced, in which case its electrical characteristics, in the sparking region, would have remained almost identical *for the immediately following experiment*. This was, in fact, the *only other experiment* during which a plasma ball ever formed. Probably, the chain was moved slightly before the third experiment was performed so that, from then on, the igniting sparks could no longer precisely match the chemical impurities in the air and/or the electrical state of the air inside the Leyden jar (11,12).

3. Energy Release and Phase Changes.

Any rational explanation for long lived lightning balls, or for their even longer-lived relatives, such as earth-lights and Unpredictable Flying Objects (UFOs), must accept that they are mainly fuelled by chemical energy stored in the air (12,13,20). This energy is presumably released by nitrogen oxidation to nitric acid. The only plausible reaction that is thermodynamically possible is

$$N_2 + 2.5\ O_2 + H_2O\ \text{(gas)} \rightarrow 2\ HNO_3\ \text{(aqueous)} \qquad (1)$$

The standard Gibbs free energies of reaction shown in Fig 1 represent three (of four) *nominally* possible ways of performing the oxidations. The others include

$$N_2 + 2.5\ O_2 + H_2O\ \text{(liquid)} \rightarrow 2\ HNO_3\ \text{(aqueous)} \qquad (2)$$

and

$$N_2 + 2.5\ O_2 + H_2O\ \text{(gas)} \rightarrow 2\ HNO_3\ \text{(gas)} \qquad (3)$$

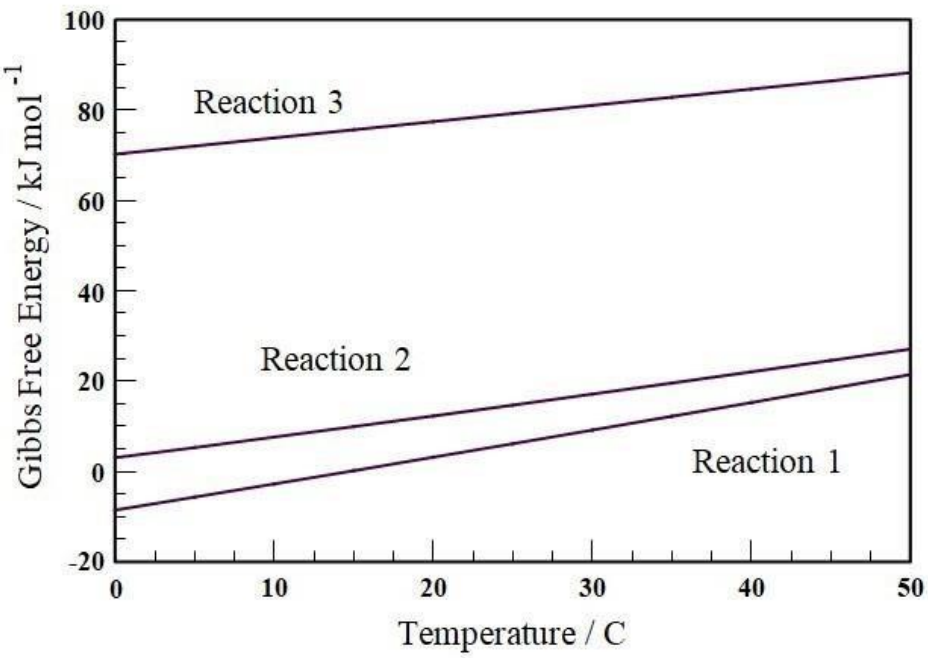

Fig 1: Free Energies for the Formation of Nitric Acid.

The free energies, calculated mainly from the NBS tables of thermodynamic properties (14), *of necessity* assume that all the species involved are in their standard states. This requirement arises because *only* standard state values of moist gas phase ions can have any practical value (18).

The basic reason for this (23-27) is that we possess no *valid* theory that can describe how to convert between the concentrations of ions and their thermodynamic activities *whenever a solution is highly compressible*. Later it was realized that this problem also applies to a moist gas. This fact led to a new ball lighting model (11). The fundamental problem is electrostriction (compression of a fluid in an electric field). It is huge for any ion in moist air (20,18).

Fortunately, because free energies are properties of state and because standard states are precisely defined quantities (if sometimes representing totally unattainable states), energy differences between them can be *calculated validly* without needing to understand any of the *details* which, theories permitting, could have described the concentration dependencies. Changes in composition, even for electrolytes, are associated with relatively small free energies and they *have to be neglected* in the systems under consideration - because the above mentioned parts of physical chemistry are missing. At any temperature in the air of the troposphere, ionized nitric acid is only thermodynamically stable in an aqueous phase - either as an aerosol or as a droplet (18).

We obviously would like to know all the detailed mechanisms and relevant rates of the various steps involved in the processes of concern. Clearly this is not currently possible, though clues have already been collected which provide fairly specific conclusions regarding what the mechanisms involved, at a plasma surface, must include (11-13). Some of these matters will be discussed in later sections of this paper.

Each of the reactions whose free energies are represented in Fig. 1 has an associated enthalpy which is given by the identity:

$$\Delta G^0 (x) = \Delta H^0 (x) - T \Delta S^0 (x)$$

Here x is the reaction number while ΔG^0, ΔH^0 and ΔS^0 are respectively the standard Gibbs free energy, enthalpy and entropy of the processes involved. T is the temperature. The standard enthalpies are the quantities of heat which would be released or absorbed *if* the reactions could be made to occur with each component in its standard state. They are slightly temperature dependent but, say at 10^{O} C, they would be -168.2, -123.6 and -27.9 kJ mol^{-1} for the three reactions respectively - based again on the NBS tables (14).

Clearly, from the data presented in Fig 1, the direct oxidation of nitrogen to nitric acid is very anomalous in that the reaction only has a negative free energy, and thus can proceed spontaneously, *if the temperature is below* 15^{O} C. The reaction product, aqueous nitric acid, still contains chemical energy (it can further react with such natural materials as calcium carbonate) so that the coexistence of N_2, O_2 and H_2O in the air *must be maintained* by some outside energy source - ultimately the Sun.

The important point is that ball lightning and its larger relatives seem to represent a means by which Nature occasionally extracts solar energy, using the air as a huge store of renewable fuel and oxidant (13,18,20). With all these air plasmas, nitric acid is being created fairly close to the plasma surface (12) and it must be formed there as an aerosol. Clearly, a hot plasma requires considerable cooling before aerosols can form near it. It will be most convenient to continue discussing the role of *nitric* acid in ball lightning stability before describing the absolutely *crucial refrigeration* mechanism, which involves *the formation of nitrous acid.*

From at least the 1830s (1), it has appeared very difficult to account for all the properties of ball lightning because it seemed that *all* its characteristics could not be explained by any *single* model without violating some law of physics. Historically, an important example of such a constraint has been thought to be the virial theorem (4). This theorem, a powerful way of expressing simultaneously the conservation laws of momentum and energy for an enclosed plasma (28) would place severe restrictions on the stability of a plasma *in the absence of chemical changes*. However, in 1994 it was shown that these restrictions do not apply to ball lightning because the ions in the plasma do not act as the simple charged particles that the virial theorem assumes them to be. Rather, they are chemicals and chemical processes can provide at least some stability (11) - just as they do in normal gas flames.

The virial theorem and other interpretational problems resulting from the disregarding of chemistry, have misled many physicists into believing that ball lightning cannot be a plasma (4,7). Whilst some have been willing to ignore the virial theorem and so have conducted valuable experiments (6,8), others simply refuse to accept that naturally contained air plasmas can exist. Our failure to agree on whether or not ball lightning is a plasma must be partly responsible for the lack of real investment in studying it. Progress is still only being made through the collection and use of those clues we can currently understand - just as it has been for well over a century.

As suggested above in the introduction, there is an equally serious problem in addition to the ignoring of chemistry. This is electrostriction. The practical importance of the phenomenon first became obvious through an attempt to understand the precise causes of a serious industrial accident during which most of a huge steam turbine went through the roof of the building housing it (23,24). It soon became clear that, because of the enormous electrostriction effects in steam, there was no valid way of quantifying the vapour phase chemistry associated with the turbine disaster (23,24).

By 1994, it was clear that the same problem limits what can be known about ionic processes *in moist air* (11) and we still lack a valid theory applicable to these systems (18). Hence the best clues in future, as in the past, are likely to come from reliable reports of such natural phenomena as ball lightning and its relatives. All naturally contained air plasmas, including earth-lights and UFOs, seem to be related, the more complex ones consisting of mutually attracting air plasmas that resemble ball lightning and are held together by precisely the same forces as those that stabilize ball lightning (21).

4. The Structures of Air Plasmas.

The more complex plasmas are unlikely be fully understood until lightning ball structures are better understood. However, they are usually far longer lived than lightning balls and nearly always seen under fair weather conditions (29,30,31). Compared with ball lightning, support for their study has been even less forthcoming - at least from most of the scientific establishment. Some are simply dismissed as unidentified flying objects or as normal objects viewed under unusual meteorological conditions. The acronym UFO is more appropriate if the “U” is taken to stand for “unpredictable” rather than “unidentified” (18,21).

It will be assumed here, based mainly on the kind of evidence assembled by Klass (29), that any real luminous object in the air, which is not a misidentification of a well-known object and which is able to move freely, is an air plasma. The phenomena called UFOs, earth-lights and earthquake lights, like ball lightning, seem to be naturally contained air plasmas (18,21). However, all the larger ones are structurally far more complex than a single lightning ball.

These plasmas are frequently described using some obvious characteristic or associated feature, and various names result (30). Among the fair weather variety are the so-called earth-lights - luminous atmospheric phenomena which are seen repeatedly in specific geographical locations. A tectonic source of energy is usually assumed, but some more recent observations (31) imply that a simultaneous contribution from cosmic ray showers, may also be required. These need only to be involved in “igniting” the plasmas - not providing them with long lives.

Decades of earth-light observations, made near Hessdalen in Norway, had been summarized in 2004, by Teodorani (31). Rather little has changed since then (32). Their study has greatly clarified the relationships between earth-lights, UFOs and lightning balls. The observations already confirm (if only indirectly) that the air provides at least some of the energy necessary to fuel these phenomena. This is because the larger ones are *nearly always* seen during fair weather. The studies also imply that the radiant optical power output (19 kW for one of the lights) (31) - can be much greater than that claimed in almost any ball lightning report.

Earth-lights differ in a number of significant ways from lightning balls (31). The detailed differences should eventually teach us much. The main advantage of earth-light study is the wide range of measurements which becomes feasible when observation is possible within a fairly well defined area (31,32). Three important points connecting the two phenomena were clearly implied in the Hessdalen studies. Earth-lights nearly always consist of groups of air plasmas (each resembling a lightning ball) and held together through similar stabilizing forces (18). They can survive for much longer than lightning balls and their occurrence is *definitely not associated with thunderstorms*.

As shown by Teodorani, (31), earth-lights seem to share detailed structural similarities with lightning balls. This conclusion resulted from measurements of light intensity profiles obtained from both still photographs and video records. Almost all of the hundreds of images available were small because of the large area being monitored. However, many of the records were of high quality. Because of light scattering in humid air, the most informative images were obtained on the very few occasions during which the air was unusually clear.

For these objects, the profiles closely resembled those characterizing brightly glowing *solid* bodies: they showed flat emissions over much of the visible area with intensities dropping off steeply at the edges (31). Under misty conditions, which predominated in the valley during the observation periods, many of the light profiles resembled those of stars - unavoidable consequences of light scattering by the intervening air in both cases. A solid body would have a similar light profile for the lights but solids cannot materialize from thin air. A more realistic explanation of the emission (31) is that the structures closely resemble those previously deduced for powerful lightning balls (11-13). The implication is that the lights observed, like lightning balls, owe their structure and stability to electrochemical processes which permit an inflow of air to produce nitric acid while, at the same time, holding the plasmas together.

Fig 2 is a schematic diagram of a lightning ball floating in the electric field of a thunderstorm with its total weight being largely (sometimes mainly) balanced by the buoyancy force of the plasma. The widths of the three zones surrounding the plasma are not to scale. Proceeding outwards from the plasma are: I, the Intermediate zone where the plasma surface is cooled; H, the hydration zone, where all the ions created by the plasma become hydrated; and R, the *absolutely crucial* refrigeration zone. The mechanism by which the air is refrigerated at the surface will be explained shortly. The + signs represent an excess of positive charges. A roughly corresponding number of electrons lie on the plasma/I-zone interface. An electric double layer at the plasma surface results.

5 The Processes Occurring at an Air Plasma Boundary.

It was early concluded that important processes occur at different distances from the surface of a lightning ball (11). The outer positive charges of Fig 2 are shown concentrated at the top of the ball. This is because of the direction of the current flow during a thunderstorm. With those naturally contained air plasma that are observed in fine weather, the distribution of charged aerosols would be reversed and would be much smaller in extent - because current in the air is in the opposite direction and is much smaller than during a thunderstorm (33).

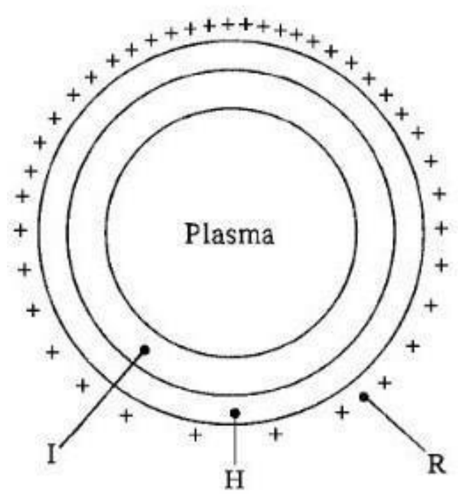

Fig 2: Schematic Diagram of a Lightning Ball During a Thunderstorm.

So-called "electrostatic guidance" of plasma balls has only been reported for ball lightning and this is consistent with the model. This form of guidance is actually an *electrochemical* effect (12), not simply an electrostatic one, but it does arise from the local electrostatic field.

When the new electrochemical model was first developed (11) - from the earlier one of Stakhanov (10) - it was realized that endothermic (heat absorbing) processes, outside the plasma, must balance the heat being produced inside it. UV radiation, created by charge neutralization inside the plasma, oxidizes nitrogen to *nitrous* acid just outside it and this acid is then further oxidized. More recently (34), it was demonstrated *experimentally* that both nitrous and nitric acids can be produced in this way and it was also shown that Reaction (4) has a vital part to play.

$$\gamma + N_2 + O_3 \rightarrow NO^+ + NO_2^- \qquad (4)$$

Here γ formally represents a mole of photons. All the other species are considered to be in their gas phase standard states. The reaction products are the lowest energy ions known that can be formed from the main components of completely pure dry air (11). The reaction can be taken to describe, symbolically, the uptake of a single photon per molecule of nitrogen *as if* the photon is in equilibrium with chemical species in dry air. Water vapour will then rapidly hydrate the ions.

Reaction (4) is more than usually symbolic for several reasons, among them that photons travel at the speed of light and so can hardly be at equilibrium. However, the *enthalpy* needed to *permit* Reaction (4) to proceed is very relevant because energy differences always accompany changes of state. Fortunately, both ions produced in Reaction (4) are well characterized thermodynamically. In an air plasma the ions are produced by the UV that results from charge annihilation within the plasma. They provide endothermic (heat absorbing) reactions in the refrigeration zone, R. In zone H, at temperatures below roughly 400 ^{O} C, ion hydration becomes increasingly important as temperatures decrease (11).

The unexpected significance of Reaction (4) was discovered accidentally when a small mercury vapour lamp was switched on very close to the silica window of a glass cell containing dust-free, water-saturated, air. The original aim of the experiments had been to replicate some of the earliest studies of C.T.R. Wilson (35) that had never been replicated. Details are provided elsewhere (34). The most important finding was that a very weak but very high energy emission line of mercury was *exactly* of the energy needed to permit Reaction (4). On hydration of the ions produced in this reaction, NO^+ changes to the hydrated proton, H_3O^+ (to which water molecules are then added), while NO_2^- is simply hydrated (11).

When this basic ball lightning model was first outlined there appeared to be no way of predicting the sizes of lightning balls but there was a plausible explanation for why established balls normally have fixed volumes. This is that changes in energy input effect the various exothermic and endothermic processes to the same degree. Hence a temporary increase (or decrease) in energy input might well be accommodated by an increase (or decrease) in the *temperature gradient* near to the refrigeration zone - but it need not produce any change in size of the plasma. It now seems that the actual size of a lightning ball is determined during its initial formation stages and depends partly on the particle content of the air, but also on other parameters such as the space charge in the air at the time of formation (13).

What is important here is that, if this explanation is correct, a very powerful lightning ball is expected to have an extremely large temperature gradient at its surface. Such balls are presumably the ones that crack circular holes in glass window panes when they pass through them while others, presumably less powerful ones, can either bounce away from or pass through the glass of closed windows without damaging the glass (36).

The steepness of the gradient at the edge of a powerful ball clearly results from the proximity of the exothermic ion hydration zone to the refrigeration zone a little further away from the plasma (11). The passage of lightning balls through windows, *without* damage to the glass (37), presumably results from population inversions (of atomic or molecular states of the species present) produced by the local emission of electromagnetic radiation (22).

As seen earlier, earth-lights seem to be close relatives of lightning balls (31). It is most likely that, as with ball lightning, energy is mainly supplied to established earth-lights by the oxidation of nitrogen to nitric acid. Earth-lights can *definitely* form in the *absence* of the large electric fields present during thunderstorms. Thus, external electric fields cannot be *necessary* for either the ignition or the stability of any air plasma - except possibly by ensuring an optimum space charge. It could be that the main role of an electric field is to “ignite” the nitrogen oxidation (13), after which chemistry supplies all the energy needed for an extended life.

It seems certain that other processes “ignite” the plasmas of an earth-light because they are almost never observed during thunderstorms (31). Tectonic processes are usually assumed to be responsible because earth-lights tend to be observed in very specific locations on Earth. However, the assistance of powerful cosmic rays has also been invoked in places where these lights are seen very frequently (31). The Hessdalen Valley, in which the studies were undertaken, is in a region of central Norway where the Earth’s magnetic field continuously directs solar particles toward the Earth. Tectonic and solar wind effects may well combine favourably near Hessdalen.

Some of these studies show clearly that electromagnetic fields occasionally add to the energy of an earth-light: a few low power earth-lights, formed in the Valley, were found to brighten considerably in a manner that reflected imposed electromagnetic disturbances (31) - and therefore also, electrical disturbances. *Changes* in input energy also seem to result from changes of local air impurities. Both probably need to be “optimal” for the continued life of an air plasma. However we cannot currently define in detail what any of these optimal conditions are.

Different environments could certainly influence production rates for both nitrous and nitric acids. Variations in electric field (at many frequencies) are well known from studies of atmospheric electricity (38), but the evidence for chemically induced effects is less clear. Changes in ball lightning colour (from white to red) have been observed very occasionally when a ball repeatedly collides with tree branches (10). This might be evidence for an altered rate of nitric acid production due to very local contamination in the air; alternatively, it might represent emission from the impurities themselves that were drawn into the plasma. There is also much evidence that lightning balls can vary widely in colour (4). This must be due to impurities in the air.

Reliable thermodynamic properties for the gas phase nitrate ion are unknown - presumably because its free energy of formation is positive and large. Neither the NBS (14) nor the JANAF tables (39) has an entry for the gas phase nitrate ion. Only estimates of unknown reliability are available and they are too imprecise to be of much use (11). Hence, processes *involving gas phase nitrate ions* are unlikely to be directly important in explaining either air plasma processes or the (low) levels of nitric acid found everywhere in the atmosphere.

Reactions (1) and (2) both involve liquid water (in aerosol form), though only Reaction (1) has a favourable free energy. The difference between the two reaction free energies mainly represents the process of condensing one mole of water, in an ideal gas state, to the liquid state according to the equilibrium process:

$$H_2O \text{ (gas)} \quad \rightleftharpoons \quad H_2O \text{ (liquid)} \qquad (4)$$

Note that the relatively small free energy change ($\Delta G^0 \approx 8.6$ kJ mol^{-1} at 25^{O} C) for this process, which is a purely physical one, has the effect of tipping the energy balance so as to permit Reaction (1). This is simply because so many water molecules per ion are involved.

The crucial *refrigeration reaction*, involves *nitrous acid* production next to the plasma (11). In this case (as we shall see later), the *number* of water molecules involved in the phase change is even more significant than it is for nitric acid. However, in both cases water vapour partly controls the processes that occur. Normal air contains water in significant quantity. The water can be present as vapour, in the form of ion hydrates and also adsorbed onto invisibly small hygroscopic aerosols which, at any instant, may or may not be electrically charged (33,19). For thermodynamic reasons which are well understood *qualitatively* (23-25,11,13,20), it is quite impossible to model ionic processes in real moist air *if a valid prediction is to be hoped for*.

6. Influences of Impurities in the Air.

Quantitative arguments are again impossible because any gaseous ions in the air will inevitably be present at very much lower concentrations than are air contaminants (18). Similar points were made, decades ago, concerning reactions of ozone with *ionic* species (40). If much progress is to be made in the foreseeable future, our options are small. It seems we are obliged to rely on observations, interpreted basically as clues, if we are ever to be in a position to *use* the abundant chemical energy that is present in the air. Trying to deal with any of the *chemical reactions* that involve ions seems unlikely to be useful for many decades (18) - unless science funding policies change considerably. However, modelling *aerosol growth rates next to an air plasma* might well prove instructive if new proposals for studies of earth-lights (32) were to be supported and extended somewhat.

Natural clouds obviously exist at temperatures below 0^{O} C and this means that nitric acid in aerosols is *thermodynamically stable* everywhere inside them. However, even at such temperatures, many reactions facilitated by radical intermediates are possible. Such reactive species as O and OH can have important chemical effects at much lower temperatures than those in clouds but impurities of far lower energy than O and OH (i.e. more stable ones) are always present and some are almost certainly capable of influencing the relevant reaction rates.

In principle, many of these contaminants could prevent the formation of nitric acid by diverting *essential intermediate species* away from either the formation of nitrous or nitric acids. It is well known that thermodynamic considerations *alone* are rarely useful. As we have seen, only standard state thermodynamic properties can be treated quantitatively. Fortunately, these data *can* be used quantitatively and they seem to be instructive in ways not considered so far.

Nitric acid formation is only possible at all because the free energy of Reaction (1) permits it and it seems that its low abundance in the atmosphere must be due to kinetic effects. In other words, the low nitric acid concentrations *always* found in the atmosphere must be due to the presence of one or more potentially reactive impurities in the air. The air always contains millions or billions of different contaminants that could, in principle, ensure that nitric acid is only ever detected in the air at the very low levels at which they are routinely detected (41).

However, despite our almost complete ignorance concerning these matters, it transpires that there is one impurity that is almost always found in the air at fairly reproducible levels. It is nitrous oxide which has been found in the air at mole fractions of around $3.5 \cdot 10^{-7}$ (42).

It is therefore desirable to discuss the following reactions:

$$N_2O + 2\,HNO_3\,(gas) \rightarrow 2\,N_2 + 3\,O_2 + H_2O\,(gas) \qquad (5)$$

and

$$N_2O + 2\,HNO_3\,(aqueous) \rightarrow 2\,N_2 + 3\,O_2 + H_2O\,(gas) \qquad (6)$$

for which ΔG^0 (5) = −62.7 kJ mol^{-1} and ΔG^0 (6) = +81.9 kJ mol^{-1} at 25^{O} C. Clearly, although Reaction (5) is strongly favoured thermodynamically, it is only favoured because HNO_3 (gas) is so very unstable that it is never likely to be present at remotely detectable levels. The considerable differences in the stabilities of the acid in the two phases were discussed in Section 3. Both the reactants in Reaction (6) are certainly present in the atmosphere but the reaction is thermodynamically impossible.

Although Reaction (5) is very unlikely to be *directly* relevant - because *gas phase* nitric acid is so unstable - *gas phase precursors* of the acid's formation might well have sufficiently long lives to produce the universally low concentrations of nitric acid regularly detected. In other words, there might be mechanisms that would *ensure* low concentrations of nitric acid everywhere in the air. It so happens that a probable role for nitrous oxide can be assessed thermodynamically and it might explain the observed *low* concentrations of nitric acid always measured in the atmosphere (41).

Of all the impurities that might be involved, only N_2O possesses a concentration that is anything like as reproducible as are the levels of oxygen and nitrogen (42). On the basis of the above clues, it seems probable that the presence in the atmosphere of nitrous oxide might *entirely* explain the low concentrations of nitric acid found in the atmosphere. Some *very important* findings of Dmitriev (43,44) may support this claim - though only indirectly.

One of his findings was that lightning balls sometimes expel nitrogen dioxide (NO_2 + N_2O_4). These two oxides are normally present at very near equilibrium concentrations. However, only NO_2 is coloured. The correct name of N_2O_4 is dinitrogen tetroxide but, because it is so cumbersome and because the two molecules are normally present at equilibrium, it has long been standard practice to *refer to both* forms of the oxide simply as nitrogen dioxide. I shall adopt this practice as did Dmitriev. The ball he watched was informative in a number of ways. For example, it displayed several typical characteristics of ball lightning - such as moving significantly *into* the prevailing wind as well as electrochemical guidance.

The *most extraordinary* aspect of Dmitriev's experience was that he happened to have with him four evacuated glass vessels while he was camping near a river and lightning struck nearby. Having been alerted by the thunder, he saw a lightning ball slowly crossing the river towards him and following a curved path directly above a line of floating logs that were chained together so as to form a "log boom" - for containing tree trunks felled further upriver.

The ball was travelling so slowly that he had time to reach the place on the riverbank where the logs were tethered and to which the ball was heading. He was thus able to take the evacuated vessels to this spot and sample the brown gases that were being released from it. The brown gas was clearly nitrogen dioxide which, as noted earlier, exists in equilibrium with its dimer, N_2O_4 (45). This brown gas is only rarely released from lightning balls in sufficient quantity to be visible, although an acrid smell, that is likely to be it, is sometimes noted when the balls are encountered indoors (9,46).

Dmitriev (apparently a chemist) took the samples to his laboratory where they were analysed. The results are shown in the table below. It should be noted that, since the samples could not be analysed immediately, the gases found need not have been the only ones released but they would most likely have been the two most stable of the compounds originally released. Any short-lived species initially present would have had ample time to change to lower energy species. However, the brown gas could only have been nitrogen dioxide.

Table 1: Analyses of Gases Released from a Lightning Ball (Dmitriev, [44]).

Sample Number	1	2	3	4
Ozone concentration / µg m^{-3}	232	1283	722	43.8
NO_2 concentration / µg m^{-3}	92.3	1645	884	34.7

The sample numbers represent the order in which the samples were collected as the ball moved past Dmitriev's position. The ball was clearly releasing highly oxidized products. Formally, nitrogen can exist in three oxidized states: III (for nitrous acid), IV (for nitrogen dioxide) and V (for nitric acid). One possible explanation of the findings is that the air flowing into the ball contained unusually *high or low* concentrations of reducing agents. However, there are many other possibilities because the final products of any complex reaction scheme depend on whether or not possibly essential reactions are being catalyzed or prevented by air contaminants. As we have seen, no lightning ball can have a significant lifetime if the inflowing air contains impurities that are unfavourable to the formation of either nitrous or nitric acids.

In no case would *gas phase nitric acid* have been able to escape from the ball because the gas phase acid is so unstable. This acid could only be present (either as droplets or aerosols) held in place by the inflow of air toward the plasma and a chemical driving force for the overall nitrogen oxidation process. As previously mentioned, there happens to be one air contaminant whose concentration is remarkable uniform: *nitrous oxide* (42). Since the reactions involved certainly involve ions, we can make no valid predictions concerning the rates of any of them. Fortunately, as we shall see shortly, some aspects of the relevant thermodynamics *can* be calculated. The results are revealing.

The ball mentioned was moving with a significant component of its motion *into* the prevailing wind. Gas molecules move enormously faster than any conceivable wind and, because the ball observed by Dmitriev (43) was moving into the wind, there will have been a flow of air past the ball that could sweep with it any gases diffusing away from the ball's surface. Fortunately, on this occasion, the process permitted actual measurements of some of the gases likely to have been released.

It has long seemed certain that ball lightning, as well as larger assemblages of air plasmas, *only* possess the very long lifetimes they sometimes do if aqueous nitric acid (in small quantities) is produced at the surface of each plasma ball (12, 20). It is therefore worth considering a number of reactions involving nitrogen oxides that might have a predictable influence on the concentration of nitric acid found in the atmosphere. There are several plausibly relevant reactions for which thermodynamic calculations can be made. They include the following:

$$N_2O_4 + 2HNO_3\ (aq.) \rightarrow 3.5\ O_2 + 2N_2O + H_2O \qquad (7)$$

$$N_2O_4 + 2HNO_3\ (aq.) \rightarrow 2.5\ O_2 + 4NO + H_2O \qquad (8)$$

and

$$N_2O_4 + 2HNO_3\ (aq.) \rightarrow 4\ O_2 + N_2 + N_2O + H_2O \qquad (9)$$

All the reaction components are in the gas phase except for nitric acid (which is taken to be present as an aerosol). For these three reactions, the standard free energies (at 25^0C) are, respectively 104.44, 242.24 and 0.24 kJ/mol. There are other plausible reactions but, apart from Reaction (9), they all have positive reaction free energies similar in magnitude to those of Reactions (7) or (8). This implies that only Reaction (9) could be involved and that the predicted level of N_2O will be very low - as is found to be the case in practice. Levels of other possible reaction components vary widely in space and time so that actual levels of N_2O cannot be predicted. Nevertheless, it seems likely that the thermodynamics of Reaction (9) basically controls how much N_2O and HNO_3 are present in the atmosphere - because its free energy is far more favourable than the others.

7. Other Observational Evidence.

Some 2002 findings regarding hailstone chemistry should be mentioned here. The results were reported only recently (18), although they were obtained much earlier, and they are fully consistent with the findings of Dmitriev (43,44). The hailstones were deposited from a supercell storm that was referred to as the La Plata storm (47). This storm had passed close to where I was living at the time and many hailstones were collected from it.

Several individuals who lived near its path kindly donated hailstones that had fallen in their gardens and had been stored in freezers. The supercell seemed a perfectly normal one in that it was moving east and the hailstones fell only to the left of the moving storm (48,49). However, it *appeared* to differ from most supercell storms in that it clearly contained, deep within it, an apparently *unfluctuating* source of light. Normal lightning strokes were also observed but they could only be seen very close to the *outside* of the immense cloud.

Like most supercell storms, this one spawned tornadoes, and tornadoes usually produce large local drops in atmospheric pressure. Sometimes these pressure drops are so large that they cause buildings to explode (49,50). Tornadoes are generally believed to require some kind of feedback mechanisms but the specific reason the hailstones were collected from the 2002 storm was that it seemed to contain one or more large air plasmas somewhere near the centre of the enormous cloud. One reason for believing this (in addition to having seen the actual cloud myself) was a much earlier study by Vonnegut and Weyer (51) who had published photographs that indicated the presence of internal plasmas above a few tornadoes. A large collection of published descriptions of lightning balls in tornadic storms is available (46).

In my opinion, the most likely cause of the large pressure drops below tornadoes is the pressure reduction *expected* if either one huge air plasma or many smaller ones are situated somewhere above the tornados (12,18). This suspicion was the reason the hailstones were sought in 2002. As will be seen in a forthcoming publication, basically the same mechanism, though on a far larger scale, probably explains two characteristics of hurricanes: the existence of what used to be called hot towers in them and the huge storm surges that can cause so much devastation under their paths. All air plasmas need *air input* for their stability (11) but such “sinks” for the air are unlikely ever to have been included in supercell models.

The three largest hailstones recovered from the 2002 storm, proved to be by far the most instructive. They were melted in stages (as evenly as possible from the outside in toward the centre) and ten samples of the resulting melt from each hailstone were analysed for four common anions. The concentrations of chloride and sulphate displayed random and enormously variable concentrations (varying over several orders of magnitude) while nitrites were undetectable. In complete contrast, *nitrate* concentrations were found to be essentially independent of radius. The results are shown in Fig. 3. Measured redox potentials showed that all the melted samples were highly oxidizing so that the absence of nitrites was easily explained.

In addition, it had previously been suggested that nitric acid production, inside tornadoes, might be associated with the not uncommon shortfall between theoretically predicted tornadic powers and those observed (12). Such a discrepancy would be expected if *chemical energy* was being supplied in addition to that from conventional meteorological sources. Unfortunately, for reasons closely related to those discussed earlier, such *extra* supplies of energy are impossible to quantify.

It was hoped that hailstone analysis might reveal a record of chemical processes that had occurred deep inside the supercell. Infrared and microwave heating, from a central plasma, would maintain large quantities of water vapour inside a characteristic region of all supercells. The discoverers of these structures, Browning and Foote, (52) called them "vaults" but they are now usually called bounded weak echo regions or BWERs.

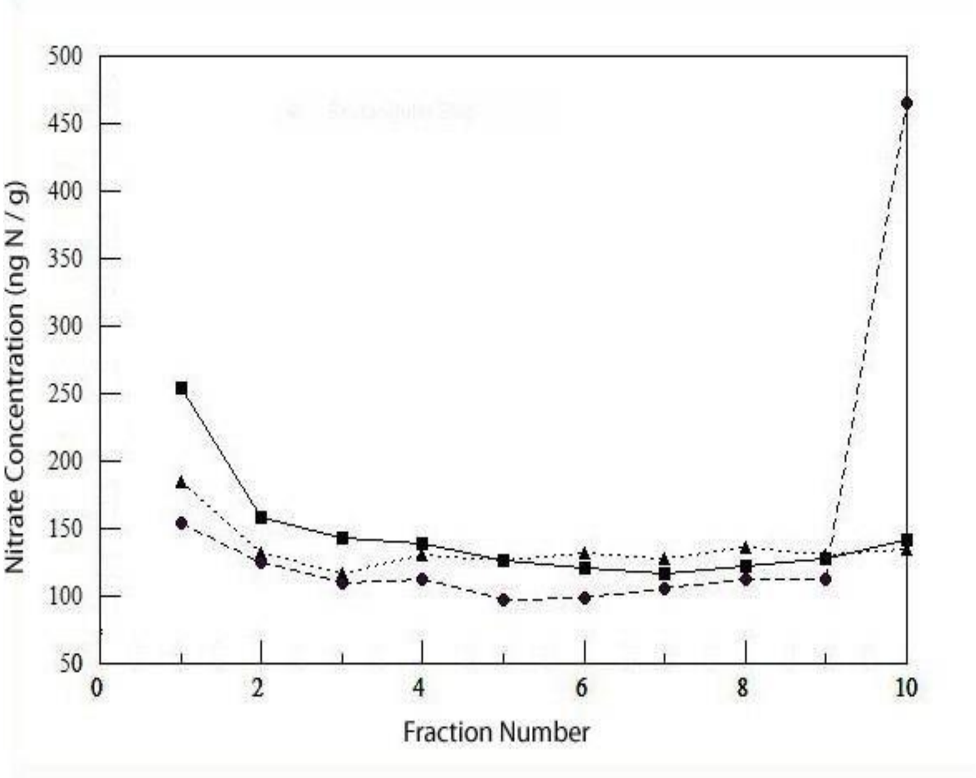

Fig.3: Nitrate concentrations as a function of depth for three hailstones.

A few *large* hailstones would be expected to grow at some distance from any plasma ball while all small, radar reflecting, particles could have evaporated completely. This was what appeared to be the situation in the storm studied by Browning and Foote (52). As we have seen, the limited analyses of hailstones from the La Plata storm revealed completely random results for chloride and sulphate but remarkably uniform patterns for nitrate concentration. There appears to be an easily understood reason why a few nitrate concentrations were higher than all the others: contamination.

One of the three innermost samples (which could have contained contaminants from the original nucleus around which the hailstones had grown) possessed a nitrate concentration far higher than all the others. Also, all the *first* samples melted possessed nitrate concentrations somewhat higher than the inner ones. These samples had probably become contaminated through contact with the ground before they had been collected. The findings indirectly support the belief that at least one powerful air plasma was present inside the La Plata storm.

The surfaces of large hailstones are never smooth - very large crystals of ice being present. Apart from the first one or two samples, all others had nitrate mole fractions near 12 (±3).10^{-8}. All the oxidation potentials were positive but they varied considerably. This appeared to be a consequence of randomly distributed blades of grass that were present in all the hailstones. These could have acted locally as strong reducing agents. Future, more refined, methods for studying hailstones from tornadic storms should prove very informative.

Large hailstones are generally assumed to form by repeated collisions and consequent surface melting (41). However, the above analyses suggest that the very large hailstones formed inside this supercell resulted from local warming by one or more large plasmas, inside the vaults, followed by freezing of new material from the vapour. If nitric acid was formed very near a plasma surface, measurements might only be expected to represent a lower limit to the acid's concentration - as a result of dilution with pure ice formed elsewhere. However, it seems *far more likely* that small nitric acid containing aerosols were present fairly far from a plasma since the nitrate concentrations measured were so very close to those typically found in rain, ice and snow (41).

It appears very relevant that the nitric acid concentrations, detected *in all precipitated forms* of atmospheric water, are always of a similar magnitude whereas concentrations of chloride and sulphate in the few studies reported in the literature seem to differ by orders of magnitude (41). In a hailstone formed (by freezing) at a considerable distance from an air plasma, an oxidizing environment is easily maintained because charge neutralization within the plasma leads to UV emission and this will produce O and OH radicals from the water vapour present. These radicals do not require high energy UV in order to oxidize nitrogen. Because H atoms normally react very slowly, an *oxidizing environment* is expected a considerable distance from any air plasma.

These claims appear to be supported by the numerous reports in the literature of lightning balls that entered rooms and expired there (4, 46). Frequently, a strong odour resembling sulphur dioxide or ozone is reported but the measurements made by Dmitriev (44), admittedly in the open air, imply that the compound responsible for all the odours was really nitrogen dioxide.

8. Refrigeration at the Surfaces of Contained Air Plasmas.

As pointed out earlier, we cannot predict how ions in real moist air behave chemically. However, we are not helpless. Thermodynamic predictions *are* possible for the most stable known pair of ions that can escape from an air plasma (11,12). It was through considerations of this fact that the basic 1994 model for ball lightning was developed - from a much earlier, very innovative, model by Stakhanov (10).

In 1994, it was shown that nitrite ions and hydrated protons in the air can combine and refrigerate the surface of an air plasma (11). The further hydration of these ions, due to surface tension effects (12), together with other inevitable processes, easily account for the mechanical stability and unpredictable motions which are so characteristic of ball lightning (11-13,20).

We have seen that established air plasmas can be thought of as oxidizing nitrogen - ultimately to nitric acid. We can burn hydrocarbons easily because a spark can ignite them and an inward pressure results from the air feeding the flame. Nitrogen "burning" is far more difficult because it can only occur at the *refrigerated surface* of an air plasma. The two acids formed are the only ones known that are thermodynamically stable under the relevant conditions. Refrigeration close to a hot plasma surface is *absolutely essential* for air plasma containment (11-13,20).

The improvements to Stakhanov's electrochemical model for ball lightning (11) were made possible by two facts. One was that the standard state thermodynamic properties of the gas phase nitrite ion and of H_3O^+ are both known (39). The second was that the thermodynamics of gas phase ion hydration are sufficiently well understood for the hydration and some of the subsequent chemistry to be predicted.

Crucially, some of the problems resulting from *using invalid thermodynamic assumptions* had been realized much earlier (24,26,27) and they were later found to be avoidable in systems such as the exteriors of lightning balls (11). The very unusual position facing us in this particular case is that, although the standard state properties are calculable by established means, those of *real* solutions (at finite concentrations) are not (13,18).

Many of the arguments which follow would apply to plasmas similar to ball lightning, such as earth-lights and Unpredictable Flying Objects (UFOs) but by far the most plentiful information relates to ball lightning. Most main-stream *ball lightning models* fall into two classes (10, 8). One group of investigators stresses their plasma-like behaviour while the other group *cannot accept* that they could possibly be plasmas - so they have sought a wide variety of alternative explanations. Fortunately, lightning balls are observed sufficiently frequently, sometimes at close range, so that good statistics on a few of their characteristics are available. Such statistics are very valuable - most importantly in providing strong evidence that ball lightning is a single real - if a poorly understood - natural phenomenon (7,53).

Energy supply is what mainly distinguishes the two types of model (8). Non-plasma models are usually aerosol models which demand a *single* injection of energy. Few of them seem important any longer. Although they can often explain several properties, they can provide no explanation for the existence of really long-lived balls - especially those whose life ends in an explosion. Such balls are by no means rare (46). In addition, they offer no explanation for earth-lights or UFOs.

Most plasma models easily explain the existence of long-lived balls within thunderstorms. However, few can explain the existence of plasma balls in clear weather or most of the *strange motions* which are so characteristic of the balls. Stakhanov (10) noted that most models fail to explain how a plasma can change in shape sufficiently to pass through a hole whose diameter is much smaller than that of the ball. Also, they can bounce, rather like a balloon, or crack holes in glass windows that seem to have exactly the same diameters as the balls themselves. In addition, they can sometimes contact people's flesh without seriously burning it.

Some of these were characteristics that led Stakhanov (10) to his *most important conclusion* : that *ball lightning possesses an effective surface tension*. However, the balls claimed by many observers to contain very large quantities of energy could not be explained *quantitatively* by his model. The improved, mainly qualitative, model of Turner (11,12), fully accepts the validity of Stakhanov's main conclusions but the limitation on power is overcome if his model is modified slightly - by considering more heavily hydrated ions than he did and by placing them on the *surface* rather than in the interior of the balls. It was also found necessary to change the assumed identity of the anions involved in order to be fully consistent with the available thermodynamic data (11).

The key to what were once seen as the most anomalous properties of ball lightning is refrigeration near the surface of any contained air plasma. This process allows nitric acid to form in the cooled regions surrounding a ball but it is the chemistry of *nitrous* acid that is responsible for the necessary refrigeration. Some of the relevant thermodynamics can be modelled approximately (11), but the rate processes cannot (13,20).

The importance of forming metastable nitrous acid close to a plasma ball was first appreciated in the 1990s (11). The role for nitric acid formation was only seen later (12). By 1998, it had been realized that the electric field of a thunderstorm is not at all necessary for air plasmas to have long lives. The *crucial requirement* for any air plasma ball to exist is that H_3O^+ and NO_2^- ions have each attracted into their electric fields more than about five water molecules per ion *before* they neutralize each other's charges. On the basis of the very favourable energies involved in charge neutralization for *very dry ions* (and also using common sense), the process has usually been expected to occur rapidly and completely. However, as shown in Fig 4, this expectation is incorrect in the case of some hydrated ions. Here, standard free energies for the neutralization of H_3O^+ and NO_2^- ions (assuming that each is hydrated by n water molecules) are plotted against n. The data sources are the same as that in ref. (11) - but they are extended to higher values of n than had been used in 1994. They show that the charge neutralization process is, as expected, thermodynamically favoured for *n less than about 25* above which it becomes totally *impossible*.

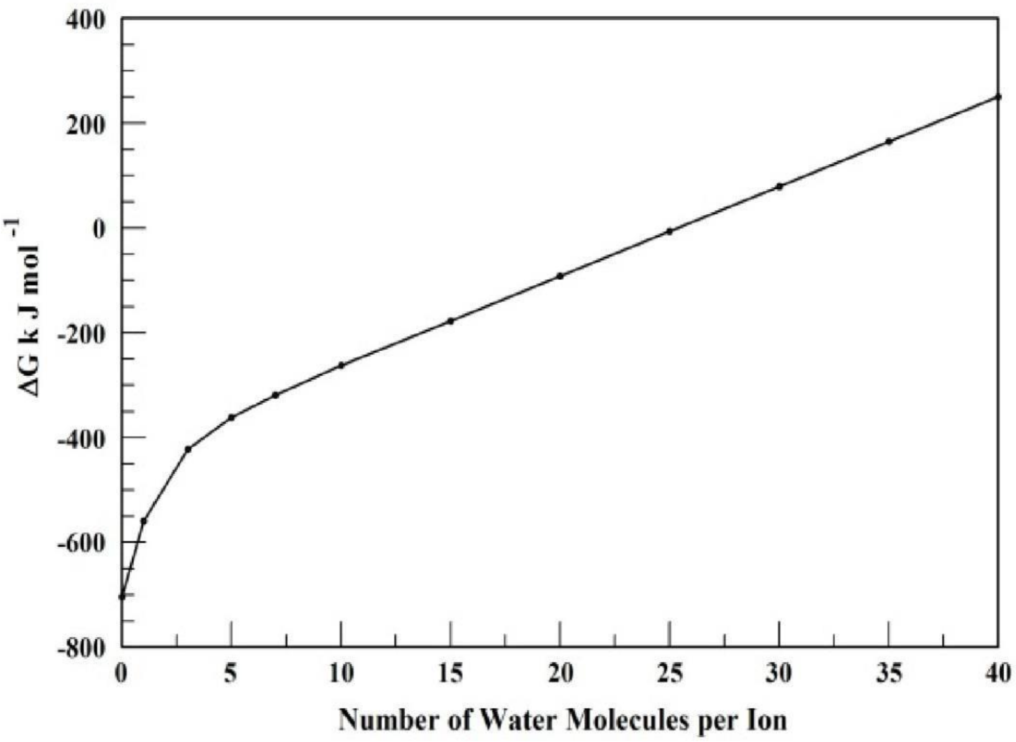

Fig 4: Gibbs Free Energies for the Charge Neutralization of Hydrated Nitrite and Hydrogen Ions.

This means that the number of water molecules per ion that are necessary for refrigeration to occur, *and* for nitric acid to be formed subsequently, is very narrow indeed (roughly between 5 and 25). Another way of saying this is that refrigeration at the surface of an air plasma is inevitable *if, and only if*, the rate of ion hydration lies in a range that can maintain optimal quantities of the ion hydrates at optimal distances from the plasma - *whatever these optima may be.*

The most crucial point is that hydration by *rather few* water molecules (about five) is needed before the charge neutralization process changes from exothermic to endothermic. However, if the degree of hydration is too high, no refrigeration of the air is possible. Unfortunately, we have little idea what the required conditions might be. Once refrigerated, aerosols of appropriate diameters surround the plasma and they will restrict the inflow of air. If other conditions are also favourable, they could (in principle) hold a plasma together *indefinitely*.

That aerosols and small droplets surrounding a ball of air plasma can span the visibility limit is shown by the comments of a few observers, who sometimes remark that the balls they saw were remarkably transparent or else that they were so cloudy that they prevented all objects behind them from being seen (4,10). It now seems clear that the requirements for a stable ball need not always be identical so long as an optimal *balance* of forces is maintained.

Any plasma ball will be negatively charged, because electrons travel much faster than ions. This charge is largely balanced by hydrated protons outside the plasma, thus providing an electric double layer at its surface. Sanduloviciu has long believed that such a structure is essential to the stability of lightning balls (54). Presumably, the positively charged aerosols surrounding an air plasma need to grow to appropriate sizes in order to provide appropriate resistance to the inflowing air.

The force produced by the inflowing reactants (that permit Reaction (1)) is opposed by the thermal forces produced by the hot plasma. Electrostatic forces are obviously crucial to stability (11) - but mainly, it is now thought, in the very early stages of a ball's formation where they help define a ball's size (13). Similar forces, plus additional electrostatic forces, are probably also important in explaining some of the differences between lightning balls, earth-lights and UFOs. No *additional* kinds of force seem needed to explain the characteristics of the other phenomena. This point will be addressed in future publications that deal more fully with the characteristics of UFOs.

For the reasons given earlier, stability probably requires the presence of suitable air contaminants and/or the absence of unsuitable ones. The space charge in the air also needs to be near optimal. Air contaminants could, in principle, prevent either the refrigeration stage or the oxidation of nitrous to nitric acid at any stage in the processes that lead to the containment of an air plasma. It is, therefore, not at all surprising that all air plasmas are rare. At increasing distances from the plasma, the cooler ions become larger as a consequence of further hydration and the effects of aerosol surface tension. These processes provide a detailed (purely qualitative) description of the double layers that were first invoked by Sanduloviciu (54) to explain several ball lightning characteristics.

In current attempts to contain plasmas on Earth, metals are used and very serious limitations result. In principle, air plasma containment would avoid all these problems. The various endothermic and exothermic processes that occur at an air plasma surface would provide "thermochemical lagging" between the plasma and the ambient air (11) and this would be an additional advantage if chemical energy could be derived from the air and used in electricity production or in the shipping industry.

9. Properties of Air Plasmas and Proposals for Studying Them.

When Stakhanov's model (10) was first refined (11), it seemed natural to assume that, as with other plasma models, a ball's energy is supplied entirely by the electric field of a thunderstorm. Later it was realized that air plasmas are frequently observed in fine weather and that this is easily explained by the formation of nitric acid close to the plasma surface (12).

It now seems that single air plasmas are best thought of as spherical flames that need very special conditions to ignite them because nitrogen can only be oxidized to nitric acid at low temperatures. The electric fields produced by a thunderstorm can supply the sparking energy needed but there have to be other ways of starting the plasma processes (22). At least a few new *experimental* approaches are certainly needed. In the meantime, molecular dynamics simulations might possibly help. Monte-Carlo simulations would probably be less useful because the problems need to be formulated so as to avoid *all* thermodynamically invalid assumptions.

The inward gas flow past the aerosols and the thermal forces opposing it impart the effective surface tension which a stable plasma ball requires. Observationally, this force can be much larger than that of a soap bubble (11). A plasma ball also possesses a far more *stable* "surface" than a soap bubble since, following a distortion, a re-minimization of an *effective* surface energy (by chemical means) is needed rather than mechanical repair to a thin liquid surface - which is impossible. Ball lightning surfaces can be remarkably strong and large balls are occasionally seen to split into smaller ones with little apparent change in total volume (55). Such processes only require a reminimizing of the effective surface energy.

The above facts, together with some qualitatively predictable chemical and physical effects, clearly explain a ball's ability to bounce and to squeeze through holes that has a smaller diameter than the ball itself (10). Also, there seem to exist a number of energetically plausible reactions, between metastable species, which can result in re-ionization of the air and could support the structure of a strongly distorted lightning ball (11, 12).

It is not currently possible to provide a useful quantitative understanding of any of the *chemical* processes involved in air plasma stability. This is because we possess no valid theory for ion-ion interactions in moist gases (11,24) and because this situation is unlikely to change in the foreseeable future (18). In principle, however, we might be able to learn a little more by restricting attention to the purely *physical* processes involved. It now seems clear the gradients of electric potential, humidity and temperature are all involved in stabilizing air plasma surfaces and in controlling their motions.

Very large temperature gradients, inevitable at some plasma surfaces, help explain why lightning balls sometimes prove relatively harmless to the touch while others can kill animals (4). They can also crack circular holes in panes of glass (36). As far as is known, the holes are always of exactly the same size as the witnessed balls. A very early example of this phenomenon was clearly displayed in experiments of Arden and Constable (16).

Structurally, *earth-lights* are significantly more complex than lightning balls (31) but their stabilizing and disruptive influences seem to have identical causes (21). Clearly, differences in behaviour between the two phenomena could prove instructive as could the more complicated motions of UFOs.

Thermodynamics, being path and mechanism independent, is not concerned with the fact that, just outside an air plasma, some of the ions are moving outwards, while the air comes from the opposite direction. Nor do the detailed mechanical forces, required to hold the plasma together, effect the thermochemical driving forces or the chemical energy delivered in response to them. The plasma can be thought of as serving as a *catalyst for nitric acid formation* (12) while the overall process can be, in effect, autocatalytic once it has begun.

It might prove instructive to investigate a few chemical aspects of nitrogen oxidation that are *free from* the complications of dealing with ions. One possible way of learning more about the *neutral molecule chemistry* involved in air plasmas might result by studying grouped air plasmas using techniques rather similar to those recently discussed by Teodorani (32).

Teodorani's proposed experiments would send drones to earth-lights in order to study them at close range. If the drones were to be fitted with small, evacuated vessels, similar measurements to those made by Dmitriev (44) should prove possible. If similar nitrogen containing gases are always found to surround an earth-light, much could be learned but even the occasional absence of such compounds could be instructive as could possibly local wind directions (and speeds) near the plasmas. Local redox potentials, in the immediate vicinity of the plasmas, could also be measured.

Eventually, much more information might be obtained on other air plasmas if drones used were to be fitted with heat seeking instrumentation and sent in search of the kinds of plasma that are likely to be found inside supercells and in hurricanes. Clearly, any of these suggested studies would be a considerable improvement on the kind of largely amateur study that has proved necessary to date.

10. Using Air Plasmas to Produce Energy.

These days, arrays of solar cells are commonly used in producing so-called "green energy". The main disadvantages of producing electricity in this way are (1) their limitation to daylight hours, (2) their very low energy density and (3) the consequent difficulty, in some cases, of avoiding conflict with land needed for agricultural purposes. All other existing "green" energy sources, except for nuclear power, are limited in similar ways.

The main advantages of using the *chemical energy in the air* over the simple use of solar cell arrays would be its availability day and night, and the high *energy density* it would provide. The standard enthalpy for Reaction (1) is close to -168 kJ mol^{-1}. This is less than half the heat released in burning carbon ($\Delta H^0 \approx 394$ kJ mol^{-1}). However, using air plasmas for energy production would still provide high *energy densities*. They would be orders of magnitude larger than is achievable from most current "green energy" sources (windmills, ocean waves, hydroelectric dams or solar cells). Solar cells in quantity would obviously be required to extract the energy as electricity. However, these are already produced in quantity and research on improved designs is currently very active (56).

There has been plenty of government funding going into research on *nuclear fusion*. However, this potential source of energy is certainly not without problems. One obvious benefit that the use of air plasmas would have over future fusion reactors is that, because no metals are used to contain the plasma, all the associated forms of radioactive contamination would be absent. It would surely be best to let the Sun's *distance from us* cope with the need to use nuclear fusion. If *even a very small fraction* of the funds directed to hydrogen fusion had ever been directed at learning more about air plasmas (and the basic science that explains them) we would surely now be in a much safer position with regard to man-made global warming than we currently are.

The experiments described by Priestley (16) imply that, to harness the chemical energy in the air, it is necessary to know now, as precisely as possible, where most of the difficulties lie. The important question is what can *realistically* be done to remedy the situation - bearing in mind our thermodynamic ignorance is very unlikely to be addressed soon (18).

11. Conclusions.

If we wish to avoid the worst consequences of global warming in forthcoming decades our best hope seems to be, among other technologies, learning how to prepare electrochemically contained air plasmas. If we could prepare and control them, we would be able to extract and use the *chemical* energy that is demonstrably present the air.

Occasional claimed simulations of ball lightning over the centuries have only twice been successful. These were in the mid-18th century, but they have never been replicated. We simply do not know how to prepare these plasmas under controlled conditions. A potentially less serious problem is that no valid theories exist that can deal quantitatively with ions in moist air. The only kind of modelling that seems feasible would be to ignore the chemistry and model the systems in terms of air resistance resulting from aerosols of different sizes at different relative humidities and different distances from the plasma surface.

New experimental approaches that should prove useful include new observations of earth-lights and of the plasmas that seem to inhabit most supercells - as well as those that probably inhabit the "hot towers" of hurricanes (paper in preparation). As much use as possible should obviously be made of modelling - but ignoring all the most relevant chemical mechanisms. It may be reasonable to hope that such work can somehow be supported - as it once was when public service was still widely valued.

Acknowledgements.

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