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The Missing Science of Ball Lightning

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Abstract --- One of the main problems in understanding ball lightning is that its properties, taken together, seem to be inconsistent with the laws of physics. This long-standing problem is completely eliminated once it is accepted that a plasma is both a phenomenon of physics and a mixture of chemicals. The processes occurring in the coolest regions surrounding a wet air-plasma will depend greatly on the temperature and on trace contaminants present in the air. This may explain why ball lightning usually forms unexpectedly and unreproducibly. Under appropriate chemical and physical conditions, a number of unusual nitrogen-oxidation reactions become possible. Phenomena result which are thermodynamically inevitable but, at first sight, totally unexpected. These can explain qualitatively all the seemingly impossible behaviour. To get much further, we need to be able to achieve, in the laboratory, conditions that will start the vital processes. We do not know how to do this and it is suggested that the reasons for our ignorance are complex and important. Considerable technological benefits might well be reaped from an ability to make ball lightning. The basic problems cast doubt on the mathematical modelling of any rate process involving the simultaneous presence of ions and saturated water vapour. If these problems were solved, light might well be thrown on other poorly understood phenomena as well, ranging all the way from star formation to the destructive power of some tornadoes and the existence of phenomena often classed as paranormal.

1 Introduction

Ball lightning normally appears during thundery weather as a free-floating globe of glowing gas, usually spherical, that can enter buildings in a variety of ways. It sometimes squeezes through spaces much smaller than its diameter and occasionally passes through closed windows which it may or may not damage. It frequently moves horizontally, at speeds between 0.1 and 10 ms^{-1}, a metre or so above the ground. Surprisingly little heat is usually sensed and contact with a ball may do no damage. Sometimes, however, considerable damage is done to objects contacted and acrid smells, white or blueish mists and bright sparks may escape from the balls. Colours and brightness vary greatly, as do sizes, which usually fall in the range 50--500 mm diameter. Usually the balls are observed for less than 50 seconds, although of roughly 1500 observations in Stakhanov's survey (1979), 70 apparently lasted more than 100 seconds. They can then either disappear quietly or explode. They have been reported rotating in the air, and rolling on or bouncing off surfaces, often damp ones. The balls can suddenly make dramatic changes in direction but they very rarely change significantly in either size or colour during their lifetime.

Clearly, any comprehensive explanation of the phenomenon needs to cover a wide variety of observational evidence. Ideally, it should explain all the properties and be at least physically reasonable and internally consistent. Until recently (Turner, 1994), all models have failed to satisfy at least one of these requirements. A significant difficulty is that the initial formation of a lightning ball is seldom seen well. A ball may form from a lightning channel in the sky, or where lightning strikes some solid on the earth; sometimes it simply grows out of and detaches itself from a solid. It has been seen to fall from the cloud base, or simply to appear out of thin air (Singer, 1971). Unfortunately, the

few detailed observations available do not offer useful guidance towards a reliable preparation method.

Two of the most characteristic features of ball lightning are the unpredictability of its behaviour and the variability of its properties. Nevertheless, there are sufficient qualitative similarities in the accepted properties to imply that ball lightning is either a single phenomenon or at least a family of related phenomena. In either case, several different forces must be involved in providing a stable structure and in explaining the accepted properties.

Detailed reports of the peculiar properties of ball lightning appear in the earliest examples of the scientific literature. The French physicist and meteorologist, Arago (1838), was one of the first to collect and re-publish some of the early observations and to use them in defining the more obvious difficulties. He found, as many have since, that the mere fact of publishing his views in reputable scientific circles supplied him with new information, both from fellow scientists and from the public. As a result, his early conclusion was reinforced that the phenomenon was "one of the most inexplicable problems within the range of physics" (Arago, 1855).

Nearly all the characteristic properties of ball lightning had been identified by the 1920s (Brand, 1923) but, as a set, they have remained difficult to reconcile with the known laws of physics (Singer, 1971; Charman, 1979; Stakhanov, 1979; Barry, 1980a; Stenhoff, 1999). Most attempts claiming a complete explanation of the phenomenon ignore certain of the reported observations or refuse to accept that they were attributable to ball lightning. Consequently, since at least the time of Arago, many scientists, aware of unexplained evidence, have been sceptical over the very existence of ball lightning as a physical entity.

It may come as a surprise to those who have not read many first-hand accounts, that the objective evidence seems quite clear concerning the great majority of properties, despite the fact that many of the witnesses are remembering an event from the past. It seems that many people can visualize and remember clearly what they actually saw; but often they cannot recollect what a scientist may later consider a very relevant fact. Clearly, there is a considerable risk that details could be inaccurate and the need to be very selective has long been recognized. Brand (1923), for example, made use of only 215 of the roughly 600 accounts available to him.

It is quite possible that Brand rejected some reports that contain important clues. Certainly, reports existed (mostly from the 19th century) of properties that he did not mention. However, his approach allowed the first statistical analysis of data on the quantifiable properties and greatly clarified the variety of things we need to explain. Most scientists who have read many of the better accounts and have examined the statistical data agree that there is probably only one basic phenomenon. There are now thousands of ball-lightning reports considered reliable enough to provide statistical data (see for example, Smirnov, 1987; Grigor'ev et al., 1989; Amirov and Bychkov, 1995; Smirnov, 2000). The properties covered include size, shape, lifetime, speed, estimated energy-content and colour. All the quantifiable properties vary over at least two orders of magnitude, but most of the mean values being obtained now are not greatly different from the values Brand (1923) obtained. Barry (1980b) collected data suggesting that energy densities can vary over a factor of 10^8. He and many other authors have tended to disbelieve the higher values (a model-dependent decision), but more recent analyses have supported some of them (Bychkov et al., 2002).

A ball-lightning sceptic would point out that several of the most puzzling claims do not lend

themselves to statistical analysis, and that these characteristics are the real challenge. They include motion possessing a component against the prevailing wind, abrupt changes in direction and vertical speed, a tendency to bounce, so-called "electrostatic guidance", and the various strange ways in which a ball may apparently choose to enter a room: for example, it may enter through a window whether the latter is open or not. Potentially, these observations now offer the prospect of teaching us most, and it is for this reason that what might be called a policy of deliberate gullibility has guided the author in recent years.

It is, of course, necessary to accept that some reports may be mistaken or fraudulent, but this can hardly be the case when the same phenomenon is described repeatedly. Also, many descriptions will contain some degree of interpretation by the witnesses. Two selections of fairly typical first-hand reports have been provided recently (Abrahamson et al., 2002; Turner, 2002). Some of these date from 250 years ago and have been re-published several times; others are very recent. Many more can be found in the various books and review articles on the subject. Brand (1923), in particular, and also Singer (1971) provide many examples.

2 Difficulties in Rationalizing Properties

The main problem in rationalizing the behaviour of ball lightning is to reconcile the reported properties with each other and with the known laws of physics. If one accepts all the evidence (Singer, 1971; Stakhanov, 1979; Turner, 1994, 1998, 2002), there are many interconnected difficulties; one of the most obvious is why a very hot plasma does not rise as a consequence of its buoyancy. Another is how it can remain the same shape, size and colour for several minutes. These difficulties have led to two quite different types of ball-lightning model, each of which tends to accept a different group of properties. They differ according to whether energy is assumed to have been provided at birth or whether it is fed to the ball continuously. Perhaps the most succinct summary of the difficulties was provided over twenty years ago by Stakhanov (1979). His conclusions have formed the basis for most of the author's arguments (Turner, 1994, 1998, 2002).

Stakhanov's main contributions followed the publication, in a popular Russian science journal in 1975, of a paper that ended with an appeal for information from any witnesses of the phenomenon. Within nine months or so, about fifteen hundred responses had been received. The results were compared with those of other surveys and published, together with a critical summary of important previous work on the subject, and Stakhanov's own model. This was based on his "cluster hypothesis", the reference being to clusters of water molecules around ions.

In addition to statistical evaluations which have since been extended by others, Stakhanov discussed a range of different kinds of report and his analysis included a consideration of the following aspects of ball lighting: the peculiar characteristics of its motion, the need for forces to balance buoyancy, the need for an effective surface-tension, the paucity of correlations between properties, the difficulties in reconciling energy content and lifetime, the inadequacies of then-current plasma models, weaknesses in then-current aerosol and chemical models, and the likely importance of ion hydration. After detailed consideration of these and related matters, including plasma instabilities and heat loss, Stakhanov came to much less dogmatic conclusions than have several later authors who cannot accept a continuous input of energy. His final conclusions were prefaced with a warning that "all the opinions on this subject belong to the realm of conjecture and are of a provisional nature." To the main question, "What is ball lightning?", he contrasted the two main views:

"First answer: Ball lightning is an autonomous body consisting of some sort of unstable matter, upon whose disintegration energy is released.

"Second answer: Ball lightning is a specific process, for example a particular form of gas discharge or wave-guide process .... from which it continuously derives its energy."

Stakhanov preferred the first alternative basically for three reasons:

"1. The nature of its movement (it moves as an independent, separate body not revealing any traces of channels connecting it with the surrounding medium).

"2. The existence of an interface between ball lightning and the surrounding medium which, apparently, has surface tension, indicates that the matter constituting the lightning forms a separate phase in the air.

"3. There is a correlation between the life span and size of a fire ball."

After considering the inevitability of ion hydration and outlining his cluster hypothesis, Stakhanov's book closed with this statement "..the matter constituting ball lightning consists of heavy positive and negative ions which, for some reason or other, in contrast to ordinary ions known to us, do not recombine. The cluster hypothesis of ball lightning is based on this fact."

If one accepts these conclusions, which stem logically from the empirical evidence used and the detailed arguments presented, one is left with three obvious questions:

1. Why do the heavy ions not recombine?
2. How can an apparently energetic body survive for more than a few seconds without an external energy supply?
3. Where does the surface tension come from?

It was a quite independent interest related to the first of these questions that initially drew the author's attention to Stakhanov's work, which led his then employer to obtain a translation of the 1979 book and which eventually led the author to his largely qualitative model for ball lightning. Unfortunately, the translation is no longer available---the company responsible for it suffered a major reorganization that included closing its research laboratories and libraries.

Most of the difficulties in attempting to answer these three questions, and in understanding ball lightning, stem from a single, basic, area of missing science. It may seem surprising that a whole area of classical physics and chemistry could have been ignored throughout most of the 20th century, but there are clear reasons for it.

To a chemist, it seems obvious that an air plasma must have chemical as well as physical properties. After the immense scientific effort that has gone into fusion research, one might have expected that we would know all we need to know about plasma containment. This is not the case, however, especially for an air plasma, because it is treated, like most other plasmas, exclusively as an assemblage of simple charged particles---the plasma's chemical properties are ignored. We do know a little about the chemical properties of the ions that must be present: specifically, we know the standard thermodynamic properties of many of them. For a high-temperature plasma, it is reasonable to assume that the most energetic charged species will all react rapidly with their neighbours in such a manner that the total free energy of the system is reduced. It turns out that thermodynamic tables contain just enough information to allow a fairly reliable answer to be given to one important question: What are the stablest ions released from a wet-air plasma? (Turner, 1994).

Towards its edge, an air plasma is only likely to contain the hydrated cations (positively charged) H_3O^+ and NO^+ and the hydrated anions (negatively charged) NO_2^- and NO_3^-. Other ions one might expect to find, such as OH^-, would be present in negligible quantities (Turner, 1994). The relative concentrations of the two cations will depend mainly on temperature and, to a lesser extent, on the quantity of water present locally. Very poor data are available for NO_3^-, but it is chemically obvious that the ratio of the two anions will be controlled by the nature and concentration of any air contaminants present. The important point is that the concentration of any kind of ion in normal air is always at least six orders of magnitude below that of any detectable contaminant. These contaminants could include aerosols or gases and behave as oxidizing agents, as reducing agents, as both, or as neither. Examples from each of these redox classes are, respectively, sulphuric-acid aerosols, methane, nitrous oxide, and silica.

If the chemistry of the ions affects either the stability or formation of ball lightning---as it seems it does---then the tremendous variations in the contaminants encountered in air immediately suggests why the formation of ball lightning is so unpredictable.

Once a blob of air plasma forms, it will immediately begin to cool, and first from the outside. The resulting chemical changes will also occur first at the edge of the blob. The most obvious fast reactions at lower temperatures in normal, humid, air are the progressive hydration of the ions. It transpires that there is a gradual change of predominant cation from hydrated NO^+ to hydrated H_3O^+ as the temperature drops below about 350^0C to near ambient temperatures (Turner, 1994) at which point all sorts of new reactions have become possible. We will postpone a discussion of these reactions until some more basic problems have been dealt with. These will show why an approach is needed that seems unnecessarily complicated.

3 Some Undeveloped Areas of Physics and Chemistry

The problems I am about to discuss are not the only ones that impede our understanding of ball lightning, but they are some of the most serious. It has been argued, by proponents of what they see as rival models, that the author's model cannot possibly be correct. They have claimed that no ions can persist where the model requires them. The arguments, in fact, represent one of the key mistakes that help make ball lightning seem so anomalous (see Appendix A and Turner, 2002). The problem is the use of a perfectly standard approximation on a system where it cannot possibly be valid: the approximation is that an ionic concentration can be substituted for an ionic activity in calculating a reaction rate.

Although often ignored, it is a fact that the activity and not the concentration of a dissolved chemical controls its thermodynamic and kinetic properties. For most normal solutes, however, the differences between activities and concentrations are small; thus the differences may be forgotten, particularly in kinetic studies, and one then tends to assume that concentrations are what really matters. But in a system containing wet vapour and ions, very large departures from any simple idealization are to be expected (Turner, 2002)---see Appendices A and B. Many of the most critical processes occurring near a ball lightning surface are therefore impossible to quantify. One unavoidable problem is that the chemical potential of an ion (its reactivity) depends on both its concentration and its local electrical environment.

One consequence of looking at the problem in this, apparently negative, way is that significant positive benefits result. Ball lightning and its close relatives can be seen as manifestations of a single set of processes that lead to properties which vary enormously, rather than as a range of separate phenomena that are almost equally difficult to explain individually. Though some authors prefer the latter choice (Stenhoff, 2001), the statistics on energy density (Barry, 1980b) are usually taken as indicative of a single phenomenon. Even the disagreements are understandable, however, once the basic problems are understood.

Perhaps more important, it seems possible to define several quite different areas of applied science where quantitative models are equally likely to prove misleading. Also, an appreciation of the basic nature of the difficulties suggests why scientists may have been too hasty in discounting some kinds of evidence. In a way, it is surprising how much can be deduced without a firm theoretical basis. However, it is necessary to understand why no theoretical basis exists. In order to see the relevance of the following arguments, it will be necessary to accept, for the time being, that both humid air and electric charges might be involved in providing stability to ball lightning.

Both technical and non-technical factors explain why our current understanding of the thermodynamic properties of ions in water vapour is so poor (Turner, 1998). Even if one became convinced that the theoretical problems could be overcome, experimental data for checking any resulting theory are lacking.

Although the discipline of electrochemistry in some respects represents a very successful collaboration between physicists and chemists, its development to date relates almost exclusively to the liquid phase. What goes on in a gas has been largely left to physicists, and they have been either unwilling to interest themselves in the peculiarities of wet electrolyte solutions or unable to see how to approach the problems.

Physicists and chemists tend to look at things in very different ways. One difference is the way they think about quantum mechanics. This stems from what they need to learn as students: physicists obviously need to learn quantum mechanics in a truly fundamental way, while chemistry courses usually teach little more than applications to atomic and molecular structure. A chemist will tend to take the inelegant complications of applied quantum mechanics for granted; thus he accepts the complexities of the Periodic Table as an unavoidable aspect of his work. By contrast, a physicist often tries to avoid dealing with such matters. This seems to have deterred good scientists from investigating areas that involve both chemistry and really messy physics. The situation is worse, of course, when the areas are experimentally difficult and of no obvious commercial interest.

I believe it is for these reasons that the basic problem of dealing with ions in wet vapours has been neglected. It was only because of the unusual research policies of my ex-employer that I was encouraged to investigate the problem. At the time, it was politically acceptable to run a company solely to look after what was perceived as the public interest. It was accepted that some research areas would inevitably progress very slowly but, so long as the work had an obvious long term goal, it would be given the necessary support. My employer was a large nationalized industry in the UK, the electric-power industry.

The first hints that there were significant gaps in classical physics came in September, 1969, when a large steam-turbine failed during over-speed testing. Parts of it literally went through the roof.

The failure was due to stress-corrosion cracking in a specific region of the turbine. Ionic contaminants carried over from the boiler into the steam were soon implicated, and our group was asked to recommend a way to modify the boiler-water chemistry to avoid future problems. This proved impossible, in part because we could not define how various important contaminants would partition into the steam. A very expensive engineering solution to the problem was eventually needed. In the following years, we experienced a number of other chemically related problems where the same lack of basic science limited what could be predicted.

These basic limitations are associated with the fact that all published mathematical treatments for electrolyte solutions assume the fluid to be incompressible. This is not true for steam and obviously not for steam near its critical point (374° C and 221 bar), where steam and water become indistinguishable and the fluid becomes infinitely compressible!---see Appendix B. With electrolyte solutions too, the compressibility is infinite at their critical points. Under these conditions dilute electrolyte solutions at equilibrium have been shown to be stratified (on earth). This is certainly not what one intuitively expects of a solution: a solution at equilibrium is normally taken to be homogenous by definition. In a gravitational field, however, this is not the case. There is no more reason to expect homogeneous solutions to result when electrolytes are dissolved in steam at sub-critical densities (Appendix B) and steam flowing round bends will be subject to large g-forces. As a result of such problems, we started to collaborate with the European Space Agency, ESA (Turner, 1983, 1988). We were able to complete three sounding-rocket experiments on super-critical salt solutions before privatization brought all long-term research by the UK electric-power industry to an end.

We were late-comers to low-gravity research, but did start in time to make a small (if ultimately fruitless) contribution to ESA's research plan for the 21st century (Walter, 1987). It became clear to me that there are, in fact, many areas of classical physics where the basic science is much less well understood than most physicists would like to believe. This knowledge reinforced my growing conviction that what we do not understand about vapour-phase electrochemistry is connected in some way with what we do not understand about ball lightning.

The basic problem in dealing with a compressible ionic solution is that the electric field near an ion is very strong, and the highly polar water molecules are strongly attracted into the field. The phenomenon is known as electrostriction and can result in enormously anomalous thermodynamic behaviour of ions when the solvent is sufficiently compressible (Turner, 1983). The most significant anomaly in the present context is that salts behave in qualitatively unexpected ways. Normally (say in water at 25°C) any solute, including a salt, will approach some sort of ideal behaviour as its concentration is reduced. By contrast, in a very compressible solvent the behaviour can become so abnormal that, instead of a thermodynamic property approaching a fixed value as concentrations are reduced, it can appear to be approaching an infinite value (see Appendix A). The reason that salts behave differently from non-electrolytes is that, in the limit of infinite dilution, they are fully dissociated into ions.

These effects have been demonstrated experimentally only in high-pressure steam above the critical point of water, where the solubilities of some salts are high enough to allow fairly accurate measurements. However, related problems would arise if one tried to study salts in steam below the critical point. In practice, even in zero gravity, one could probably not conduct a thermodynamically meaningful experiment on significantly sub-critical steam, because salt solubilities, even at fairly high

temperatures and pressures, are very small. It is currently impossible to define the thermodynamic properties of ions at infinite dilution in saturated water-vapour (Turner, 1990, 2002).

It may seem easy to dismiss these considerations as trivial thermodynamic inconveniences, but not if one needs usable thermodynamic or kinetic properties. A clearly defined standard state is necessary to define an activity (Appendix A). Since thermodynamics is really what drives any process, whether chemical or diffusional, activity gradients and not concentration gradients control rates. If activities cannot be defined, because the standard state cannot be, then it is impossible to model validly the behaviour of ionic impurities in any system involving saturated water-vapour. Neither thermodynamic states nor rate processes can be treated quantitatively---or rather, if they are, using currently available methods, they will only produce meaningless numbers and potentially misleading conclusions.

4 Available Information

In practice, the situation is not quite as hopeless as indicated above. When the author first read Stakhanov's (1979) book, he was intrigued to note that what Stakhanov called his cluster hypothesis was based on early studies of Kebarle. The starting points for Stakhanov's model were the gas-phase-hydration studies of ions that Kebarle and his colleagues began in the 1960s (see Kebarle, 1974). These led to the availability of standard-state thermodynamic data for the step-wise hydration of several simple ions. Stakhanov (1979) considered that these data could be directly relevant to ball lightning because they might be able to explain how ions could avoid combining in a few milliseconds.

The formation of these hydrate clusters could also help explain the strange lack of buoyancy exhibited by ball lightning, provided that the ball's average temperature did not exceed 500--700 K. Kebarle's hydration studies extend to the addition of no more than six water molecules for most ions. (surface wetting inside the mass spectrometer imposes this limit on the experiments). Stakhanov was impressed by some independent results of *in situ* mass-spectral measurements in the ionosphere. These provided direct evidence for the presence of heavily hydrated ion-clusters even though the water content there is minuscule. The atmosphere contains vastly more water vapour than the ionosphere, which suggests that much larger clusters might be stable near the earth's surface. An exploration of this implication seemed desirable.

The author had previously used Kebarle's data to develop estimation procedures for equilibria in high-temperature liquid water (Turner, 1981, and Appendix C). A thermodynamic cycle involving a single well characterized ion (H_3O^+) was used. The study supported Kebarle's suggestion that most of the trends in hydration enthalpies for a liquid-phase ion are established within the first couple of hydration layers (Kebarle, 1974). The initial relevance to the present problem was that the author had became convinced of the quantitative value of gas-phase-hydration data in bridging the gap between the solvent behaviour of liquid water and of water vapour. The reason for this confidence (outlined in Appendix C) was that the data on the gas-phase hydration, when combined with data covering other predictable influences, correctly predicted the thermodynamics of proton transfer from gas to liquid. The initial procedure was elaborate and specific to the proton, but a much simpler and more widely applicable one was developed. This extended to any ion, of any cluster size, whose hydration had been studied in the gas phase (Turner, 1994). Note that we are here dealing with standard-state properties for well defined systems, avoiding the theoretical problems mentioned earlier.

Stakhanov (1979) had illustrated his cluster hypothesis as applied to ball lightning by assuming that a lightning ball was filled with clusters of hydrated H_3O^+ and OH^- ions held together by an independently estimated surface-tension. This description seemed unsatisfactory to me because it assumed that a phase comprising water vapour plus the hydrated ions completely displaced the air inside the ball. Also, it seemed clear that clusters of much more than seven water molecules must exist. There is good evidence that some lightning balls have temperatures well over 1300K, so a ball much hotter than 700K could only be held down against the inevitable buoyancy force by such larger clusters. Further, because the cluster-forming reactions are very exothermic, cluster sizes will be extremely sensitive to temperature and clustering will only be important in the coolest regions near the surface of a ball (Turner, 1994).

If the centre of any lightning ball is an air plasma, it can be treated as a mixture of chemicals. As mentioned earlier, we needed to know what chemical species were likely to exist towards the edge of a ball after completion of all the rapid high-temperature reactions. Combining available (standard state) thermodynamic data with some estimated as above, it transpired that, above about 350^0C, the only ions finally expected are unhydrated and lightly hydrated NO^+, NO_2^- and NO_3^-. Below this temperature, ion hydrates become increasingly important and hydrates of H_3O^+ gradually replace those of NO^+ (Turner, 1994). At 25^0C, the same thermodynamic data predict that transformation of NO^+ to H_3O^+ cannot take place in the gas phase until the ion is solvated by four water molecules. This is precisely what Puckett and Teague (1971) had concluded from their rate studies, so that there was independent confirmation that the thermodynamic estimation procedure can make valid predictions.

Note that the kinetic experiments were conducted using ion-containing mixtures at finite concentrations. The correct prediction of the kinetic behaviour on the basis of standard-state values suggests that the (potentially large) differences in reaction free-energies between real and standard-state conditions were smaller than those calculated for the standard state. This is normally the case so that, in this sense, the assumption that standard-state thermodynamic properties have a real meaning is justified, even when we do not know how to define them in terms of directly measurable properties. Clearly, however, we can only expect useful predictions when standard free-energy differences are large. Because of the logarithmic relation between activities and free-energy differences (see Appendix A), the kinetic problems are much more serious than the thermodynamic limitations. Fortunately, the rates of ionic reactions are normally diffusion-controlled (very fast), and the various hydrates will compete for the water molecules available locally, their relative concentrations being fixed by the local thermodynamic conditions.

This is not the case for the various uncharged molecules produced in an air plasma. Their decomposition to more stable species can be slow, with rates that can be catalysed by traces of contaminants whose concentrations will greatly exceed those of ions. They can act directly as oxidizing or reducing agents or simply as catalysts for the decomposition of such metastable molecules as ozone or nitrogen oxides. Thus the relative concentrations of many important species, including NO_2^- and NO_3^-, will depend on numerous processes that are unpredictable for moist and arbitrarily contaminated air.

As a result, little reproducibility in the chemistry at the edge of a lightning ball can normally be expected. This fact probably explains (at a molecular level) the general lack of reproducibility not only in the formation of lightning balls but also in air breakdown generally. Quite possibly, the lifetime of an established lightning ball is determined by the length of time the internal plasma processes can

themselves maintain an appropriate chemical environment locally.

More definitely, NO_2^- and its hydrates will greatly predominate over any form of OH^- (Turner, 1994). This conclusion provided a very plausible explanation for the slow charge-neutralization which any model must provide if it relies, even partly, on stored energy. Stakhanov (1979) had speculated that some unidentified process greatly slows down the recombination of the ions he assumed to be present: H_3O^+ and OH^- hydrates. In normal solutions, this reaction is one of the fastest known. On the other hand, a charge-neutralization process involving the vastly more abundant nitrite ion provides very plausible thermochemical reasons for anticipating a fairly slow reaction between ion clusters (Turner, 1994).

A prediction for the thermodynamics of charge neutralization of nitrite ions was initially more surprising. It was also even more significant, in part because it helped explain the slow charge-neutralization just referred to and in part because it led to an answer to the second and third questions raised by Stakhanov's analysis. The reaction can conveniently be approximated thus:

$$H_3O^+.nH_2O + NO_2^-.nH_2O = HNO_2 + (2n+1)H_2O \qquad (1)$$

Although it is quite possible that n is not the same for both ions, our existing knowledge does not allow this possibility to be investigated. The estimated thermodynamic consequences of reaction 1 (for the ions in their standard states and at 25° C) are shown in Table 1 (Turner, 1994).

Table 1 near here

ΔH^o, ΔS^o and ΔG^o are respectively the standard enthalpy, entropy and Gibbs free-energy for the processes. They are related by the thermodynamic identity $\Delta G^o = \Delta H^o - T\Delta S^o$. The standard enthalpy, ΔH^o, can be thought of as the energy that would be released as heat during reaction 1 if each component represented in the equation were present in its standard state. Though this is a hypothetical concept, what matters is the sign and magnitude. All the values listed are large and for n=0, the heat given out is very large. For n=15, the heat taken in from the surroundings is also very large. In the first case, the enthalpy is helping the reaction proceed from left to right, while for n=15 it is pushing the reaction to the left.

What actually determines whether a reaction will go to the left or the right is not the sign of the enthalpy but that of the free energy, ΔG^o. Table 1 shows that, for all the listed values of n, the reaction will go to the right because the free energy is negative. What allows the effect of the unfavourable enthalpy for n=15 to be overridden is the huge positive entropy contribution. A positive entropy is a measure of the extra freedom that the molecules in the system gain when the reaction occurs. The reaction resembles the evaporation of water, which also has a positive standard enthalpy and positive standard entropy: that is why water will evaporate from your hand while cooling it at the same time. The reactions represented by the entries to the right of Table 1 proceed mainly because water molecules are released.

Essentially then, while the charge-neutralization reaction of unhydrated ions is (as normal) strongly exothermic, that of the most heavily hydrated ions of Table 1 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 whereas the heavily hydrated ions react because of entropy production. The necessary heat must be found from the surroundings. The surroundings are therefore cooled locally when the heavily hydrated ions combine. These conclusions seem unavoidable. They are crucial to the electrochemical model for ball lightning.

The calculations are approximate but the magnitudes of the predicted effects are so large that they can hardly be grossly in error. The missing electrochemistry means that no realistic estimates of the relevant kinetics can be made. The important thing in the present context is that, if the ions can survive long enough to become hydrated by more than five or six water molecules, their subsequent neutralization should significantly cool the air locally. Furthermore, there exist a number of thermodynamically allowed reaction-paths that can lead to the spontaneous formation of hydrated ions from metastable molecules at low temperatures (Turner, 1994). It should be pointed out that any ion having similar thermodynamic properties to nitrite could behave in the same way; however, nitrite is the only known ion likely to be present in pure air that could produce thermochemical refrigeration.

Water droplets close to the plasma will tend to evaporate, whereas those further away will have a tendency to condense if the humidity is great enough and the temperature sufficiently low. In this case, water droplets located at a specific distance from the plasma would be in a state of kinetic equilibrium. As long as the relevant physical and chemical conditions were correct and sufficiently stable, these steady-state conditions could, once established, last indefinitely. Correct conditions might include optimal values of the space-charge-density in the air, the local (time-dependent) electric field, the local relative humidity and humidity gradient plus the nature and concentration of contaminant molecules and aerosols in the atmosphere (Turner, 1998, 2002). Generally we know none of these.

5 Structure and Related Properties of Ball Lightning

The author believes that, if the local physics and chemistry allow it, chemically induced refrigeration inevitably occurs around a wet air-plasma and that this process can stabilize droplets on the surface of a lightning ball. The droplets restrict the inflow of air needed for nitrogen oxidation to nitric-acid droplets and the inflow holds the ball together (Turner, 1994). This inward force (opposed by electrostatic and thermal forces) is what provides a ball with an effective surface tension. Furthermore, the spontaneous formation of ions near the surface of a ball can stabilize it to such an extent that it can bounce and squeeze through small holes with a greater tendency to resist collapse than a soap bubble. Thus, predictable electrochemical phenomena and their consequences can answer qualitatively the second and third questions raised by Stakhanov's analysis and can explain many of the other apparent anomalies in the properties of ball lightning. Once it is realized that gradients in temperature, humidity and electric field can modify the symmetry of the structure, all the other apparent anomalies disappear (Turner, 1998, 2002).

Despite thousands of observations that have allowed the ranges of some properties of ball lightning to be clearly defined, certain other properties are not amenable to statistical analysis. These may be too qualitative, such as aspects of a ball's motion (discussed in Section 7), or of a kind where reliable numerical estimates have proved impossible to make. It is convenient to discuss the structural aspects of a lightning ball separately from its size, energy content and motion; at least in principle, the separation can help differentiate those problems that need addressing *before* we can be confident of making ball lightning from those that we *might* be able to leave until afterwards.

From a structural point of view, the most important missing property is a ball's surface-charge. The problem here is that there is no independent way of deciding what contribution to the forces moving a specific ball arose from electrostatic influences (see Section 7). Clearly, the charge on the water clusters surrounding a lightning ball could have a large influence on its stability. The author has not changed his original view that most balls are positively charged (Turner, 1994), but whether a large net positive charge is essential at some stage in its formation is still not known. (The plasma surface will have an electrical double-layer and this might allow stable structures with a minimal net positive charge).

The structure of a somewhat idealized lightning ball is shown in Figure 1. Next to the hot central plasma is the intermediate zone, I, where most of the ions recombine and metastable molecules are produced. Further out is the hydration zone, H, where cooling allows the hydration of any remaining ions and the formation of pairs of new cluster-ions from some of the metastable species made in the I zone. Which reactions are most important we do not know, as several of the reactions between likely metastable plasma products are favoured thermodynamically (Turner, 1994). The reaction products are, of course, the cluster ions already considered. Ions formed in this way can provide stability for balls that depart significantly from spherical symmetry (Turner, 1994). Both the I and H zones liberate heat. Outside the hydration zone is the refrigeration zone, R, where the chemical, electrostatic and hydrodynamic forces meet and impose a stable shape on the ball. The refrigeration process (reaction 1) leads to locally elevated levels of water vapour and consequently to any surplus ions being heavily hydrated. Witnesses sometimes comment that a specific lightning-ball was transparent, and sometimes that it appeared cloudy. This suggests that water clusters, although only near the surface, can sometimes be large enough to be visible. However, the droplets need not be visible for the total ball-weight to balance any conceivable buoyancy force whatever the plasma temperature (Turner, 1994).

Fig 1 near here

The cross section illustrated in Figure 1 is purely schematic. The outer zones may be very thin. That the division between the H and R zones can be sharply defined is suggested by the kind of damage a lightning ball sometimes does when passing through glass: either there is a clean fracture and ejection of a disc, or the glass is crushed to powder (Turner 1997, 2002). Often, however, the temperature gradient may be too low to cause any damage. On the basis of dozens of witnessed accounts of ball passage through windows (Grigor'ev et al., 1992), it seems that the three outer zones can be very narrow, because the reported sizes of the balls are often about the same size as the holes produced. This was also true of the oldest known laboratory simulation of ball lightning, which was made (by accident) in 1757 (Turner, 2002). In this case, a broken disc was removed in one experiment and powdered glass fell out in the second. After these two experiments all attempts to repeat the findings failed.

The ball illustrated is assumed to be suspended in a thunderstorm (dc) field of moderate magnitude. A net positive charge on the surface of the ball is assumed, since this is the sign of the space charge during a thunderstorm. Furthermore, there is some evidence in favour of positively charged balls and none supporting negatively charged ones. Thus an excess of cations is indicated, and these are expected to be concentrated predominantly at the top of the ball (Turner, 1994). In a normal thunderstorm field, positive current passes from the earth to the clouds. In the air outside the ball, the

current is carried almost equally by cations travelling upwards and anions moving downwards. However, inside a hot plasma, most of the current will be carried by electrons which will, like the anions outside the ball, travel downwards. Thus cations are preferentially neutralized at the bottom because of the asymmetric mode of current flow inside the ball. If the ions on the surface are very heavily hydrated, the ball will become top heavy and a slow rotation can result. According to Stakhanov (1979), a slow rotation characterizes about 30% of ball-lightning observations.

If local currents are strongly concentrated as a result of issuing from rough surfaces or sharp points or edges, rotation may be replaced by an inertial force towards the source of the current (Turner 1998, 2002). This could easily be mistaken for electrostatic attraction. Faraday believed that ball lightning exists but did not believe it to be an electrical phenomenon. This was probably because what was then called "electrostatic guidance" would have been seen as inconsistent with the laws of electrostatics.

The model requires an internal pressure somewhat lower than atmospheric to maintain an inflow of air, and this is maintained by the production of nitric-acid droplets. It was originally suggested (Turner 1994) that the magnitude of the pressure differential might approach that involved in holding a child's balloon in shape. Many reports describe the motion of ball lightning as similar to that of a child's balloon. Related arguments used recently (Turner, 2002) imply a much smaller pressure-difference. The analogy with a soap bubble is better. Because the "surface" of a lightning ball is permeable to the gases whose electrochemistry forms it, it can, under the right conditions, be repaired easily and be much more stable than a soap bubble of equivalent surface-tension. Thus lightning balls have repeatedly been seen to split up into smaller balls, whereas soap bubbles do not behave in that way.

6 Energy Supply

Many models attribute the stability of lightning balls to a light-weight network of aerosols (Stakhanov, 1979; Smirnov, 1987, 2000; Bychkov, 1994, 2002; Abrahamson and Dinniss, 2000; Abrahamson , 2002). I can readily accept that such models may describe the earliest stages in the formation of lightning balls, but I cannot accept claims by some authors that such models give a complete explanation of the behaviour of ball lightning (Turner, 2001). For example, the models cannot account for a ball lasting for at least three minutes and then having energy left to explode with the sound of a cannon (Brand, 1923; Singer, 1971; Turner, 2002). Nor can they explain how a ball can pass through a window without damaging it. More important in the present context, rejecting the possibility that energy can be continuously supplied to a ball seems to result in so-called "explanations" of energy content that are based more on hope than anything else.

If, on the other hand, one is prepared to accept an external supply of energy, at least for long-lived balls and those that can pass through windows, then the concept of an energy density loses its straightforward meaning. It can still be a useful concept but it can only mean the energy density that the ball would have if it were not being continuously supplied with energy. One of the reasons that Barry (1980b) and those of his persuasion cannot accept energy densities much over 2×10^8 Jm^{-3} is that this is the limit defined by a fully ionized plasma. But values much higher than this have been observed (Bychkov et al., 2002).

The question of energy supply to a lightning ball is largely one of energy conversion since, in a

thermodynamic sense, there is plenty of energy available---arising ultimately from the sun's power to separate electrical charges and to maintain a chemically metastable state in the air. The century over which vapour-phase electrochemistry has been neglected seems most wasted here: we know virtually nothing except that electrochemical processes can (in a liquid solution sometimes) result in very efficient energy conversion. Some processes by which energy could be supplied to a ball have received attention recently and it seems very likely that both the discontinuous-current route of Lowke (1996, 2001) and a maser route, perhaps of the type discussed by Handel (1997) and Leitner and Handel (1994, 2001), have a part to play.

Lowke's explanation for the powering of ball lightning seems perfectly reasonable, in particular as a basis for explaining how some balls can do damage that is not readily explicable by internal-energy models such as those of Bychkov (2002) and Abrahamson (2002). Well witnessed events exist, such as that reported by Gerasimenko (1956), where the damage would undoubtedly have been attributed to normal lightning were it not for the fact that there were 11 independent witnesses to the involvement of ball lightning (Turner, 2002). The model (Lowke, 1996, 2001) is perfectly consistent with the author's electrochemical model, but it is desirable to elaborate here on one general aspect of the physics of electrical conductance in a wet vapour.

In the atmosphere, the currents of the global circuit, which maintain the charge on the earth, must often be inhomogeneous although, for convenience, the opposite is usually assumed. Inhomogeneous currents are obvious in the case of lightning, including its leader strokes. Invisible currents must also be inhomogeneous during a storm where they are being emitted as point discharges from irregular surfaces. Even in fair weather, currents cannot be homogenous on a molecular scale because ion production is localized and the mobilities of the ions actually found in air samples vary greatly (see, for example Gringel et al., 1986).

One might argue, on the basis of well understood low-pressure phenomena (Alfvén, 1950, 1981), that larger-scale inhomogeneous currents in the atmosphere result from free electrons magnetically concentrated into current filaments, and this can obviously be relevant in lightning strokes. However, at atmospheric pressure and fields smaller than the breakdown value, free electrons contribute very little to the conductance because the mean-free-path is so small. Thus magnetic influences probably contribute rather little to filament formation in normal air. It seems that some very peculiar observations made during and prior to one of the low gravity experiments referred to earlier may be relevant in this connection.

At mean fluid-densities more than 200 times greater than those of air, indirect evidence was accidentally obtained for what seem to be current filaments. Rapidly fluctuating currents, indicative of electrical breakdown, were observed in solutions at a mean ac field of less than 5 Vm^{-1} (Turner, 1988). This is a ridiculously low field-strength for electrical breakdown. The relevant experiments involved measuring the conductance of near-critical solutions of sodium chloride. The peculiar effects appeared while re-heating cells in which salt had temporally precipitated out. It seems that the thermal effects associated with ion hydration and phase changes resulted in extremely non-homogeneous and rapidly changing currents. The densities of the solutions, roughly one third that of room-temperature water, as well as the low field-strength, imply that the current was conducted entirely by ions.

Thus it seems that something like localized current-filaments can be produced in saturated water-vapour in the absence of significant magnetic fields. These filaments would, of course, be

invisible. One cannot help wondering whether some of the difficulties in explaining lightning initiation (usually assumed to start from bare electrons produced, for example, by cosmic rays) might not be removed by the inclusion of a mechanism that includes electron attachment, hydration, and field-induced dehydration processes. Similar processes could also be important in ball-lightning formation and in the supply of energy to a lightning ball.

The author's model allows for a continuous input of energy to a lightning ball and, like the models of Lowke (1996, 2001) and Handel (1997), does this without requiring any visible connection to its energy source. One conclusion of the author's first paper on ball lightning (Turner, 1994) was that ball lightning is a thermochemical heat-pump powered by the electric field of a thunderstorm. Both the electrical and chemical sources of energy ultimately come from the sun and the energy can probably be supplied, on different occasions, from any or all of the appropriate forms (Turner, 1994, 2002). It should be noted that the sun's energy maintains the existence of free oxygen and nitrogen in the atmosphere. Below about 15^0C, these two gases in the presence of water are unstable with respect to a nitric-acid solution (Turner, 1998). This is why chemical energy can, in principle, be extracted from the air. (Of course, the nitric acid is not stable either; it can react with any amine or other base in the air or with the components of rock, soil or organic matter once it contacts them).

Thus any wet air-plasma that can be contained and cooled sufficiently at its outer surface could act effectively as a catalyst in the energy-extraction process. Thunderclouds discharge through visible lightning-strikes and, much more effectively, through silent discharges (Mason, 1971). The fainter precursors to an actual stroke and inter-cloud discharges are electrically noisy phenomena and plasmas are capable of absorbing electrical energy over a very wide frequency-range (Stenhoff, 1999). Furthermore, it seems certain that low-frequency electromagnetic radiation fed by some kind of population inversion must be involved in the passage of a lightning ball through a closed window (Handel and Leitner, 1994, 2001; Handel, 1997; Turner, 1998, 2002). There appear to be many ways in which energy can be fed to the plasma of a lightning ball. An observation that suggests a possible way for someone suitably qualified to help advance our ideas on this matter is discussed in Section 8.

7 Movement and Electrostatic Charge

Calling a lightning ball a thermochemical heat-pump seems fully justified, but the definition is incomplete because it says nothing about the strange ways in which ball lightning moves. To explain these, one must consider the electrochemical and hydrodynamic forces responsible for a ball's stability. Bouncing is fairly easy to explain because the surface deformation just pushes a layer of droplets into a hotter region, providing an outward force to restore the symmetry. Electrostatic as well as thermal forces are probably involved.

The wide variety of observed properties suggests that there are at least four different types of force capable of controlling the motion of an established ball (as a macroscopic unit). In a vertical direction, these are the buoyancy force, F_b, the total weight of the droplets, F_w, an electrostatic force, F_e (which could be in either direction) and a force induced by a local electric current which can produce a reactive force, F_r. This last force is probably what makes the motion of some lightning balls seem so very strange, and the force responsible for what used to be called "electrostatic guidance".

One of the best examples of such guidance was provided in the almost unbelievably detailed description given by Dmitriev (1967) and re-published several times since. The ball's motion was

clearly under the influence of a line of wet logs floating in a river and attached to the bank near to Dmitriev's position. As a consequence of the river's flow, the logs formed a gentle curve which the ball followed precisely while apparently ignoring the influence of a slight cross-wind. Later, Dmitriev (1969)---making the usual assumption of a perfectly conducting earth and implicitly neglecting any space charge---assumed that electrostatic attraction to the logs was being exactly balanced by the buoyancy force. Since he could estimate this quite reliably, he calculated the charge he thought must have been on the ball.

The assumptions made, however, do not reflect conditions that normally apply during a thunderstorm when a large positive space-charge and a positively charged earth might be expected. If, however, one accepts the author's model which allows the weight of a positively charged ball, balanced by electrostatic repulsion, to determine the height at which it floats, then the explanation of the horizontal guidance observed by Dmitriev has to be different. The present author reasoned that the apparent attraction was really the result of localized currents issuing from the logs which, due to charge neutralization on the surface facing them (see above), resulted in a smaller resistance to the air inflow in that direction and a reactive force on the ball towards the logs (Turner, 1998). The ball would behave rather like a jet engine except that, since the gas flow is inwards, the force on the ball will be towards the effective nozzle. The reactive force would hold the ball firmly a fixed distance from the source of the current because of electrostatic repulsion between logs and ball. The suggestion is consistent with the fact that guidance was only evident over the line of logs and that, when the river bank was reached, the ball wandered about, apparently randomly. Similar reactive forces acting on ball lightning are implied also by other evidence (Turner, 1989, 2002).

8 Size

We now turn to the range of sizes observed for ball lightning. In my first ball-lightning paper (Turner, 1994), I only attempted to explain why lightning balls so rarely change in size after they have been formed. The explanation is that, as the external energy supply is either decreased or increased, the chemical processes in the central plasma and in the refrigeration zone parallel one another. Thus we would expect an increase in temperature gradient as energy is added but not necessarily an increase in overall size. I also expressed the view that, since so few aspects of the phenomenon can be quantified, it was impossible to use the model to predict the range of sizes observed for lightning balls. I am now less pessimistic about circumventing this problem (Turner, 2002).

In previous illustrative calculations (Turner, 1994), it was assumed that established balls can be surrounded by clusters whose sizes are close to the visibility limit and whose total droplet-weight balances the buoyancy force. Calculations, using droplet radii of 0.2 and 1.0 m, showed that a gravitationally balanced ball could easily yield an effective surface-tension consistent with the strange motion often reported for lightning balls. Droplets approaching a size where they are visible are appropriate for an established ball. However, at the beginning of a ball's life, the droplets surrounding a plasma are likely to be much smaller.If we accept the author's explanation for the fixed size of an established ball (parallel rate changes in the plasma and in the refrigeration zone), then the size must have been established in the very early stages of the ball's life. Other assumptions are, therefore, needed to predict a ball's size. Presumably, a single particle suspended in the air could provide a nucleus for electrical breakdown, but what happens next? Usually, at least while a ball is stably floating near the earth, the electrostatic force is repulsive between earth and ball, so that near the

ground there are two upward and two downward forces such that

$$F_b + F_e = F_w + F_r \qquad (2)$$

all these terms being positive. There is fairly clear evidence that each term can sometimes exert a major influence. An obvious difficulty in trying to calculate many properties of ball lightning is that there is seldom any way of distinguishing the causes of the total force in either direction.

One needs a set of mutually consistent assumptions or approximations. Of the terms in equation 2, the one whose range can be estimated most accurately is the buoyancy force, which depends only on the volume ($4\pi r_b^3/3$) and on the density difference between the air and the plasma ($\rho_a - \rho_p$). A single ball-radius, r_b, the visible plasma radius, is assumed. The ball weight, can be expressed in terms of the number (n_d) and radius (r_d) of the surrounding droplets. Neither the electrostatic force nor the reactive force will be effective for a ball suspended well away from the earth and, since their effects cannot be distinguished observationally, we shall only consider balls formed either in the clouds or in mid air, well above the ground. This means that we will be considering balls formed rather gently.

As in the earlier calculations, we assume that the hydrodynamic force acting on each droplet and holding it in place against the outward-directed thermal forces are given by Stokes' law,

$$f_h = 6\pi r_d \eta u \qquad (3)$$

where is the viscosity of the air and u is the inward velocity. If we knew enough about the details of the oxidation processes involved, the inward velocity for a spherically symmetrical flow might be independently predictable, but we do not.

It seems that u can vary greatly with direction in an established ball, sometimes being orders of magnitude higher in one direction than in directions normal to it (Turner, 2002). Impossibly high reaction-rates are implied if one assumes u to be radially symmetrical and equal to the highest observed ball-velocities. Previous calculations (Turner, 1994) have suggested that a very small radial velocity is needed to provide a healthy "surface tension"; and before the ion-production and refrigeration rates start to speed up as the plasma heats up, u could not possibly be high. We accept that u is unknown and that we will need to assign it a range of what seem realistic values appropriate to a ball's early life.

For a spherically symmetrical ball, the total inward pressure being ÄP and the effective surface tension being , we have

$$\Delta P = 1.5\eta r_d n_d u / r_b^2 = 2\sigma / r_b \qquad (4)$$

Several estimates have been made of σ (Stakhanov, 1979; Smirnov, 1987; Turner, 1994). We shall adopt Stakhanov's lower estimate because this is the lowest and therefore most appropriate to a low flow-rate.

Ball-lightning sizes are known to vary widely and so are the concentrations of Aitken nuclei (small condensation nuclei) around which droplets normally condense. Thus it seems reasonable to

consider the possibility that there might be some correlation between the two. Aerosols of the types envisioned by Bychkov (2002) or by Abrahamson (2002) might well control the developing ball in its early stages, i. e. up to the stage where its size can be controlled by electrochemical forces. However, there seems no way of quantifying their role here.

We assume that all the nuclei needed to stabilize the surface of a ball initially are derived from those Aitken nuclei originally inside the eventual radius. This is clearly arbitrary and may not be realistic, but it avoids introducing yet another unknown. With this assumption and defining the concentration of Aitken nuclei in the air as c, the above relationships can be combined to yield

$$r_b^2 = \frac{3^{2/3}(4\pi cB)^{1/3}}{4\pi cHu} \qquad (5)$$

B is the function $\rho_w/(\rho_a - \rho_p)$ which contributes to the buoyancy force and H, defined as $0.75\eta/\sigma$, controls the hydrodynamic force. ρ_w , ρ_a and ρ_p are respectively the densities of water, air and the plasma. B contains one temperature-dependant term, the plasma density. The value assumed for B is 1.72×10^3, which corresponds to an average plasma-temperature of 600K. Thus it is being assumed that the ball size is fixed by a balance of the forces considered above when the plasma temperature first reaches 600 K. After that, control of the size is assumed to switch to the chemical reactions which, as seen earlier, can apparently control heating and cooling processes so that the radius remains constant. Since the temperature-dependent term occurs in the ball-radius expression only as the sixth power, the degree of arbitrariness over the choice of switch-over temperature is relatively small.

The assumed values for η and σ are, respectively, 1.86×10^{-5} Nsm^{-2} and 10^{-3} Nm^{-1}. The range of c values was selected from those quoted by Mason (1971). They went from claims of zero to a maximum (city) concentration of 4.0×10^{12} m^{-3}. The latter was taken as the highest reasonable value while the average concentration over the ocean (9.4×10^8 m^{-3}) was taken as a realistic minimum. Table 2 shows radii calculated from equation 5 for the above range of c values and a range of u values.

Table 2 about here

The fact that realistic (low) inward velocities predict balls of the observed size-range suggests that the size is largely determined by the aerosol content of the air. We almost never know the dust concentration of the air, but the impression provided from the locations of some ball-lightning sightings (see for example the collections of Singer, 1971, and of Corliss, 1982, 1986) is that really large balls are reported less frequently from very polluted than from very clean areas such as over the ocean.

The low velocities required to balance the radial forces during the formation stages would not necessarily change much once the droplet sizes and concentrations come under the control of chemical processes. There seems no way at present of predicting such velocities. However, inflow velocities are relevant to the behaviour sometimes exhibited by fabrics when lightning balls pass close to them. Typically a curtain, for example, will be attracted to a passing ball. Either rapidly inflowing air or electrostatic attraction could explain this. On the other hand, what can only be electrostatic repulsion has occasionally been reported also. Brand (1923), among others, has quoted an example from 1791 in which a lightning ball formed on the ground a few metres from a young girl and then made its way up her skirt, causing it to open out like an umbrella. The obvious explanation for the skirt's behaviour is

that electrostatic repulsion between it and the ball greatly exceeded the inward force arising from the air flow. Of course, this does not mean that the radial flow-rate into established balls is always small. There is plenty of indirect evidence that the inflow can be very large, at least in one direction (Turner, 2002). Perhaps the clearest evidence comes from accounts of lightning balls observed from the passenger windows of aircraft. These will sometimes remain above the aircraft's wings for several seconds. This is readily explained only if air is flowing into the front of the ball at about the speed of the plane.

One last calculation relates to the suggestion that a lightning ball could be considered as a hole in the positive space-charge beneath a thunderstorm (Turner, 1994). Except for the direction of the force, electrostatics does not distinguish between a small spherical hole in a large volume of space charge and a similarly sized charged sphere in a space otherwise free of charges. The high plasma-conductivity needed for this model to be realistic means that the temperature has to be very much higher than that considered above. It is therefore more likely to be applicable to the violent ways in which lightning balls can form than to the gentle ones considered so far.

The simplest approach to quantifying the effect is to estimate the maximum likely inward pressure difference, ΔP_m, from the maximum likely field, E_m, taking this to be the measured break-down field for clean air (3×10^6 Vm^{-1}). The electrostatic force per unit area across the charged "surface" (the mechanical force on a charged condenser-plate) will be

$$\Delta P_m = E_m^2 / 72\pi 10^9 \qquad (6)$$

which represents a maximum inward pressure-difference of 4×10^{-4} bar. The pressure difference given by equation 4, for an "average" ball of radius 230 mm (Smirnov, 2000), would be 1.7×10^{-7} bar if we assumed the same surface-tension as before. ΔP_m is two thousand times larger, which implies a significant stabilizing force from the space charge even at more realistic (lower) charge-densities. It seems quite possible that some lightning balls could lose their structural integrity eventually because the space charge has dropped so much that the ball's surface-charge-density is too low to provide electrostatic rigidity.

A significant space-charge could help hold together the specific kinds of aerosol structure favoured by several groups (see Smirnov, 2000; Abrahamson, 2002; Bychkov, 2002), provided that their internal temperatures were sufficiently high. It does not seem that it could provide the main inward force for an established ball, however, because the charge density in the air is likely to change over the lifetime of a ball, and it is very rare for a ball to change in size, as it would have to in response to such a change. Space-charge stabilization could be very relevant to the model of Abrahamson and Dinnis (2000), at least during the formation stages. This model describes the more violent formation of ball lightning following a normal lightning-strike. In this case, the electrons would go rapidly to earth and inevitably leave behind a positive space-charge that could provide stability at a crucial stage in a ball's formation.

8 Towards Laboratory Ball-Lightning

Ball lightning is obviously a multi-faceted phenomenon, but scientists are now very specialized. This poses a rather general kind of problem discussed in more detail elsewhere (Turner,

2002). Unless we can pay more attention to disciplines remote from our own, a realistic laboratory simulation of ball lightning could continue to elude us, as it has done since the early attempts of Benjamin Franklin and Joseph Priestley (Priestley, 1781). They and other contemporary scientists failed to duplicate the 1757 simulations that John Arden and William Constable had produced, inside Leyden jars, by accident. Until we can make fully characteristic ball-lightning and study it in the laboratory, there will probably continue to be arguments over what, exactly, it is.

Before we can properly characterize ball lightning, we have to make and control it. This requires at least a willingness to consider using any or all of the relevant facts available.

The main fact is that ball lightning can form in six fairly distinct ways. It can sometimes develop from the rare spheroidal form of St. Elmo's fire. This is the method that the present author has so far felt might be pursued most profitably. Balls formed indoors in this way do not usually seem to be very powerful, and this is an advantage from a safety viewpoint. Rather few have given much direct indication of their power and, even then, the evidence is not always straightforwardly interpreted.

One example, about the size of a golf ball, after detaching itself from a light fitting, moved across a room towards a television set and then blew the latter's 2 A fuse (Emsley, 1993). Remarkably, a somewhat smaller lightning-ball had appeared in roughly the same part of the same room about a year previously. A storm had again been in progress and this ball had ended its life in precisely the same way. Unfortunately, without knowing all the relevant details of Dr. Emsley's house and of the two storms involved, we cannot know what factors led to repeat appearances of the phenomenon.

Since neither ball appeared to have discharged itself directly through the set, the fuse must have blown because of induced currents. Television engineers have suggested to the author that the overloading would most likely have originated in the line-scanning circuitry. This could have drawn the required fusing current from the mains, and so no simple inference can be drawn about the energy flow through the balls from the fact that fuses were blown. However, an interested electronics engineer, with time to spare for experimentation, might be able to deduce valuable information regarding the spectrum of the radio emission from the ball. This could be relevant to the matter of energy input discussed in Section 6. The components of the line-driver circuit that is likely to have been involved are, apparently, fairly standard.

Ball lightning can also form at the site of an ordinary lightning strike or some metres away from it. It can be formed from bead lightning, which itself is a rare phenomenon remaining in the air after the passage of an ordinary lightning-bolt. Bead lightning occasionally forms as a string of spheres or ellipsoids along the path previously used by the return stroke of a lightning discharge. Most often, it expires without moving far, but sometimes its beads are stable enough to be seen falling slowly to earth. Lighting balls can form at one of the sharp angles that lead to the description of ordinary lightning as zig-zag lightning; and it can apparently form out of thin air when a thunderstorm is in the vicinity. Sometimes Nature seems able to produce lightning balls of remarkable uniformity (Turner, 1996, 1998) but this is rare and, on these occasions, she seems to prefer to do it up in the clouds where no one can see what is going on.

Few of these natural methods of formation seem more promising for adaption to laboratory use than the St.-Elmo's-fire method but, of these, the approach investigated by Abrahamson and Dinniss (2000) could well prove the best. It simulates a lightning strike into a closely confined region, and such

confinement of a collapsing plasma within media of controllable composition allows some control of the chemistry during the vital early stages of plasma collapse. As mentioned earlier, the method should automatically provide space-charge stabilization shortly after electrical contact to the earth is made. It might, therefore, only be necessary to provide a continuous supply of energy for fully characteristic, long-lived, ball lightning to be produced. A disadvantage is that, to be practically useful, it may require large voltages at high current---hence the availability of a high-voltage facility.

There may be something significant in one matter of consistency in the various past attempts to make laboratory ball-lightning: the lifetime of about two seconds that characterizes the best examples over the last few decades. Besides Barry's electrically ignited flame (Barry, 1968), roughly spherical discharges have been produced from variously initiated air-plasmas and from interactions of plasmas with solids (Powell and Finkelstein, 1969; Ohtsuki and Ofuruton, 1991; Bychkov, 1994).

It is often stated that ball lightning has never been made in the laboratory, suggesting that the plasmas produced so far merely resemble ball lightning. Admittely, few of them closely resemble the classic form. However, it is quite possible that most of them represent the successful completion of the construction and ignition phases of ball lightning and that it is only the optimizing of the chemistry and physics for long-term running that is missing. Alternatively, the balls may succumb to intrinsic instabilities after two seconds because, during the first few microseconds, the local chemistry was never correctly balanced against the electrical input and aerosol content. For example, if nitric-acid-droplet formation is essential early on, the surface needs to be cooled below about 15^0C. The processes leading to the production of the crucial anions will depend on the right metastable molecules being present in appropriate amounts, and it is quite possible that the wrong initial redox conditions will always lead to collapse after one or two seconds. And, of course, a lightning ball may well need a continuous supply of electrical energy and, surrounding it, a stable space-charge of exactly the right amount. Clearly, the extent of our ignorance on these matters is considerable.

Over the last few years, the author has occasionally attempted to prepare St. Elmo’s fire in a spherical form, hoping that ball lightning could then be detached from the conductor. He has obtained some potentially useful clues, in this way and others, but has never been able to control more than a few of the essential variables (Turner, 2002). Probably for this reason he has not even succeeded in making the large spherical kinds of stable corona-discharge to which he believes the phenomenon is related. Nor has he found from the literature that anyone else has been more successful.

It seems inescapable that electrochemical processes play a crucial role in explaining many properties of ball lightning. This could be a depressing conclusion since vapour-phase electrochemistry barely exists as a discipline; and the situation seems unlikely to change quickly because the current lack of interest in this basic chemistry means that nothing is being done to reverse a century of neglect. Furthermore, no testable quantitative theory seems likely to be developed without new experiments and these, compared with computer modelling, can be very expensive indeed.

There are, however, two aspects of the overall problem where we might know enough to derive some small benefits in future. First. Even in its present largely qualitative form, the electrochemical model can help decide which properties are best addressed or ignored by specialists in particular disciplines. By using these hints, we might be able both to advance ball-lightning research more quickly than in the past (by avoiding futile exercises) and, at the same time, find a realistic way to approach the wider areas of ignorance.

Second. There is probably still much untapped information in the literature if only we have the patience to find and interpret it. Some evidence of this type, superficially unconnected with ball lightning, has already suggested possible future studies (Turner, 1998). Information available from a wider field may or may not help advance our understanding of ball lightning or of vapour-phase electrochemistry. However, it could at least provide warnings of areas where modelling should be treated with great caution. In the remaining sections, I will indicate some areas where the missing electrochemistry is likely to be involved and where a better understanding of its possible involvement could prove informative.

It should be borne in mind that some of the problems discussed earlier are generic limitations of physical chemistry while others arise only because we are short of information regarding specific chemical reactions. Furthermore, the chemical reactions are of two rather different kinds: some are specific to the complexities of nitrogen oxidation while others relate to anomalous heats of charge neutralization and would apply to other systems. So far, we have been assuming that formation of the nitrite ion is a necessary precursor of thermochemical refrigeration. However, this has only been assumed because the ion is almost certain to be present in normal clean air. As mentioned previously, there is no reason to assume that the nitrite ion is the only one which can produce refrigeration. If, for example, the air happened to be heavily contaminated with organic materials then any anion formed by oxidation or nitration that has the correct thermodynamic properties could serve the same purpose. It does not help, of course, that there is no tabulated information on such ions in the gas phase.

9 Phenomena Related to Ball Lightning

What would normally be referred to as a lightning ball emits light in its central region. This is believed to consist of an air plasma whose energy content varies widely and whose temperature is, therefore, expected also to vary widely. The temperature is generally very difficult to estimate and in only a few cases have such attempts been made (Barry, 1980a). The range of central temperatures that will sustain a ball is not known but appears to be very large. Some balls are undoubtedly very hot and energetic and temperatures as high as 15,000K have been suggested through visual assessment by a witness with years of plasma experience (Dmitriev, 1967). In nature, there may be a continuum of phenomena related to ball lightning which have temperatures as high as those measured in ordinary lightning (up to 30,000 K), since there seems to be little difference between what is sometimes called slow, or rocket, lightning and what is reported as fast-moving ball-lightning (Turner, 1998). Bead lightning, which certainly forms directly from ordinary lightning, can---if it lasts long enough---look very similar to ball lightning in general appearance and rate of fall. It could, therefore, be an intermediate between the two forms.

However, according to the electrochemical model, there is no need for high temperatures in the central plasma; it is only required that sufficiently energetic metastable molecules of appropriate kinds be present and able to react with one another in the right place. As we have seen, this can lead to spontaneous ionization and hence the possibility of further water addition to the new ions as they cool. The observational evidence is that light can be produced on the surface of some balls with very cool centres. This is not surprising since, once a chemical species has been ionized, it will be energetic enough to emit ultra-violet light on recombination and this ability is not lost when hydration slows down the recombination. Neither thermodynamically nor observationally does a ball's formation, or light emission near its surface, require a high-temperature plasma (Turner, 1998).

The low-temperature forms would not usually be called ball lightning but rather St Elmo's fire, for fixed spheres, and some descriptive title such as a light bubble, for free-floating ones. One of these examples, quoted in Singer's book (1971) as an example of ball lightning, was of a German engineer and his wife who, during a storm, became surrounded by an unusually large globe of light. This had approached them after sinking through some telegraph wires and was moving at about 10 m/sec. It was 4 m in diameter and absolutely no harm was done to them during the brief period they were inside it. They had time to note that the wind appeared to cease, that there was no sensation of heat, and that the man's lighted cigar seemed unaffected. Clearly, it is partly up to the reporter of such incidents to decide how to classify the observation.

Since there now appears to be no reason to think that this kind of observation violates any law of physics, there is every reason to take such reports seriously. A somewhat similar account, apparently of a significantly hotter globe, was given by a group of seamen (Anon., 1887). They felt stifling heat at the same time that anomalous freezing on the rigging was observed, suggesting that they could have been, for a time, located inside the outer two zones of a large lightning-ball. There was no mention of a visible ball at the time of the observations although, immediately before it, a large and very powerful lightning-ball, accompanied by St Elmo's fire all around the ship, had fallen into the sea alongside the vessel and caused huge waves to break over it.

Clearly, many scientists will be very sceptical about the validity of such unique accounts, especially when the observers were not themselves scientists. However, the author believes that we risk cutting ourselves off from vital clues by being too sceptical. Since barely luminous analogues of ball lightning seem to exist, they may play a role in explaining a few reports of "paranormal" activity. For example, if conditions happen to be stormy at the time, some reported ghostly appearances or poltergeist effects might be manifestations of ball-lightning analogues rather than the purely psychological effects that most scientists usually assume all such "sightings" to be. If the conditions were not stormy at the time of the effects, the cause may more closely resemble the phenomena about to be described.

There is a huge literature on unidentified flying objects (UFOs), much of it seeking to sensationalise the phenomenon or to address some political or social agenda. One of the earliest and best books to attempt a scientific approach was that of Klass (1968). Some of the easiest evidence to believe comes from a small but credible set of UFO sightings by aircraft pilots. A number of these were backed up by an independent source such as a simultaneously obtained report from a ground-based radar facility (Smith, 1997). These phenomena appear to resemble ball lightning less than they do a phenomenon for which there does not seem to be an agreed name. This phenomenon is often given a local name or it may be called an earth light by some (Devereux ,1982; Long, 1990) or a ghost or nocturnal light by others (Corliss, 2001).

Compared with ball lightning, these phenomena display several fairly clear differences: the phenomena are not associated with thundery weather, they can occasionally last for hours and (apart from high-level UFOs) they are usually associated with a very local area. In these localities, they may have been seen hundreds of times. In most other respects, this type of UFO seems to resemble ball lightning.

Bearing in mind how many different processes need to proceed at correctly balanced rates and how many chemical options there are, it would not be at all surprising if there were to be more than

one set of conditions which could lead to a stable ball. It may be relevant to note that there is usually a marked difference in the space-charge concentration at the earth's surface depending on whether there is a thundercloud overhead or not. But there could also be trace amounts of chemicals in localized regions that might facilitate the formation process. It is important to realize that there are two quite distinct types of constraint on making ball lightning. These are birth criteria and stability criteria. They might well depend on quite different environmental conditions and both need to be satisfied before a long-lived lightning-ball can result. Presumably this is true of some UFOs.

The agreed properties of the nocturnal lights have been fairly well-documented (Corliss, 2001); the motion seems very similar to that of low-energy ball lightning. Ignis fatuus (Will-o'-the-wisp) behaves slightly differently from the brighter forms of nocturnal light and seems to form only in marshy or boggy locations. In its typical form, it is a very mobile and unstable flame. Its form is probably the result of the flame's dependence on a significant quantity of methane or other organic fuel. However, the normal cold flames of ignis fatuus have sometimes been seen to rise and float in a roughly spherical form; they may owe their spherical shape to basically the same mechanisms as other nocturnal lights.

Similar but much more powerful phenomena have been reported to interact with people in strange and unpleasant ways. Following some UFO encounters, there exist several apparently reliable reports of facial burning or damage to the nervous system. Such reports are potentially useful, but it seems unwise, at present, to attempt to use most of them in refining the ball-lightning model. The situation is slightly different with the phenomenon to be discussed next.

10 Spontaneous Human Combustion

Most of the phenomena described in the last section have been much less studied by scientists than has ball lightning. As a result, and because the better reported ones rarely leave any permanent record, not much usable new information is available from them, whether the reports are old or new. However, this is not necessarily the case with another rare phenomenon that may possibly have mechanistic similarities to ball lightning: the phenomenon of spontaneous human combustion (SHC). I have relied almost exclusively on information from the book by Randles and Hough (1992) because these authors made an unusually determined effort to be objective. They relied mostly on forensic evidence, court records, the direct questioning of witnesses, and consulting any scientists who would talk to them. However, their policy also meant that they felt the need to mention some fairly incredible theories, and they were obviously not doing so from a physicist's viewpoint.

SHC may not be as rare as we tend to think; by 1890, there were 73 cases that at least some medical doctors accepted as valid. We can compare this with the results of Brand's (1923) ball-lightning survey, making some simple assumptions to correct for the fact that the data were collected at different dates. If one assumes that the efficiency of collection for SHC and ball-lightning reports was the same up to1923, that the average collection rate was constant, and that the collection of such data by scientists started in 1660 (when the Royal Society was founded), then we can estimate how many SHC cases would have been accepted in 1923: the number is 83. Of course, the assumptions are all questionable but it is probably the best we can do, and the number is not significantly different from the actually known 73.

Brand (1923) had accepted 215 of 600 reports available to him. Others might have accepted many more. On the basis of this kind of evidence, SHC seems to be between about 3 and 8 times less common than ball lightning. The death rate from ball lightning is extremely low while that for SHC it is very high; thus these numbers suggest that one is at a significantly greater risk of death by SHC than from ball lightning. Both risks are statistically small for any individual although they might cause some people concern.

It is extremely difficult to obtain realistic statistics on SHC using more recent data because there are now huge establishment pressures to avoid citing SHC as a cause of death. It is, after all, hardly an explanation. There seems to be a remarkably consistent pattern relating to those professionals who have investigated an incineration case involving seemingly impossible evidence. If they were heretical enough to mention SCH early in the investigation, they would tend not to be called on to testify at the inquest. Also, the general impression these days, fed by the press and by some of the most frequently quoted scientific journals, is that only at the "cutting edge" of science should a scientist admit to any doubts about a hypothesis. It is hardly surprising that a scientist advising a coroner would suggest a verdict of accidental death or an open verdict rather than one that cites the limits of current scientific knowledge.

Although it is not always clear, in these very odd cases, that the adjective "spontaneous" is appropriate, it is often clear that something very strange has occurred. Usually the charred extremities of a human body are found with a pile of ash in between and remarkably littl e damage in the immediate vicinity; for example, the chair or bed in which the death occurred may be largely undamaged. Bodies have also been found similarly destroyed, lying on straw or leaves, and in this case only combustible material very close to the body will have been burnt. Indoors, a foul smell will be reported by those finding the body and the walls will be dirty, greasy and damp---more like the result of steam distillation than a normal fire.

Witnesses to the fire often describe flames coming from the upper body or stomach. The former is usually reported when the victim is still standing and the latter when he is on the ground. The flames can be extinguished by water and by smothering; but the victim will not generally survive more than a few hours; rarely a few weeks. When the process has gone to completion, the ash remaining indicates burning at least as thorough as is achieved in a modern, two-stage, crematorium. A number of photographs have been published but little useful information seems to have been derived recently from the bodies themselves or from a detailed chemical examination of the surroundings. However, it may be more accurate to say that not much information has been made available to those trying to investigate the phenomenon.

As far as can be judged, the flames look nothing like ball lightning or UFOs yet there are obvious hints that something similar is going on, most obviously the apparently very large temperature-gradient at the edge of the plasma. The combustion process, which can reduce flesh and bones to ash overnight, proceeds in the presence of much water and the phenomenon appears to be able to start without an obvious source of ignition. The evidence for this is almost certainly less plentiful than it might be, as all forensic teams try hard to find a potential source of fire in the vicinity. This will certainly be mentioned in court, however improbable it may have been for the flame to have reached the victim over the intervening distance. Whether deliberately or inadvertently, a coroner's court will not usually have a witness available to explain that there is no known mechanism by which some proposed cause of the fire can start a person burning to ash.

Once one accepts that ball lightning and roughly spherical UFOs exist and have the properties generally attributed to them, there seems no reason to disbelieve SHC. In a thermodynamic sense, all the phenomena are equally possible and related mechanisms seem applicable in all three cases. However, in SHC the probability is greater that some organic acid is involved, possibly in addition to nitrous acid, in the surface-cooling mechanism of the plasma, because in the typical phenomenon, the fire often seems to have started from within.

Both stomach and lungs have been suggested as the initiation site, but it is easier to believe that oxidation could start in the lungs than in the stomach. There is also some evidence (in cases that may or may not be related) that a fire can start between a victim's skin and an item of clothing. This may, in fact, be the way most such incinerations begin. It is to be hoped that, some time in the future, there will be much more thorough forensic examinations in cases of suspected SHC than are currently carried out. Clearly, however, the phenomenon will first need to be more generally accepted as at least plausible. There is also the problem, pointed out by Randles and Hough (1992), that consideration needs to be given to the feelings of relatives who may not welcome what could seem an unnecessarily long forensic investigation.

11 Other Meteorological Phenomena

Meteorology considers processes ranging from global down to molecular scales. Inevitably, it is now split into so many specialty areas and scientific approaches that it is increasingly difficult, if not impossible, for a non-specialist to maintain an up-to-date and balanced view of advances in all the separate fields. The author did attempt to discover whether there exists information to disprove or modify some aspect of his electrochemical model. In the event, he found nothing to contradict it but several hints supporting his views and suggesting clues to extending it.

The systems considered (Turner, 1998) included any in which ions and near-saturated water-vapour co-exist. Evidence from the field as well as from experiments aimed at explaining it were considered for processes related to the following:

- the separation of charges to provide a positively charged upper atmosphere and a negatively charged earth;
- water condensation in clouds;
- the relationship between lightning and cloud-bursts;
- tornadoes and related vortex phenomena.

It may be no coincidence that controversy still surrounds these areas of meteorology. Among those listed, most closely related to ball lightning seem to be certain tornadoes.

Not all reports of ball lightning are spherical or even elliptical with the long axis vertical. One might attribute the latter geometry to distortion resulting from a large dc field. However, reports exist of elliptical shapes aligned at a range of angles between vertical and horizontal; and that applies also to tornadoes. Presumably, if a lightning ball is rotating sufficiently rapidly and the effective rigidity of the shell of charged droplets is sufficiently slight, the spinning charges would be drawn towards the equator by electromagnetic forces. In some circumstances, the inward pressure might add to the electromagnetic effects and increase the forces tending to elongate the oval.

The extent of the elongation would depend on the magnitudes of the various electrostatic, electromagnetic, chemical, thermal and hydrodynamic forces. For this explanation to hold, an elongated lightning-ball would always have to be associated with rotation. Such rotation has sometimes been noted but not always. However, since a healthy effective surface-tension can result from aerosols far too small to be visible, rotation of the central plasma need not be noticeable.

A very unusual observation (Needham, 1993; and subsequent correspondence) seems relevant. There have been dozens of reports of lightning balls removing circular holes from windows (Grigor'ev et al., 1992). Sometimes both pieces of glass are collected and saved. Needham's example was of this type but very unusual in that a strongly elliptical hole was made and this hole was oriented horizontally, 30 cm wide by 12 cm high. There do not seem to be many possible explanations other than rotation of the ball, which was not noticed, however. In this particular case, the ball assumed responsible for the damage had been seen bouncing down the sloped roof above the window, and this may have imparted sufficient angular momentum about the required axis (Turner, 1997).

A tornado is normally modelled, these days, as a wind vortex (Davies-Jones, 1985; Trapp and Davies-Jones, 1997), apparently with no allowance for the fact that the moving fluid could contain charged particles. If such particles were present, then one might well expect the rotating air containing them to have a structure similar to that of a rotating lightning-ball, which means that there would be a continuous net flow of air into the plasma region. Although it is currently fashionable to model tornadoes by ignoring their electrical properties, this would have surprised many physicists 150 years ago. In 1841, Peltier published a book on tornadoes that was very influential in France (Flammarion, 1888; Planté, 1888; Chauveau, 1922). His ideas were also influential, for a while, elsewhere (Hare, 1840). However, some of his arguments were flawed because he did not realize that air is a conductor of electricity; his meteorological ideas have been largely ignored (Chauveau, 1922).

Peltier (1841) listed 66 examples of water spouts, 71 of land-based tornadoes and 52 phenomena he called analogues of tornadoes. On the basis of these, particularly the evidence for scorching, it is nearly impossible not to agree with him that the phenomenon can be largely electrical. Such evidence is not confined to earlier centuries. Remarkably similar accounts to some of the historic ones are provided by Corliss (1983,1986). More recent examples include luminous glows inside or well above a tornado funnel; near-horizontal tornadoes between a pair of clouds; the singeing, desiccating, and burning of vegetation by the passing funnel; and the presence of an acrid smell resembling sulphur oxides. All these were reported by Peltier.

It has been known for many years that tornadoes present severe problems to modellers (Brooks, 1951; Fujita, 1960; Vonnegut, 1960). The concentration of energy is a particularly serious problem. Some more recent tornadoes have been unusually well monitored, yet modelling these tornadoes with entirely hydrodynamic and thermal forces (e.g. Brandes, 1984) does not seen to have done much more than confirm basic inconsistencies. Nor have attempts to model tornadoes as mainly electrical phenomena fared much better (Watkins et al., 1978).

In 1995, a phenomenon was attributed to a tornado on the basis of the damage it caused (Weeks, 1995), although no funnel cloud was apparently seen. The whole event was, however, witnessed by two people on a hill above the site. They saw a large lightning-ball passing along the road of damaged houses just above the height of their roofs. In this case, the connection between the two phenomena appears to have been so close that it is difficult to know what the phenomenon should

have been called (Turner, 2002).

More recently, a much more powerful tornado devastated the small town of La Plata, in southern Maryland. The atmospheric super-cell thar powered it began its life in the mountains of north-west Virginia, causing damage in four Virginia and three Maryland counties as it travelled roughly east. It ended its life after dark, on the eastern shore of the Chesapeake Bay, by which time what appeared to be a large glowing mass was clearly visible in the cloud high above the funnel. A witness in La Plata, who was awakened by the tornado and had no time to seek safety, had earlier seen a strong white light coming from above him through the damaged roof of his home. I also watched a very unusual bright patch through the surrounding clouds of this event for half an hour; I was in a position about half-way between these two observations. It seems possible that the plasma was present for at least the 1 1/2 hours the tornado took to travel across Maryland. Thus this tornado could be thought of as influenced by an exceptionally long-lived lightning-ball or by a very powerful UFO. I plan to publish some of the details on this tornado in the future.

It may be that tornadoes will eventually teach us a great deal about ball lightning. They may be unpredictable but at least they are more predictable than are appearances of ball lightning.

12 Comets

Comets may be the closest extra-terrestrial objects to us where ions in the presence of saturated water-vapour are to be expected. Historically, what were classed as bolides were divided into slow- and fast-moving varieties. The slower ones were early seen to come in two varieties, depending on whether or not they moved in straight lines (Bertholon, 1787). If the nucleus around which a plasma ball has formed could be guaranteed to remain within the fireball, then, from the point of view of the light-producing processes, there is little difference between the three basic forms of "bolide": meteorites, comets and lightning balls. They all involve what Bertholon (1787) called "electric fire" and we now call plasma. The plasma processes would presumably be fairly simple for dry meteorites: the generation of light following vaporization and ionization. However, for comets entering the atmosphere, the presence of ice might allow some of the peculiar chemical phenomena described earlier to occur.

In this connection, some of the findings of the various missions to Halley's comet may be relevant. Superficially, comets out in space are distinctly different from lightning balls: they are surrounded by plasma instead of by air. However, they still contain a boundary in which the plasma interacts with molecules. The temperature measurements made in the inner coma of the comet, near to the stagnant plasma region, revealed a significantly higher temperature-gradient than expected (Galeev, 1987). This may have a similar cause to the much larger gradients seemingly found in lightning balls. Note that the relative and not the absolute humidity is responsible for the poorly understood electrochemistry and is believed to control many of the peculiar properties of ball lightning. There is no evidence that the nitrite ion was responsible for this temperature gradient, but an organic anion or hydroxide might be. Unfortunately, the mass spectrometers used for the close encounters with Halley's comet were not designed to detect anions.

The formation of ion hydrates is so exothermic that, well inside the coma, hydrate clusters should be thermodynamically stable. (An exothermic reaction inevitably becomes more strongly favoured the lower the temperature). Calculated temperature profiles for the region near the nucleus

(Ip and Axford, 1990) suggested temperatures between about 30 and 200K, these temperatures being the same for both electrons and neutral gas. The minimum temperature applies at about 300 km from the nucleus while the higher one applies at its surface. Not until a distance of nearly 1000 km from the nucleus do the predicted electron and gas temperatures begin to diverge.

Let us suppose, for argument's sake, that the inner 300 km of the coma contained only saturated water-vapour, plus H_3O^+ ions, unspecified anions and hydrates of these species. A strict thermodynamic treatment of the equilibrium state is impossible because valid treatments for ions in a saturated vapour are not available. The problem can be avoided to some extent by considering separately the volatility of ice and the vapour-phase reactions. We can then assume a common temperature but, for the hydration reactions, a vapour pressure significantly lower than for saturation. In this way we could hope to reduce the problems resulting from the absence of a theory but could be sure we had underestimated the hydrate concentrations. One is then only left with the problems of a crude extrapolation of the thermodynamic data. Using this approach, it can be shown that H_3O^+ hydrate ions should predominate within 300 km of the nucleus. This seems to be true despite the considerable uncertainties in the hydration data (Keesey and Castleman, 1986).

The Giotto spacecraft approached within 1000 km of the nucleus, but few mass-spectrometric measurements could be made during the short time it was this close. Apart from a clear demonstration of the preponderance of water (Krankowsky et al.,1986), a number of interesting results were obtained on the ions present. One relevant and very clear result is that, of the ions present, unhydrated H_3O^+ increased in importance between about 10^5 and 2×10^4 km from the nucleus, becoming the dominant ion clearly detected inside this range (Balsiger et al., 1986). Another result is that, inside the coma, ions with mass numbers up to the detection limit of the apparatus (200 atomic-mass-units) were present. If some of the ions at this limit were H_3O^+ hydrates, that would correspond to 10 water molecules per central ion.

However, this would not have been predicted on the basis of the above-mentioned estimation procedure for the equilibrium state. If the heaviest ions found at 1000 km were, in fact, large clusters of polar molecules, then either the lack of a basic theory is very serious and the hydration data more uncertain than believed or else the clusters were slow in decomposing. Either or both could be true but we may not learn much more before extensive in situ measurements inside the coma of a comet are made. For comet Halley, few of the heavy ions have been positively identified although some are believed to be heavy metals, sulphur compounds or hydrocarbon-related ions (Korth et al., 1986). Based on the above considerations, the author believes that some of them could be clusters of water and probably other dipolar molecules around H_3O^+ ions.

Thermodynamically, one would expect few free electrons to emerge from the inner coma because of their attachment to any molecular fragments that could be stabilized thereby. As a consequence, we would expect anions, such as OH^- and HCO_3^-,to predominate greatly over electrons inside the coma. The Giotto mass-spectrometers could not detect anions, and the author is not aware that either anion has ever been detected in an astronomical object. This is perhaps not surprising since anions would probably only be stable well inside rather dense clouds. If the above speculations are correct, it seems quite possible that, somewhere in the coma, a zone would exist where anomalous thermal processes could occur and produce higher than expected temperature-gradients. As mentioned earlier, this effect was indeed observed. It is to be hoped that a future mission to a comet will be equipped with a mass spectrometer that can detect anions.

The fact, that the coma of a comet is fairly compact and has roughly spherical symmetry, could have relevance to one of the most spectacular and perplexing events of the last century: the explosion, equivalent to a 10-to-40 megaton hydrogen bomb, that devastated a huge area of taiga in the Tunguska region of Siberia in1908. The cause of this explosion has been the centre of much dispute ever since1958 when it was firmly established that the explosion occurred well above the ground. The early history of the controversies and many of the (often bizarre) attempts to reconcile all the facts are discussed in the book by Baxter and Atkins (1976). A more recent analysis has been made of all the data collected by the interdisciplinary institute set up in 1958 to investigate the phenomenon (Vasilyev, 1994, 1995). The analysis suggests that most of the long-standing problems still remain---at least if one excludes such explanations as the explosion of a nuclear-powered space-craft from another planet! That possibility was seriously considered at one stage, based on similarities between the ground damage there and at Hiroshima (Zigel, 1961).

More conventional candidates for the incoming object include either a meteorite or a small comet. The first expeditions, in the 1920s and 1930s, were looking for the remains of a meteorite, and for some time this was the preferred candidate. As more evidence was collected, it gradually became clear that this explanation did not fit all of what appeared to be the relevant facts. By the early 1980s, most---though not all---of these findings were thought to favour a comet that had exploded in a very inhomogeneous and peculiar way. Then, in 1983, detailed calculations (Sekanina, 1983) suggested that a comet could not have been responsible. This conclusion has been confirmed several times by other calculations and, as Vasilyev (1995) points out, we are again confronted with a whole set of seemingly irreconcilable facts.

But only a few difficulties remained while it was believed that the bolide was a comet, and it may be premature to discount the comet hypothesis. The extensive calculations of Sekanina (1983) and later computer simulations such as those of Chyba et al. (1993) rule out a comet largely on the grounds that its mechanical strength would not allow it to penetrate the earth's atmosphere to anything like 5.5 to 8 km of the surface, the height range of the explosion implied by the ground evidence. However, it seems unlikely that a comet entering the earth's atmosphere could avoid being influenced by forces other than those considered in these calculations. It would also be subject to chemically produced hydrodynamic forces, similar to those that give ball lightning its unexpected stability.

In the case of a comet entering the earth’s atmosphere, a central plasma would already be in place and be of the correct symmetry. It would contain plenty of solid particles of various types and plenty of water. It would then encounter cold air of ever-increasing density and would, it seems, lack nothing required to start the electrochemical processes that explain ball lightning.

The electrochemically derived forces would help hold the comet together and presumably the effective surface-tension would be very great. It should be noted that ball lightning can apparently travel very fast without breaking up (see Section 9). The low temperature of the surrounding air (well below freezing at the relevant heights) would ensure that the formation of nitric acid is strongly favoured thermodynamically. This also applies to the condensation of a liquid or solid phase from the ample water-vapour that a comet would be releasing. There seems no way of calculating a realistic maximum temperature for the system, so even a self-ignited nuclear-fusion reaction cannot be ruled out. Zigel (1961) calculated the temperature of whatever caused the devastation to be tens of millions of degrees.

At Tunguska, there have been exhaustive studies of the spatial and temporal effects of the event on the local biology and geochemistry (Vasilyev, 1994, 1995). Among the effects found was an accelerated rate of tree growth starting immediately after 1908 and an increase in the ^{14}C count for the 1909 tree-rings (also found worldwide). The former effect was well above that expected simply from improved access to light (Vasilyev, 1994). If nitric-acid production in a comet was involved, then there would be an obvious explanation in terms of the spreading of a nitrate or nitrite fertilizer. Some of these matters have been discussed in a little more detail elsewhere (Turner, 1998).

13 Star Formation

Roughly spherical contained plasmas can be seen in ball lightning, in some tornadoes and in the vastly larger comae of comets. An obvious question is whether there could be any related processes occurring on an even larger scale, in stars. An advantage of asking this question is that the number of stars available for study is vastly larger than the number of lightning balls ever seen. Also, the total number of man-hours that have been devoted to their study over the millennia is much larger. Thus there is at least a hope that useful clues could be available by now in the astrophysical literature.

Any clues would come from rather specialized new areas, and might be quite indirect because the stabilizing and disruptive forces would combine in different ways in the various plasmas. The fact that the distance and time-scales are so large for stars is, however, a potential advantage because any remotely similar processes occurring around the smaller plasmas on earth proceed so very fast.

There are formal similarities between the processes that must occur in the two-phase region adjacent to any plasma. Stars form deep inside giant “molecular clouds” composed of molecular hydrogen and ice-covered dust particles. (In this context, “ices” are any solids more volatile than water ice; less volatile solids are classified as dust or grains.) Both the physics (Harpaz,1994; Hartmann,1998) and, increasingly, the chemistry (Hartquist, 1990; Hartquist and Williams, 1995; Faraday Society, 1998) of star-forming regions have been studied over the last few decades. However, it is only possible to study the clouds directly at relatively low densities, that is at hydrogen-number densities less than about 10^{13} m^{-3}. The clouds protect the inner regions from the heating effects of starlight and allow them to drop to temperatures below 10K.

The molecular clouds can be studied in regions where, as yet, no stars have formed and also where stars have recently been born. Least observational information is available for the pre-star-birth regions where the clouds are thick. Particularly detailed pictures of the chemistry can be obtained where a new star has moved out of the dusty ice envelope in which it formed. Useful information can also be extracted from the surroundings of the brightest young stars at a molecular-hydrogen density of about 10^{13} m^{3} (Hartquist and Williams, 1995), because dozens of powerful OH masers can surround these stars: the hydrogen density can be deduced from its best fit to models for maser emission. To put this density into context, it can be compared with the mean density of the sun, 4.3×10^{29} m^{3}.

A very interesting feature of the OH masers is that they are all found 10^{14} to 10^{15} m from a new star, just where there is a dramatic change in the physics and chemistry (Elitzur, 1992; Hartquist and Williams, 1995). This boundary is referred to as the HII/OH region, HII being the name given by astrophysicists to regions that consist predominantly of hydrogen ions. Inside this boundary the hydrogen is ionized, whereas outside it the region is cold enough that molecular hydrogen is the main

constituent. Ice-coated dust is also an important constituent in these outer regions, and the OH is believed to be produced in reactions between H_2 and O. The rate is controlled by the radiation coming from the new star and is significantly temperature-dependent. The local OH concentration is surprisingly high, between 1 and 10% of the likely O concentration. The fact, that the masers do not have significant motions away from the new star, suggested that the early shock-wave models, which seemed to explain the behaviour of other masers (Elitzur, 1992), are unsatisfactory in this case.

The recent model of Thissen et al. (1999) seems to remove all the anomalies by invoking, rather than a shock wave, the combined influences of infra-red and ultraviolet irradiation arriving continuously from the new star. Sublimation of the warmed ice under the conditions expected at the HII/OH boundary and photo-dissociation of the products appears able to explain all currently available measurements making only very reasonable assumptions. The model defines a "small-grain border" and explains the stability of the maser position in terms of the thermal and other processes taking place on ice-covered grains of an assumed size-distribution. Some of the processes seem to be somewhat analogous to those in the refrigeration zone of a lightning ball.

The stages leading up to the formation of a star are less clear. Somehow, the hydrogen present in the molecular cloud has first to increase its density by something like 16 orders of magnitude over the densities where observations are possible. At the moment, there is no general agreement about the later stages of collapse, and we are at the mercy of models over a huge concentration-range. If icy dust plays an important role, it is unlikely that a valid model of relevant rate-processes can be developed at present. Thus, it seems necessary to consider the question of how important the icy-dust phase might be.

To explain the longevity of the dark clouds from which new stars develop, it is generally accepted that local magnetic fields inhibit the collapse that would otherwise occur rapidly once the local mass exceeds the so-called Jeans mass. For a medium of uniform particle-density (n) and temperature (T), this mass is proportional to $(T^3/n)^{1/2}$. Above this theoretically well-defined limit, a gravitational instability could arise and lead to collapse. It is believed that, in the initial phase of gravitational collapse, an elevated magnetic field holds off the collapse until the neutral molecules present have had time to diffuse through it. The resistance to diffusion is caused by interactions between neutral molecules and the ions coupled to the field. It is believed that reasonable limits can be placed on the time-scale for this process, known as ambipolar diffusion. Once the gases have penetrated this barrier, the collapse is assumed to be "rapid", being constrained only by rotation, turbulence and the escape of heat.

At present, there are no observational data to define just how fast are these final stages. The collapse is unlikely to occur either perfectly isothermally or adiabatically, and which of the two it most closely resembles will obviously depend on the unknown rate of collapse and the rate at which heat is being transported away. Clearly the physics is very complex and it is difficult to see how the icy dust could not be directly involved in most of the rate-determining processes. Even if electrochemistry were to be of only marginal importance, there are other serious difficulties. Systems involving heat and mass transport, where two phases are involved, are just the kind of systems where present physical and engineering models are least reliable.

They are, in fact, largely empirical and can often yield quite wrong predictions, for example, in low gravity fields (Walter, 1987). This is because the models were originally developed in the

presence of earth's gravity. In my opinion, we are unlikely to really understand star birth until much more experimental work has been completed at low g. The assessments made for the future of micro-gravity research by the European Space Agency (Walter, 1987) were carried out at a time when it was possible to be optimistic about the future of long-term fluid-physics and physical-chemistry research. This was true, at least in mainland Europe, even when the research lacked glamour, was experimentally difficult and was unlikely to produce a rapid payback. However, the political climate is very different now and there has been an ever-decreasing level of support for this kind of work.

It therefore seems that a credible quantitative model for star birth is as far off as is one for ball lightning. New experiments may help us decide whether electrochemistry offers a viable means for containing a fusion plasma. But we need to make ball lightning first. Perhaps our most realistic hope for relevant new knowledge will come from future missions to comets and from future work on tornadoes. It might even be possible to find support for realistic attempts to make ball lightning. However, it must be admitted that rapid success cannot yet be guaranteed.

Appendix A: Processes in Solution

Reactions in solution are often reversible, and both the equilibrium state and the rate of equilibration can be important. The equilibrium state will be the main consideration here. It is governed by the laws of thermodynamics. Thermodynamics (including statistical thermodynamics) can be considered as a detailed mathematical statement of the facts relevant to the inter-conversion of energy and work. At its most rudimentary, it explains why it would be a waste of time to attempt to construct a perpetual-motion machine by any means whatever. It applies to all forms of energy: heat, other forms of kinetic energy, gravitational, nuclear, electrical or chemical energy. Of these, the most complicated to deal with can be chemical systems, because so many different chemical compounds exist and we do not have data on all of them. Although chemical thermodynamics and kinetics are intimately connected, they are treated using quite different methods and using different types of approximation. Some of the rigorous definitions needed in the development of thermodynamic arguments may appear unduly complicated and pedantic to those more familiar with the rates of chemical change; however, the resulting relationships can be simple and profoundly important. Unfortunately, the importance of chemical thermodynamics is not appreciated in much applied, as opposed to basic, research.

Different kinds of energy change call for different definitions. In most cases where chemistry is involved, the Gibbs free energy is most appropriate. Just as water flows down a waterfall to reduce its gravitational potential energy so, in a chemical system, the chemicals present react with one another to minimize the Gibbs free energy of the system. The property that determines how reactive any component will be is called its chemical potential. It can usefully be thought of as the "escaping tendency" of that component (Lewis and Randall, 1961) and is exactly analogous to a gravitational potential. (Of course, an object's gravitational potential is much simpler, on earth depending only on its mass and height above the earth.)

The chemical potential of any substance, i, can be defined as

Eqn. A1 here

where G is the Gibbs free energy of the whole system. Its change for an infinitesimally small change in the number of moles of component i at constant temperature, pressure and composition is given by the partial derivative. (The chemical potential can also be expressed in terms of other definitions of a system's energy if this is more convenient.)

The condition for equilibrium is that G be as small as possible, which means that no small changes in composition will raise it. This is expressed by the Gibbs-Duhem equation,

Eqn. A2 here

Here, x_i is the mole fraction of i and the mixture is assumed to have r components. Like a gravitational potential, a chemical potential is measured indirectly. However, it differs in depending on many more properties and variables. In dealing with chemical equilibria in solution, it is usually more convenient to use an activity, a_i, for each component instead of μ_i. The relationship to the chemical potential is given by

$$\mu_i = \mu^0_i(T,p) + RT\ln a_i \qquad \text{(A3a)}$$

$$\mu_i = \mu^0_i(T,p) + RT\ln x_i f_i \qquad \text{(A3b)}$$

The identity in (A3b) provides the connection with the mole fraction at equilibrium, x_i, a property that is measurable in principle at least. (Although there are other ways of measuring concentrations, only mole fractions need be considered here.) f_i is the activity coefficient, and $\mu^0_i(T,p)$ is the standard-state chemical potential; for many solutions, it can conveniently be considered as the potential at infinite dilution, where there would be no interactions except with a solvent. The definition of an equilibrium constant, K, comes directly from these relationships.

To illustrate some of the strengths and limitations of thermodynamics in understanding solution properties, consider a simple hypothetical reaction for which all required experiments are assumed to be possible. Two reactive chemical compounds, A and B, are dissolved in a solvent that allows some of the less reactive compounds C and D to be formed via the simple reaction

$$A + B = C + D \qquad \text{(R1)}$$

At equilibrium, the solution will have a composition in which each component has a fixed concentration, and these equilibrium concentrations can define the equilibrium state. The equilibrium quotient, Q, is defined by

$$Q = x_c.x_d / x_a\, x_b \qquad \text{(A4)}$$

If similar experiments were to be conducted with different starting concentrations of A and B, then somewhat similar, though not identical, values of Q would be obtained. However, if we also knew what all the activity coefficients were as a function of composition, we could calculate the thermodynamic equilibrium constant,

$$K = a_c.a_d / a_a\, a_b \qquad \text{(A5)}$$

for the reaction. This would have the same value for whatever amounts of A and B were dissolved in the solvent. (That equation A5 is equivalent to A2 is readily seen from the above definitions.)

K is thus a thermodynamic quantity characteristic of the chemical system. It is independent of the concentrations, x_i , and dependent only on temperature and pressure. K is in principle much more important than Q, and not only because it is a constant . It is an integral part of thermodynamics, no exception to which has ever been found. It is related, also via the relations given above, to what is called the standard free energy of reaction, ΔG^0, by the relationship

$$\Delta G^0 = -RT \ln K \qquad \text{(A6)}$$

Because K and ΔG^0 are clearly defined thermodynamic properties of a system, they obey the general thermodynamic relations that define, for example, their temperature and pressure dependence. The relationship defining the temperature dependence of the free energy,

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \text{(A7)}$$

was used in obtaining some of the results of Table 1 in the main text. Again, the standard enthalpy, ΔH^o, and the standard entropy, ΔS^o, nominally refer to an infinitely dilute solution. For many systems, both these quantities have a rather small temperature-dependence which can be neglected over small temperature ranges.

As a solution is diluted, it is normally to be expected that any associated molar property (its value per unit mole) will eventually approach a constant value. So long as we can either conduct experiments close enough to zero concentration to ensure that the limiting value can be defined, or can estimate deviations owing to non-ideality using some theory, we can obtain standard-state properties.

ΔG^0 values are additive in the same way that heats of reaction (enthalpies) are, so ΔG^0 for reaction (R1) can be obtained from the formula

$$\Delta G^0 = \Delta_f G^0(C) + \Delta_f G^0(D) - \Delta_f G^0(A) - \Delta_f G^0(B) \qquad \text{(A8)}$$

where the free energies on the right are the standard free energies of formation of the various components of reaction (R1). For many compounds, values of these and related properties have been repeatedly measured and assessed and tables of recommended values exist. Note that, for dissolved substances, all these values refer to changes involving one mole of each chemical component and that *these changes are taken to occur at infinite dilution where all the solutes are behaving in an ideal manner.*

In principle, each free energy could be considered calculable by extrapolating ln Q to infinite dilution. More often, because of experimental difficulties, other thermodynamic relations are needed to fill in or improve some of the missing data. The problem of missing data is probably one of the main reasons that thermodynamic arguments are not more frequently used in chemistry. Many systems simply cannot be studied experimentally by available methods. As a result, users of thermodynamics often find it necessary either to estimate any missing data they need or to try to make new measurements themselves. Once one has obtained experimental data, however, one still needs a method for relating what one has measured to a standard-state value and then back to actual conditions

of interest. There is no other practical approach if one wishes to take full advantage of the power of thermodynamics and of already-existing data.

For illustrative purposes we can confine our attention to the direct measurement of K. Clearly we cannot derive K from Q unless we can either extrapolate the data to infinite dilution or estimate the activity coefficients. The former approach is restricted to methods that are reliable at sufficiently low concentrations. If these are unavailable, the latter approach is needed. For many solutions, the problems are not serious because the activity coefficients are fairly close to unity and so Q is not very different from K. Electrolyte solutions are not so easily dealt with, but simple extensions to the Debye-Huckel theory will often prove satisfactory.

The important thing to realize is that the standard states for electrolyte solutions are significantly different from those of other substances, because electrolytes are fully dissociated at infinite dilution. In normal solutions, the fact that there can be an increase in the number of particles on dilution does not matter because such solutions, being liquids, are essentially incompressible. In a gas, however, this would not be the case and we can anticipate that problems might arise from this cause.

There are several strong hints that such problems do exist (Turner, 1983, 1990), but the hints all come from measurements under rather unusual conditions. Most of the chemically related problems with which scientists and engineers are asked to deal can be solved without considering the presence of ions in the gas phase, because the temperatures of interest are often far too low for gas-phase ions to be present in detectable amounts. However, if one is interested in the behaviour of very low concentrations of a particular substance, for example, if one is assessing the risks associated with a low-level radioactive contaminant like hydriodic acid, then very low levels do matter.

It was in this context that my colleagues and I first realized how misplaced the above assumption could be. We began with what at first appeared to be a simple though potentially serious problem. Some measurements on the partitioning of hydriodic acid between water and steam had been made at the Oak Ridge National Laboratory in Tennessee (Clinton and Simmons, 1987). At first we could not believe the results because they appeared to violate all scientific common sense. In fact we undertook a range of experiments to disprove the findings but without success. All the evidence eventually pointed to the fact that iodides, including hydriodic acid, are fully ionized in steam at 285^0C. This is far below the temperature at which one normally expects ionization in a gas, and the obvious explanation invokes the powerful effects of ionic hydration. This is, of course, what makes liquid water a good solvent for salts.

The clearest available picture of the physical processes involved comes from measurements on the densities of common salt solutions under super-critical conditions (Benson et. al., 1953; Copeland et. al., 1953). Other relevant aspects of solvent behaviour under such conditions are discussed in Appendix B.

An advantage of measuring solution densities and deriving thermodynamic quantities from them is that density is a quantity that is particularly easily pictured. From sufficiently detailed and precise measurements of densities, it is possible to derive partial molar volumes, which are the pressure derivatives of chemical potentials. Although the measurements referred to above were not sufficiently precise for the authors to derive these quantities from their data, the observed effects were

so large that a less demanding analysis of the data proves very informative. Apparent molar volumes are, as the name implies, the volume each mole of a solute seems to occupy on the basis of differences in density between the solution and the pure solvent. The results shown in Fig. A1 are plots of apparent molar volumes as a function of salt concentration (in mol kg^{-1}) for one of the sets of temperature and pressure studied.

Fig A1 near here.

Two things are noticeable at once. One is the fact that the apparent molar volume, ϕ, does not approach zero concentration with a finite value. By contrast, a similar plot at 25^0C would show a line almost indistinguishable (on the scale of the graph) from the x axis but actually intercepting the y axis at 16.63 cm^3 mol^{-1}. The other thing to note is the negative sign and huge magnitude of the apparent volumes measured at each concentration (–24 dm^3 mol^{-1} at the lowest one). The fact that, at 25^0C, the molar volume of a salt is less than the actual volume of one mole of the solid has long been attributed to electrostriction, and the phenomenon has been studied extensively for many salts (mostly at 25^0C). The almost unavoidable conclusion of the above findings is that the electric fields of the dissociated ions are able, because of the large compressibility of the solvent at 385^0C and 243 bar, to bind large numbers of water molecules to themselves.

If one makes the seemingly realistic approximation that an electrostatically compressed cluster of water molecules close to each ion would have an average density of 1 gcm^{-3} , then the number of water molecules in each cluster can be estimated. The results are shown in Table A1 (Turner, 1983, 1990). Also shown are the concentrations, the apparent molar volumes and the mole ratios of water to salt represented by each concentration.

Table A1 about here

From the similarity in the entries of the last two columns for the three highest concentrations, it appears that the clusters (as defined above) are in contact. At lower concentrations, the hydration numbers increase with dilution less fast than the mole ratios, implying that free water is appearing between the clusters as the clusters grow larger. (In reality, the local density will be a little greater than 1 gcm^{-3} near the ion and less than this further away.) However, despite the crudity of the model, it seems clear that the ions are binding a large number of water molecules and that this number increases with increasing dilution. What matters most in the present context, however, is that a finite intercept on the y axis is not obtainable and that this appears to be directly associated with ion hydration.

The slope of the curve is becoming increasingly negative as the concentration is decreased. This slope is proportional to the partial molar volume of the salt, which is the pressure derivative of the chemical potential. Therfore there is no reason to expect the chemical potential itself, or its temperature derivatives, to behave normally. In that case, no standard state can be defined and there is no reason to expect any simple relationship between concentration and activity. Other relevant evidence from the behaviour of high-temperature solutions exists (Turner, 1983, Turner, 1990); some of it is mentioned in Appendix B.

We can also look at the problem of establishing solute activities in another way, which does not use considerations of high-temperature solution-chemistry. It is clear from equations A3, which are equally applicable to gaseous and liquid mixtures, that a standard state is chosen so that the solute has

unit activity and unit concentration there. If an extrapolation procedure has been well chosen, the mixture will behave as would an ideal mixture and the activity coefficient will approach unity for a concentration range high enough for accurate experimentation. For gas-phase mixtures, Dalton's law of partial pressures provides the required ideal behaviour and, at the level of approximation of the gas laws, there are normally no difficulties in treating gaseous systems either thermodynamically or kinetically.

When it comes to systems containing ions in a gas or vapour at low temperatures, there are no relevant measurements at all. However, even if there were, it is easy to show that they could not be treated in the conventional manner, because Dalton's law of partial pressures could not apply to such a system. This law states that each component of a non-reacting mixture of gases contributes to the total pressure an amount proportional to its mole fraction; but a mixture of ions with a condensable vapour, like water, is not a non-reacting mixture.

As mentioned elsewhere, electrostriction results in a local increase in density as a fluid is drawn into the very-high-field region near an ion. It is a general property of electrostatic fields and, on a molecular scale, influences any nearby molecule. However, it will exert a much stronger influence on a molecule with a large permanent dipole, like water, than on a molecule like nitrogen or oxygen. Based on a tabulation of thermodynamic data for reactions between ions and neutral molecules (Keesee and Castleman, 1986), it seems that water is attracted to relevant ions between 10^6 and 10^9 times more strongly than is oxygen (Turner, 1998).

Suppose, first of all, that one could somehow introduce, in small steps, a small fraction of ionized gas to dry air in a closed vessel. Assume that the temperature is just high enough to ensure that, say, 99% of the ions remain free at equilibrium. There would be a positive contribution to the pressure from the addition of new particles at each addition but also a slight negative one because of the electrostriction of the nitrogen and oxygen. The total pressure would increase with concentration---although not precisely in the way expected for an ideal system. If the experiment could be repeated with wet air at 25^0C in the absence of gravitational sedimentation (see Appendix B), the deviations from Dalton's law would be catastrophic, because the much larger electrostriction expected for water vapour will unambiguously *lower* the total pressure at each addition as long as any water remains to be removed.

These are only imaginary experiments, of course, but it is difficult to see anything wrong with the prediction of gross abnormalities in thermodynamic behaviour for low-temperature wet air, closely parallel to those observed in super-critical solutions. In particular, it seems unlikely that any procedure for obtaining standard free-energies by the use of equation A1 could be easily modified so as to yield usable standard chemical potentials in cases like this.

The important point is this: There is no reason to believe that a system including ions and water vapour will behave like a normal system in which reasonably valid approximations can result if activities are replaced by concentrations. We have no idea how to define thermodynamic activities or standard-state chemical potentials in these systems. The author's approach to ball lightning (Turner, 1994) was designed to avoid problems like this. (There are also related problems resulting from the known complexities of nitrogen chemistry in wet systems; discussed elsewhere (Turner, 1994, 2002)).

Now we can consider the connection between thermodynamics and rate processes in solution.

The considerations apply equally whether the processes are occurring in a liquid or gaseous phase. The driving force for any chemical or diffusional change results from the thermodynamic requirement that the process thereby reduces the total free energy of the system. As a reaction proceeds, the free-energy difference driving it decreases and this free energy can be considered to depend on a so-called progress variable (Kirkwood and Oppenheim, 1962),

$$\lambda = (x_i n - n_i^o) / v_i \qquad \text{(A9)}$$

where n_i^o is the number of moles of component i at time zero, x_i is its mole fraction at some later time, v_i the number of moles of i formed in the reaction (negative for reactants), and n the total number of moles in the system. The driving force at any stage of the reaction can be described in terms of this variable---in principle, though rarely in practice. If there are concurrent chemical reactions, each will have its own separate progress variable.

In normal solution-phase reactions, any consideration of the progress variable is rare, presumably because parallel reaction paths are much less common in a liquid than in the gas phase and because the variable cannot be measured. When the solvent for ionic species is very wet air, such considerations can be used to show that simple kinetic models must be invalid because the presence of parallel reactions is unavoidable (Turner, 2002).

Consider now the rate of any reaction that is moving towards some equilibrium state. At equilibrium, the rates of the forward and reverse processes are the same (an alternative and equally valid definition of the state of equilibrium is based on this fact). However, the actual driving forces for the both the forward and reverse processes are thermodynamic. Thus the definition in terms of rate processes can only be valid if reaction rates are expressed in terms of activities and not concentrations. This has long been known, but it is usually neglected because the distinction can be negligible. For the systems we are considering, which involve humid air, the distinction cannot be neglected. We simply do not know how to relate activities to concentrations and, as seen above, the reason is associated with the fact that the solvent for the ions is compressible. There is no reason to suppose that the usual formulations of rate equations in terms of concentrations have any validity in the systems which concern us.

Appendix B : Water and Steam as Solvents.

The importance of water in biology, agriculture and industry has been long appreciated, and for this reason its solvent properties have been much studied; but the great majority of studies have been confined to the liquid phase at temperatures near 25^0C. In fact, a gaseous mixture is not usually referred to as a solution at all, the word “solution” normally implying a liquid. Nevertheless, for a condensable fluid like steam, there is no fundamental difference between the two types of mixture because of the phase continuity that exists above the critical point.

Fig. B1 near here.

The gas-liquid critical point of a fluid can be defined in several ways. The basis for several of them is illustrated in Figure B1, which shows the densities of water and steam (in g cm^{-3}) as a function

of pressure for selected temperatures up to 400^0C. The region represented covers much higher densities than those where the ideal gas laws apply; these would be at the extreme left of the plot and the isotherms would resemble nearly vertical straight lines next to the y axis. The region enclosed by the dotted line and the x axis is unavailable to a real homogeneous fluid because of phase separation.

Suppose that we half fill an autoclave with water and heat it to 350^0C. (Assume that, before filling the vessel, it was evacuated so that any complications from the presence of air were avoided; and assume that the vessel is transparent and non-corrosive.) The fluid would remain separated into two phases and these would have the densities given by the two intercepts of the horizontal line marked 350 with the dotted line. If one were then to raise the temperature further, the density of the liquid would continue to fall and that of the steam would rise. However, the fractional fill of the autoclave would start to change dramatically as the temperature neared 374^0C and before this temperature was reached the autoclave would be full of liquid water. If we continued to raise the temperature to 400^0C the (now water-like) fluid would have a pressure of about 380 bar.

If we had started with the autoclave only a quarter full, the liquid phase instead of the steam phase would have disappeared by 374^0C and this time the meniscus would have disappeared from the bottom of the autoclave. On further heating the steam-like fluid to 400^0C, it would acquire a pressure of nearly 280 bar.

We could then do a third experiment, starting with the autoclave initially fractionally filled at the equivalent of what is called the critical density. For water, this would be a fractional fill of 0.322. In this case, we would find that neither steam nor water predominated when a temperature of 374^0C was reached. The meniscus would simply disappear at this temperature and, if we had been very careful about control of the temperature, percentage fill and purity of the water, we could, in principle at least, observe the phenomenon of critical opalescence. This phenomenon would arise because we had arrived exactly at the critical point where the fluid essentially could not decide whether it was really a liquid or a gas. The temperature at which the distinction between the two phases disappears is, not surprisingly, called the critical temperature and the pressure at which it occurs, the critical pressure.

Figure B1 also illustrates a related aspect of the near-critical region, that the slope of an isotherm at the critical temperature is zero. This means that the compressibility of the fluid (the slope's reciprocal) is infinite at the critical point.

Solutions also have critical points, but their critical parameters depend on the properties of the solute and its concentration. If one attempted to define a solute standard-state at the solution's critical point, using an activity coefficient theory valid only for an incompressible solution, one is hardly likely to obtain a meaningful result. This is another example of the problems referred to in Appendix A.

Another unusual property of a pure fluid at its critical point arises from the fact that its compressibility is infinite. As a result, the small pressure-difference arising from the height of any realistically sized sample yields a super-critical pressure at the bottom of the cell and a sub-critical pressure at the top. This is why physicists interested in the details of critical behaviour can learn so much more by working in a low-gravity environment than they can on earth.

As early as 1927, some very informative experiments were performed on the behaviour of salts in water near their critical points (Shröer, 1927). Using solutions of coloured salts and employing extremely precise temperature control, evidence for stratification of the solvent with sedimentation of the electrolyte was obtained. The results of later conductance studies by Corwin et al. (1960) imply that for very dilute solutions of common salt, the stratification effects extend much further from the critical point than they would for the solvent alone. These authors in fact observed sedimentation at 390^0C and the critical pressure, which is about 16^0C above the solution's critical point. No pure liquid is detectably stratified even 0.01^0C above its critical point. It seems obvious that the presence of the salt greatly enhances the stratification in a non-linear manner, presumably as a consequence of the greater solvating power of water at higher densities combined with enhanced density differences. In steam of lower densities, we expect the clusters around the ions to be no less dense but the surrounding fluid to be much less dense. Thus the expected sedimentation would be greater and would lead to even larger field-dependent concentration-gradients for sub-critical steam.

The shaded areas of Fig B1 represent the approximate regions where ionic equilibria have been studied with sufficient care to provide useful thermodynamic data. There is a notable absence of data in the low-density vapour region (on the left) and in the whole region surrounding the critical point. In view of what has been said above and in Appendix A about the problems of dealing with compressible solutions, this is not surprising.

The problems of defining the standard-state thermodynamic properties of normal (liquid-phase) electrolyte solutions only become serious if their compressibilities are significant. In water, the problem only starts to become apparent at temperatures above about 250^0C. Above that temperature, the activity coefficients and standard-state properties begin to suffer from compressibility effects (Turner, 1983). At higher temperatures, these problems become increasingly serious until, as we have seen, at the critical points of the solutions, they appear to become insurmountable.

It seems, then, that whether ions are dissolved in water, super-critical steam, water vapour or wet air, they present serious problems to the physical chemist. Routinely used assumptions and approximations should not be used in such systems without great care.

Appendix C: Theoretical Approaches

In Appendices A and B, the considerable present limitations of vapour-phase electrochemistry have been outlined. Knowledge is more advanced in certain other sub-disciplines of physical chemistry on which the author's ball-lightning model draws. This Appendix will show that the main chemical approximation on which the model is based is at least qualitatively realistic.

A characteristic of any fluid is that its properties can be changed *continuously* from one state to another by appropriately altering its temperature and pressure. This property is referred to as its continuity of states. Suppose we started with water at 25^0C and raised its pressure well above that of the critical pressure (see Appendix B for definition). We could then raise its temperature to well above the critical temperature. Now we could drastically reduce the pressure to 1 bar and cool the steam produced to 100^0C. So long as we had ensured that none of the relevant variables had fallen below the critical parameters at the wrong stage (i.e. we had avoided the two-phase zone below the dotted line in Figure B1), we would have changed the water into steam without there ever having been a change of

phase. We could, of course, have accomplished the same thing more directly, but there would have been a phase change (boiling). By using the roundabout route, no step has involved a phase change and no phase boundaries need to be considered.

The fact that this can be done has proved very important theoretically (Rowlinson and Swinton, 1982), because of the considerable problems that face a theoretician when dealing with liquids. Solids and gases are much better understood than are liquids, because very simple and accurate models describing their idealized behaviours exist and these have, for over a century, provided a basis for theoretical development. This is not true of any liquid and, because of its large dipole moment, water is a particularly difficult liquid to treat theoretically.

Statistical mechanics provides the theoretical link between the properties of molecules and thermodynamics. Intermolecular forces and their dependence on intermolecular distances are obviously of crucial importance and the continuity of states means that experimental conditions can be adjusted to provide severe tests of the theories.

In dealing with gaseous atoms and molecules in their standard states (no intermolecular forces), statistical mechanics can produce results of astonishing accuracy. For example, calculated standard entropies for gaseous molecules are often far more accurate than those obtained experimentally; for gaseous ions, statistical mechanics usually provides the only way of obtaining them accurately. The theoretical problems with liquids arise because intermolecular forces are too strong to ignore but much weaker and less precisely defined than those found in isolated molecules or solids.

Significant advances have been made in understanding simple molecular fluids theoretically (see for example, Rowlinson and Swinton, 1982; Gray and Gubbins, 1984), but even with the help of the fastest computers, formally correct theories cannot meet the needs of an applied scientist interested in the behaviour of very dilute electrolyte systems. Simple models and empirical relationships still provide the only realistic approaches. These mostly exploit the abundant supply of experimental data available on aqueous systems at 25^0C.

One obvious approach to understanding the behaviour of electrolyte solutions is the thermodynamics of ion hydration. Progress has been slow, but a reasonably detailed understanding of where the problems lie has been achieved. Thermodynamic cycles and simplified substitutes for them have been tried. These can involve different ways of splitting up and treating the various expected contributions to the energies and entropies. The circuitous route just described to illustrate the continuity of states can be considered to be part of a thermodynamic cycle. If we had gone a little further by cooling the steam from 100^0C to 25^0C and then increasing the pressure (this time allowing a phase change), we would have completed the cycle. If, for some specific calculable or measurable property, such as an enthalpy, we added the contributions (algebraically) from all the steps round the cycle, we would know that the final sum should be zero. This has the potential to provide a good check on the accuracy of each component in the cycle. Alternatively, if just one of the steps cannot be quantified, either by measurement or theoretically, the value relating to that step could be estimated from data on the remainder of the cycle.

One great strength of thermodynamics is that it allows the use of this kind of cycle for properties like those discussed in Appendix A. Of course, a related weakness is that filling in one small gap may not seem exciting either to a scientist or to a potential funding agency. This problem is much

more serious when there are two gaps and, if there are more than two, one would probably have to wait until the whole field had advanced considerably.

Studying the thermodynamics of ion hydration usually involves a cycle of some sort and the cycles can be constructed in different ways. The complications of coping with activity coefficients as well as standard-state properties has meant that attention has been confined to the latter properties. Studies of hydration thermodynamics thus involve a purely hypothetical process, that of removing an ion from its standard state in the gas phase (see Appendix A) and placing it in the appropriate standard state in solution. In this thermodynamic sense, hydration is still considered to have a precise meaning.

Although non-thermodynamic approaches cannot use cycles like this because the properties are not additive, the information they do provide is crucial. For example, the structure of a solution can be studied using various kinds of scattering techniques. Also, the rate of exchange of a solvent near an ion and the ion's mobility have proved instructive. Only a model consistent with all relevant non-thermodynamic data could provide reliable quantitative predictions. Intuitively we would expect such a model to be rather complicated.

Such models can be very informative, but there are conceptual difficulties not so far considered. In Appendix A, it was implicitly assumed that all the solutions are electrically neutral. In practice, it is impossible to study any liquid-phase solution where an ion imbalance is detectable by chemical means. However, in the gas phase, this limitation does not apply. In fact, some of the studies of ion hydration discussed in Section 4 of the main text were made under conditions where only ions of the same charge needed to be considered.

Obviously, if we wish to study the thermodynamic effects of moving an individual ion from a gas into a liquid solvent, we need a way of establishing the thermodynamic state of the dissolved ion. This cannot be done rigorously because, in solution, we can only obtain strictly valid thermodynamic data on uncharged *pairs* of ions (Guggenheim, 1967). Various approximate methods for estimating single-ion contributions to the thermodynamic properties of electrolytes have, nevertheless, been devised and have been used to establish so called "absolute" values for the thermodynamics of ion hydration. These can be informative, but the absolute values are far less precisely known than are the relative ones (obtained from pairs of ions).

One of the most detailed analyses of the basic problems of ion hydration (Bernal and Fowler, 1933) confirmed the expectation, mentioned earlier, that hydration is a complicated process. Nevertheless, many people over the years have tried to find simpler formalisms, and these have helped to rationalize the available data on solutions, both aqueous and non-aqueous, and much has been learned from these attempts. They are, however, still very limited in their predicting ability. Most of them have started from the Born equation

Equation C1 here

which describes the purely electrostatic consequences of moving a charged sphere of radius r from vacuum to a liquid. Here ze is the charge on the ion, N is Avogadro's number, ϵ_0 is the permittivity of free space and D is the dielectric constant of the fluid. If we take r to represent the radius of an ionic solute, this equation can be used to estimate the electrostatic contribution to its free energy of solution and hence, by differentiation, the corresponding enthalpies and entropies.

All simple models of this type fail in the sense that they require empirical fitting parameters because the model of a spherical charged sphere in a continuum dielectric is not realistic when r is of molecular dimensions. It is necessary to allow for at least two unavoidable facts. First, the electric fields near an ion are so large that the dielectric constant of the solvent is significantly reduced locally. Second, the dielectric constant is a property of a continuum fluid and is not applicable near an ion where the molecular structure exerts a major influence. The main importance of water in science and engineering arises from its unique properties which, in turn, arise from its unique structure. The relevant properties include water's excellent solvating power for ions and its unusually high critical temperature.

At the time my colleagues and I embarked on hydration studies, one long-term objective of the industry for which we worked (the electric-power industry) was a better understanding of boiler-water chemistry. Our most valuable boilers operated at 350^0C and almost nothing was known about solution chemistry at that temperature (see Figure B1). Our concerns with the theoretical problems of steam-phase electrolytes (Appendix A) became dominant a little later. Since the only temperature for which extensive sets of thermodynamic data are available is 25^0C, it was obviously desirable at least to assess the possibilities for estimating high-temperature data from those at 25^0C. It was clearly necessary to try to circumvent most of the known problems including those just described. We decided to try a new approach which, instead of concentrating on modifications to simple Born-equation models, examined, in some detail, the thermodynamics of a single very-well-studied ion.

The hydrogen ion, by far the most important ion in biological, chemical, and many physical systems, has been studied more extensively than any other. In aqueous solution, a proton is immediately changed into the exceptionally strongly hydrated form H_3O^+ which somewhat resembles Li^+ in size. Both are very small, so we know that the structure and effective dielectric-constant in their vicinity will invalidate any simple Born model. This is less certain for the ion $H_9O_4^+$ which, in solution, represents H_3O^+ hydrated by one complete sheath of water molecules. Its properties in the gas phase have been the subject of many theoretical calculations as well as experimental studies, some of which were referred to in Section 4 of the text.

We decided to investigate whether the problems associated with the Born equation were still significant for ions of the size of this hydrate, by calculating all the relevant contributions to the process of proton hydration using relationships that involve no arbitrary fitting parameters. The long-term plan was to perform a similar exercise for the hydroxide ion (the second most studied ion) and then to compare predictions of the model with data on the self-dissociation of water. The equilibrium constant for this reaction (K_w) has been far more studied than any other, and good data are available up to 300^0C. There are also some data well above the critical point, as well as interpolations for in-between conditions. A rough test would also be possible at an earlier stage, once predictions for the hydration of the proton were available. This test would, for the reasons given above, be much less stringent than K_w, but still useful. It was hoped that the deviations of predicted values from the experimental ones would indicate which parameters should most realistic be adjusted during subsequent attempts. In the event, we got no further than this first phase because of the turbine failure mentioned in Section 3 of the text. This directed our subsequent attention from the problems of boiler water to those of turbine steam. Some of the subsequent work has been referred to in Sections 3 and 4.

For the proton, the many available measurements and calculations made it possible to consider its hydration enthalpy and entropy in unusual detail. Several of the terms involved required

approximations and, in every case but one, these could be made objectively and on a basis that few would challenge. However, the exception involved one of the largest terms and required the choice of a fluid model in which many theoreticians had little faith. This was a development of the scaled-particle theory first applied to aqueous systems by Pierotti (1965). Our interest was exclusively in the solute, the specific aim being to estimate the size of the cavity into which $H_9O_4^+$ was to be put; the enthalpy and entropy associated with the cavity formation could then be calculated. Thus our purposes were significantly different from those of most theoreticians, and the model's advantages seemed to outweigh its limitations.

An attractive point, conceptually, was that scaled-particle theory is based on departures from an ideal hard-sphere model for a liquid. Thus it provides a rather natural first approximation for predicting the behaviour of any liquid whose compressibility is low. It can also be simple to use and, more important for aqueous solutions of non-electrolytes, it had proved surprisingly successful. Most significant was its apparent success in treating entropies of solution in water since, for many years, such entropies had been considered highly anomalous (Frank and Evans, 1945), which had appeared to preclude realistically estimating high-temperature properties from those at 25^0C.

Pierotti (1965) had checked his calculations using data on the dissolution of some simple non-electrolytes in water. These were basically the same properties that Frank and Evans had concluded could only be explained by invoking specific structural influences for each solute. However, Pierotti had fitted the data using scaled-particle theory. Hard-sphere diameters were needed in the theory, and he used gas-phase collision-diameters for the solutes. These differ significantly from any diameter applicable to a condensed phase, and their use seemed to introduce an internal inconsistency into the model. Nevertheless, the agreement found for all the relevant thermodynamic properties was remarkably good. The implication Pierotti drew was that the hard-sphere model takes complete account of the structure-making abilities of specific solutes in describing the size of the cavity into which the solute must be placed when it is moved from gas to liquid.

Assuming this implication to be true, a method was still needed by which the effective size of an ion cluster could be obtained. Gas-phase collision-diameters are not available, so a method was developed based on tabulated inter-nuclear distances and the Van-der-Waals radii of Pauling (1960). However, no molecule is strictly spherical and only methane (where the protons are well embedded into the electrons of the carbon atom) would be a good approximation to a sphere. Thus it was necessary to ensure that the sizes would be consistent with the rare-gas sizes.

The condition for consistency was taken to be that a non-spherical solute should have the same surface-area as its equivalent hard sphere. This condition would be more realistic than one based on a similarity of volumes because, in our model, a cavity resembled a surface. For tetrahedral, pyramidal and octahedral molecules, the additional assumption was made that the outer surface could not be anywhere concave. This simplified the calculation of the surface area and is likely to be more realistic than an indented surface. Calculations of average electron contours in some of the poly-atomic molecules have suggested that the degree of indentation is not great.

Figure C1 compares the diameters obtained in this way with those calculated from scaled-particle theory using available solution entropies. The latter represent the nineteen simplest non-ionic solutes whose solution entropies were, at the time, known reasonably reliably; they varied in size from neon to sulphur hexafluoride.

Fig. C1 near here.

The straight line has unit slope but it is apparent that a small correction to the geometric diameters is needed to allow the cavity diameters to be obtained from them. The only point far off the line was for acetylene, which is perhaps not well characterized as a hard sphere. Assuming that the straight line can be extrapolated to slightly larger diameters than sulphur hexafluoride, and that the conclusions of the then-current theoretical calculations on the dimensions of $H_9O_4^+$ were reliable, the diameter was estimated to lie between 6.0 and 6.2 angstroms. Hydration enthalpies and entropies were calculated for both of these cavity diameters.

The cycle used in the enthalpy calculations is summarized schematically in Fig. C2. It mainly follows the water round the cycle, but the phase transfer of the proton can be inferred from it. ΔH_D is the enthalpy change associated with the dissolution of the $H_9O_4^+$ cluster ion in water. This term includes the effects of creating the cavity and inserting the structurally unaltered cluster into it plus those associated with electrostatically discharging the ion in the gas and re-charging it in the liquid (Born charging contribution). In addition, contributions must be added to cover the interactions of the inserted cluster ion with its environment. These include changes that necessarily accompany the transformation of free rotations (in the gas) into hydrogen-bond-bending modes (in the liquid). The interaction term was taken to be the enthalpy of formation of six half-hydrogen-bonds and the others were obtained from fairly standard, though approximate, treatments of available spectroscopic data. In other words our model assumed no actual breaking of hydrogen bonds on hydration.

Fig. C2 near here

A complete cycle for the water molecules involves evaporation from the infinite sink of water (the $4\Delta H_0$ term), reaction in the gas phase with the proton (ΔH_G), dissolution of the cluster as just described and the return of the four water molecules to the pure solvent. At the same time, the proton is removed from the solution back to the gas, the reverse of hydration of the proton. In this case the arrow representing the missing step in the cycle, $\Delta H_{H,}$ is shown in the reversed direction to signify that, after all these processes, the effect on the proton has been to transfer it from gas to liquid.

An analogous process is involved in calculating the entropy of hydration but an extra step is needed to allow for the fact that the four water molecules carried into the solution with the cluster ion are not really distinguishable from the other water molecules present. Also, so as to use the most accurate data, the terms had to be added in a slightly different way. For the entropy, the uncertainties in both the cavity size and in some of the vibrational frequencies lead to relatively larger errors than for the enthalpy. The problem with the vibrational frequencies is both the weakness of the hydrogen bonds compared with normal covalent bonds and the fact that their motion deviates markedly from an ideal simple-harmonic-motion.

The calculated contributions to the enthalpies and entropies are shown in Tables C1 and C2. The agreement between the experimental and calculated values was unexpectedly good in both cases. As a result, the exercise did not help in guiding us to where any adjustments might best be applied in future. Clearly, this is not the place to discuss the reliability of the model or the validity of the various choices necessary. However, it does indicate that it is worthwhile to develop a similarly based but simpler model. This eventually provided the crucial step in understanding ball lightning.

Tables C1, C2 about here

At the time these calculations were performed, experimental values for ΔH_H were believed to lie between –1084 and –1128 kJmole and those for ΔS_H between –118 and –134 J/K/mole. The dominant role of the enthalpy contribution from the gas-phase reaction is apparent in Table C1.

Pierotti's (1965) suggestion that scaled-particle theory allows one to dispense with the concept of structure-making is not universally accepted, although others have come to the same conclusion. At least at the level of approximation that the above calculations allow, and at least for the hydrogen ion, the agreement between experiment and calculation does appear to support his claim. It was partly because of the lack of clarity still surrounding these issues that no attempt was made, in Section 4, to consider any other scenario than equal hydration numbers for the H_3O^+ and nitrite ions.

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Table 1: Standard-state thermodynamics of reaction (1)

n	0	1	3	5	7	10	15
ΔH^o/kJmol^{-1}	-700	-487	-217	-11	169	433	872
ΔS^o/Jmol^{-1}K^{-1}	14	241	687	1174	1640	2332	3521
ΔG^o/kJmol^{-1}	-704	-559	-422	-361	-320	-262	-177

Table 2: Estimated ball lightning radii

Inward Velocity u /m.s^{-1}	Dirty City r_b /mm	Over Ocean r_b /mm
10^{-1}	3.6	59
10^{-2}	12	186
10^{-3}	36	586
10^{-4}	115	1860

Table A1: Apparent Molar Volumes of NaCl Solutions at 385^0 C and 243 bar.

Concentration (mol kg^{-1})	$-\phi$ dm^3 mol^{-1}	Hydration Number	Mole Ratio
0.034	24.9	657	1630
0.173	7.69	212	321
0 529	3.58	99	105
1.237	1.81	50	45
2.325	1.04	29	24

Table C1: Contributions to hydration enthalpy of the proton at 25^0 C

Contribution *		Designation	Value (k joule /mole)
Water evaporation		$4\Delta H_V$	+ 176.1
Gas phase hydration		ΔH_G	- 1005.4
Interaction with cavity		ΔH_I	- 66.0
Restricted rotation		ΔH_R	+ 2.3
Cavity formation	(6.0 Å)	ΔH_C	+ 7.8
	(6.2 Å)		+ 8.3
Born charging	(6.0 Å)	ΔH_B	- 247.0
	(6.2 Å)		- 238.9
Total	(6.0 Å)	ΔH_H	- 1132.2
	(6.2 Å)		- 1123.6

* The enthalpy of dissolution, $\Delta H_D = \Delta H_I + \Delta H_R + \Delta H_C + \Delta H_B$.

Table C2: Contributions to the hydration entropy of the proton

Contribution		Designation *	Value (joule /K /mole)
Water evaporation		$4\Delta S_V$	+ 475.2
Gas phase hydration		$\Delta S_G^{\#}$	- 488.5
Restricted rotation		ΔS_R	- 59.5
Standard state change			- 34.9
H_2O indistinguishability			+ 133.6
Cavity formation	(6.0 Å)	ΔS_C	- 135.0
	(6.2 Å)		- 143.0
Born charging	(6.0 Å)	$\Delta S_B + \Delta S_I$	- 20.1
	(6.2 Å)		- 19.2
Total	(6.0 Å)	ΔS_H	- 129.2
	(6.2 Å)		- 136.3

* The suffices refer to processes roughly analogous to the those yielding the corresponding enthalpies.

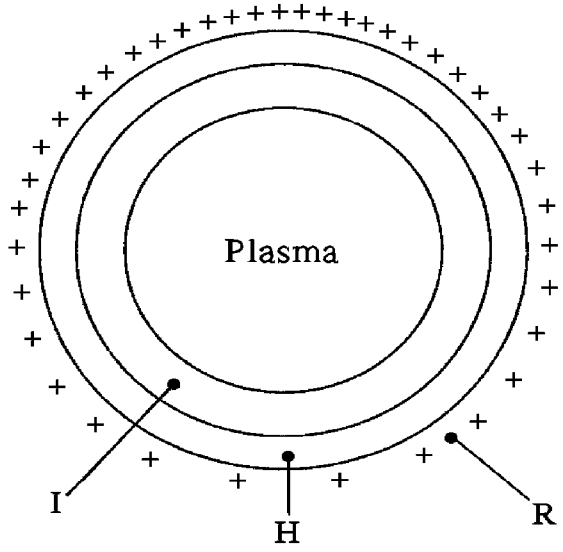

Fig 1: Structure of an idealized spherical lightning ball.

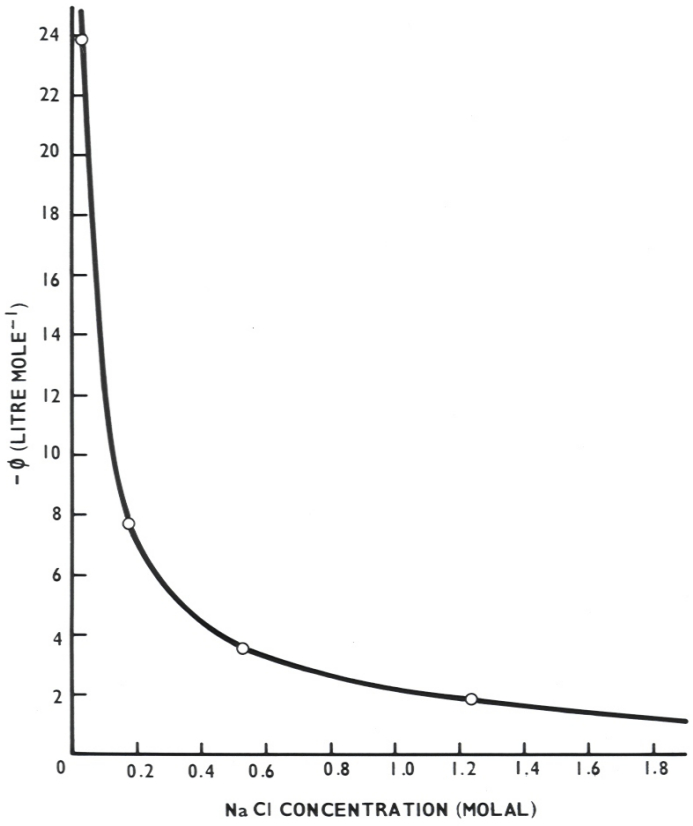

Fig. A1: Apparent molar volume of aqueous NaCl, ϕ, at 385^0 C and 243 atm.

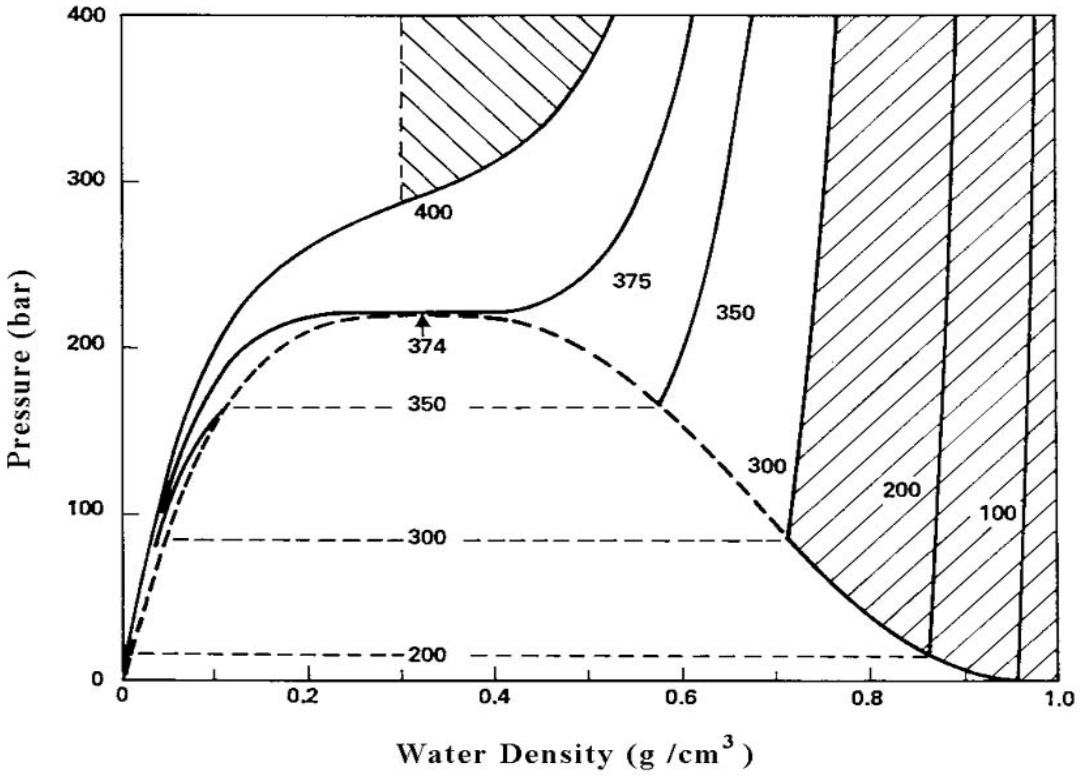

Fig .B1: Phase diagram for water with regions of electrolyte study.

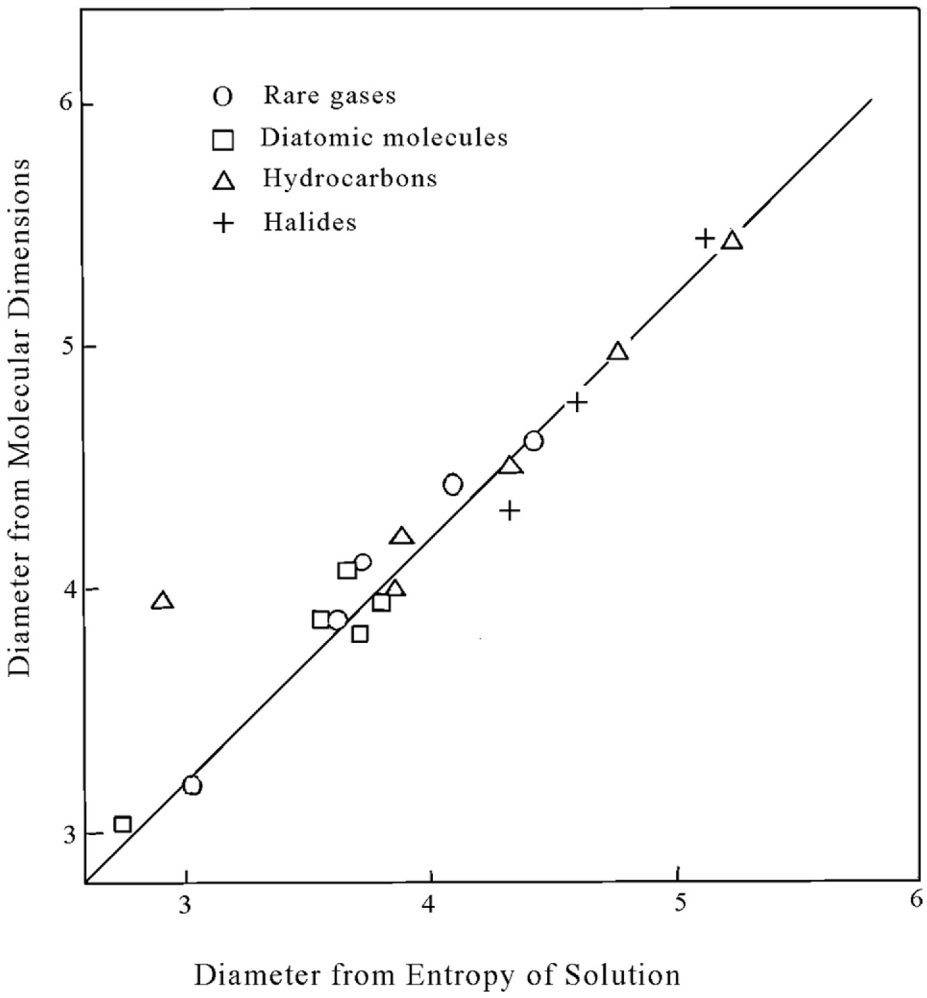

Fig. C1: Molecular diameters (in Å) from Van der Waals radii and entropies of solution.

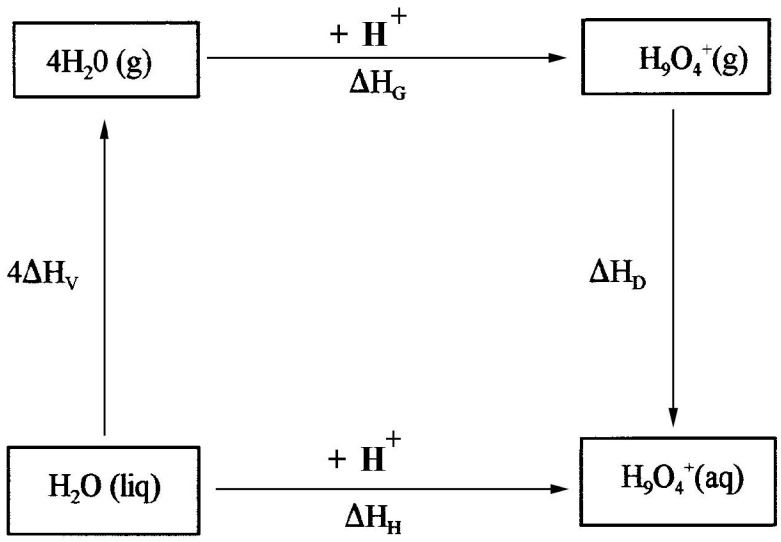

Fig. C2: Cycle for estimating the hydration enthalpy of the proton.

Graphics Equations

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad (A1)$$

Definition of chemical potential

$$\sum_{i=1}^{r} x_i \mu_i = 0 \qquad (A2)$$

Gibbs-Duhem equation

$$\Delta \mathbf{G} = - \frac{(\mathbf{z}e)^2 N}{\mathbf{8}\pi\varepsilon_{\mathbf{0}}\mathbf{r}}\left(\mathbf{1} - \frac{\mathbf{1}}{\mathbf{D}}\right) \qquad (C1)$$

Born equation