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Vapor Phase Electrochemistry: The Missing Science

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HIGHLIGHTS

Evidence suggests that the atmospheric and earth sciences lack a correct understanding of the link between the electrostatic fields of ions and chemical processes in moist air and steam.

ABSTRACT

Several aspects of physics have been adversely effected by the fact that vapor phase electrochemistry has proved impossible to quantify. By the end of the 19th century, physicists had encountered several strange observations that appeared to involve chemistry. Eventually, it was realized that, in a moist gas, no rate process involving ions is quantifiable since we possess no valid relationship between the concentrations of electrolytes and their thermodynamic activities. There are both technical and societal reasons for this problem. Until both problems have been addressed, no reliable quantitative conclusions can be drawn for any system where ionic electrostriction in a moist gas is important. The most obvious consequences of the *missing science* are misconceptions concerning naturally contained air plasmas such as ball lightning, tornadic lights, and unpredictable flying objects (UFOs). None of these phenomena violates *any* known law of physics, but this only becomes clear once the absence of applicable, strictly valid theories is accepted. Fortunately, partial solutions to the problem exist if use is made of qualitative arguments. Using this approach, it can be seen that all the *apparently* anomalous characteristics of atmospheric plasmas result from a balance between different physical and chemical driving forces. A better understanding of the chemical consequences of electrostriction should have two long-term benefits. One relates to understanding the corrosive properties of high-pressure steam. The other concerns the specific chemical processes that stabilize air plasmas. If stable air plasmas could be simulated, a plentiful supply of carbon-free energy would become available.

KEYWORDS

Electrostriction, thermodynamics, condensation, air plasmas.

INTRODUCTION

In any current scientific study, it is usually unnecessary to investigate experiments from long ago. This is because scientific disciplines have become very specialized as they matured and all the most useful early studies are believed, by now, to have been incorporated into accepted paradigms. The implication of the material to be discussed is that disciplines exist where this process has failed. Exciting new facts are being discovered all the time, but a few long-known facts are still largely unexplained.

The present study resulted from the identification, beginning in the late 1970s, of a small area of physical chemistry, mainly chemical thermodynamics, that has never been developed. Some of the most serious consequences of the missing science were first identified at the Central Electricity Research Laboratory (CERL), a laboratory of the Central Electricity Generating Board (CEGB) in the UK.

Various different aspects of the problem were identified later, and by 2003, several different ways of describing them had been employed (Turner, 1980; Gates, Wood, & Quint, 1982; Wood, Smith-Magowan, Pitzer, & Rogers, 1983; Turner, 1983; Beysens, Straub, & Turner, 1987; Turner, 1987, 1988a,b, 1990a,b, 1992, 1994, 1996, 1998, 2003). The connection between steam-related problems in the electric power industry and the strange behavior of ball lightning was first seen in the 1990s (Turner, 1994), although the full significance of the relationship was not appreciated until much later. The most obvious manifestations of the basic problem concern the properties of air plasmas which erroneously appear anomalous because valid theories do not exist. The missing science will here be referred to as vapor phase electrochemistry.

The main problems of concern in what follows apply to *all electrolyte solutions in moist gases*. A linguistic problem that is closely related to the scientific one should be noted here. It is not normal to refer to *solutions* in gases, but it seems the appropriate word here because *ions at equilibrium* would not exist in the gas phase near room temperature (at any detectable level) were it not for solvation (electrostriction) in a moist gas.

One of the clearest ways of seeing the connection between the two phases of any fluid uses a concept known as the continuity of states. This expresses the fact that the properties of gases and liquids are very closely related. In fact, the thermodynamic properties of any sufficiently dilute room temperature solution can be changed (without suffering any change of phase) to those in the gas phase. This can be accomplished by pressurizing and heating the dense fluid above its critical point and then de-pressurizing and cooling it (now in the gas phase) back down to room temperature. This fact implies that, in any system involving ions in a moist gas, it might prove necessary to accept the importance of *undetectable* quantities of ions *at equilibrium* (Turner, 2003).

In this context, the most crucial parameter of an electrolyte solution is its compressibility, this being infinite at a fluid's critical point. For the systems to be considered here, the simplest way of describing most of the basic problems is to refer to the missing science as vapor phase electrochemistry. The missing science as vapor phase electrochemistry - even though this description ignores lack of generality of the problem. In fact, exactly the same limitations apply to liquid phase solutions of electrolytes near their critical points as to solutions in steam and in moist air.

At present, it seems that studies in moist air are far more likely to receive support than any directly relevant study on high-pressure fluids. A summary of the scientific problems, all of which are basically thermodynamic, is provided later. The seemingly crucial societal problems are summarized in Appendix A (https://naturalplasmas.com/files/VPE1_AppendixA).

It will be argued that the wide failure of scientists to acknowledge the extent of our ignorance in this field is having a variety of serious consequences for science and society. One very inconvenient consequence for any scientist addressing these problems is that a wide variety of empirical facts need to be drawn together before arguments are clear. This can require publications of an unacceptably long length, and this tends to make it impossible to include all the relevant facts at once in any peer-reviewed journal. One result is that referees of papers on the subject have totally failed to understand the full significance of the missing science.

Water in Industry and the Atmosphere

We shall be seeing that one of the factors that has led to the overlooking of a crucial part of physical chemistry is specialization. The problem has, of course become increasingly difficult to address with time. By the end of the nineteenth century, much was already understood about the properties of electrolytes in water and a considerable number of experiments on moist air had been described . Several of the latter studies had been attempts to understand the role of ions in cloud condensation."

Among these were descriptions of incompletely explained phenomena that have long since been forgotten (Tyndall, 1868; von Helmholtz, 1887; von Helmholtz & Richarz, 1890; Thomson, 1893; Rutherford, 1898; Thomson, 1898; Townsend, 1897a,b, 1898, 1915; Wilson 1897;

Wilson, 1899a,b). Conclusions from a few of these studies were subsequently used to estimate the electric charge of the electron (Thomson, 1906; Townsend, 1915), but otherwise, they have been forgotten. All these studies were conducted by physicists, but many of the findings appeared to be complicated by chemistry.

These early observations and more recent studies of *apparently* anomalous phenomena, imply that our understanding of cloud condensation is very far from complete (Turner, 1998, 2002, 2003). For over a century, hardly anyone has felt the need to address the subject of vapor phase electrochemistry. Some of the reasons this situation has arisen are easily understood, and they will be indicated where appropriate. An important reason is fashion since both scientists and those funding science greatly value novel ideas. In addition, the vast quantities of new information now being collected can encourage the belief that interpreting this new data by modeling is more important than understanding basic principles. The need truly to understand how quite different pieces of information fit together seems particularly clear in the systems referred to here.

Fortunately, there are hints in the late 19th and early 20th-century literature of phenomena which, if followed up in new ways, might advance our understanding of how electrostriction influences chemical processes in humid air. In addition, a number of new experiments which support some of the arguments made here have been completed recently. They are described elsewhere. First, it is necessary to explain the connections that exist between relevant studies from the late 19th century and those of the mid-20th and early 21st centuries. A basically historical approach is used but not a strictly chronological one.

The electric power industry relies heavily on the use of high-pressure boiling water for driving steam turbines, whether the energy source is coal, oil, or nuclear power. There was (Staehle, 1977), and continues to be, a crippling shortage of relevant thermodynamic data on electrolyte solutions in high-temperature water under conditions where the liquid and vapor phases are in equilibrium. Electrolytes dissolved in boiling water can lead to serious corrosion and corrosion-related problems, while, in steam, the consequences of stress corrosion have occasionally proved catastrophic (e.g., Hearn & Jones, 1971). In neither case are the roles of electrolytes well understood. Our ignorance is even greater regarding the very low concentrations of electrolytes that are *always present at equilibrium* in moist air (Turner, 1994, 1996, 1998, 2002).

The main cause of all the modeling problems is electrostriction, through which immense numbers of water molecules are drawn into the electric fields of any ions present. Such conditions arise in highly compressible water, in steam, and in moist air. Staehle's (1977) comments referred specifically to the thermodynamic data needed in studies of liquid phase corrosion, these data providing the driving forces for the processes that lead to corrosion. Related processes that have serious consequences are the transport and deposition of corrosion products in high-temperature water circuits. At the time of Staehle's comments, attempts to study the dissociation of electrolyte solutions near the critical point of water had only just begun, and reliable data from which dissociation constants might have been estimated were also unavailable.

Beginning in the 1990s, hints of serious mistakes in scientific and technological areas *other than electricity generation* began to be collected. They were from diverse reports in the literature, and all seemed to result from the same missing science (Turner, 2003). This realization followed an earlier, very unexpected conclusion: *no well-established property of ball lightning violates any known law of physics* (Chown, 1993; Turner, 1994; Matthews, 1994; Anonymous, 1994).

Later it was revealed that the same is true of the real objects (as opposed to psychological effects) usually called unidentified flying objects or UFOs (Turner, 2003, 2023a). These objects are sometimes more accurately described in other ways, such as unidentified aerial objects or UAOs. However, the more familiar term will be used here since the acronym also stands for unpredictable flying objects. One factor that probably perpetuates our ignorance in these fields is a difference in the kinds of systems that physicists and chemists are trained to study. There are always better supported, better understood, or more convenient problems to study. Furthermore, many people like to believe in the existence of perpetually unexplained mysteries.

Technical and Societal Difficulties

The sciences can be crudely divided on the basis of three very different concepts, which are, in effect, different articles of faith. Physicists tend to believe that mathematics controls everything of importance in physics.

Chemists believe equally firmly that atoms and molecules provide the basis for reality, while life scientists and those in the medical profession put their faith in the molecular processes that occur in cells. Electrochemistry fits poorly into such classifications because the concepts of *both particles and fields* are equally important, while physical or chemical fields are otherwise of little concern to most chemists. Both chemists and physicists seem to have difficulty believing in the importance of *chemical fields* at the boundary between an air plasma (or a normal flame) and ordinary moist air. In fact, they are very important.

Electrochemistry is normally considered to be concerned only with the liquid phase. The practical problems with which it deals usually relate either to processes that occur at the electrode surfaces of batteries or with those associated with corrosion. In both cases, a state of kinetic equilibrium can be set up in which there is a stable concentration gradient. This can be considered a chemical field precisely analogous to the electric field, which will also be present at any metal-water interface. A chemical field is analogous to an electric field, where the concentration of a chemical species is thought of as separate from the electrical field (the spatial derivative of the electrical potential). In these systems, all the ions are in the liquid phase, and any differences there may be between concentrations and activities are not normally considered important. Crucially, we shall see that we have no idea how to calculate the activity gradients of any ionic species that are present at a gas-plasma boundary when water vapor is present (as it normally is in the open air).

Unfortunately, specialization is not the only societal problem involved. Chemistry can provide a wonderfully clear picture of the shapes of molecules and how these relate to the molecular orbitals predicted by quantum mechanics. In the present context, many of the difficulties seem to arise from a more primitive concept: that of a chemical bond (Pauling, 1945). Strong chemical bonds are the result of paired electrons in low-energy states. If a chemical entity has an unpaired electron, it can either remain in its unstable state, lose the electron or acquire an extra one. The result is the existence of the entities known as a radials, cations, and anions. The rates of numerous chemical reactions that proceed *through radical intermediates* are known, but there are hardly any published rates *when the intermediates are likely to be gas-phase ions*.

The relative magnitudes of the energies of these species and their consequences can easily be seen (if sought) in tabulations of thermodynamic properties such as those of Wagman et al. (1982) and of Chase et al. (1985). Apart from ions of the elements, whose properties are usually readily obtainable, the content of these tables is very revealing concerning the relative ease of obtaining different kinds of thermodynamic data. The great majority of data available are on stable compounds that are easy to obtain and purify, while information on radicals is far less plentiful.

By comparison, thermodynamic data on molecular ions are almost non-existent. It was, in part, frequent use of these tables that led me to appreciate how very poorly molecular ions in the gas phase have been characterized. One result that used data on some of the few ions that have been characterized was the electrochemical model for ball lightning (Turner, 1994). Much later, I obtained an appreciation of what seem to be related areas of ignorance in other fields of science.

Electrostriction in Meteorology

There appear to be many areas of study that are adversely influenced by our quantitative ignorance concerning the effects of electrostriction. The associated phenomena include tornadic lights, the "hot towers" of hurricanes and the strange behavior of UFOs as well as some much better-researched meteorological phenomena. These are discussed at https://naturalplasmas.com/. The associated phenomena include tornadic lights, the "hot towers" of hurricanes, and the strange behavior of UFOs (Turner, 2023a,b), as well as some much better-researched meteorological phenomena (Turner, 2023d). Related problems also arise in explaining some aspects of planetary chemistry, the properties of molecular clouds, and the formation of stars and planets within them (Turner, 2023e).

A statement by members of the International Panel on Climate Change (Houghton et al.,1996) supports some of the more limited claims made earlier - though on completely different grounds. On page 345 It reads: "The single largest uncertainties in determining the climate sensitivity to either natural or anthropogenic changes are clouds and their effects on radiation and their role in the hydrological cycle". The situation has not changed significantly since this statement was made (Rossow & Schiffer, 1999; Boucher et al., 2013). Were it not for the *long neglect* of some of the 19th-century findings to be discussed here, and the ignorance resulting from it, our understanding of cloud physics might by now be much better than it is. Important matters addressed here, and in Appendix A, are how this problem developed and what can be done to rectify it.

All the long-claimed anomalies in the reported properties of ball lightning (Arago, 1885; Flammarion, 1888; Brand, 1923; Singer, 1971; Charman, 1979; Stakhanov, 1979; Barry, 1980; Stenhoff, 1999) disappear once three facts are accepted: 1, that free ions necessarily exist *at equilibrium* in the air; 2, that the equilibrium levels of these electrolytes are always far too small to detect by conventional means; 3, that the reported properties of ball lightning can *only* be understood once it is accepted that a number of routinely used assumptions are not always appropriate.

These sometimes inappropriate assumptions include the following (Turner, 2002) :

1. That the *chemical* properties of ions can be safely ignored,

2. That chemical thermodynamics can be safely ignored,
3. That electrolytes in gases *only* become fully dissociated at very high temperatures,
4. That an electrolyte solution at equilibrium is inevitably homogeneous,
5. That the Earth can be treated as a near-perfect conductor of electricity,
6. That electric currents in the air can usefully be treated as homogeneous and
7. That the absolute electric potential of the Earth is zero.

Only items 5 and 7 from the above list are never adversely influenced by electrostriction. The diverse nature of these facts implies that there are likely to be other seemingly anomalous natural phenomena that violate no known law of physics, and there seems to be good evidence that this is the case (Turner, 1998, 2003; Bauer, 2003; Teodorani, 2004). As implied above, one of the main societal problems results from differences in the way physicists and chemists are trained to approach problems. Chemistry can be thought of as a branch of physics whose dependence on quantum mechanics is far too complicated to yield useful theoretical predictions. This is a significantly different situation from that in particle and nuclear physics, where a combination of theories based on centuries of mathematical discoveries plus decades of expensive experimental study has led to major advances (e.g., Penrose, 2005, 2016; Farmelo, 2019). It seems obvious that the success results from the close approximations to the reality of most of the relevant theories.

This *quantitative* ignorance in chemistry is the main reason that the rationalizations of chemical properties provided by the Periodic Table are still so important to chemists. Perhaps more importantly, it is the reason for the types of problems that most physicists *choose not to study*. When a system cannot be reliably quantified, it is more likely to be investigated by chemists than by physicists, but few chemists have seen any reason to study the basic physical chemistry of *electrolyte solutions in the air*. On the other hand, chemists working in the electric power industry worldwide slowly began to accept that there can be serious problems whose study is inhibited by aspects of the missing electrochemistry.

Societal and Political Influences

Unfortunately, almost all support for this kind of work ceased in the 1990s as politicians in all countries began putting their faith entirely in market-driven decisions based purely on profit rather than decisions based on science. Appendix A discusses many of the political and other societal forces that seem to explain our current level of ignorance concerning vapor phase electrochemistry. When Staehle (1977) made his comments about the state of high-temperature aqueous chemistry, the situation was very different and there was growing support for studies aimed at trying to solve some of the very basic problems. In the electric power industry prior to 1970, considerably more attention had been given to fundamental studies of steam-water systems in the USSR than anywhere in the West, and whenever conferences on relevant matters were organized in Europe, one measure of success was frequently how many Soviet scientists had been allowed to attend.

It was very clear to most participants at these conferences that a very large and well-integrated industry was in the best position to support the needed experimental studies aimed at understanding power station problems. The electric power system in the Soviet Union was, at the time, very large and extremely well-integrated, and it employed many excellent scientists and engineers. For two decades, the large unified structure of the CEGB also allowed some progress to be made, while scientists in other countries, notably in the USA, Canada, and Argentina, continued to make important contributions with their own quite different ways of funding research. One mainstay of work in the USA was, from early on, provided by several groups of chemists at the Oak Ridge National Laboratory (ORNL) in Tennessee.

However, as illustrated below and in Appendix A, there is no longer much interest, either by academics or by engineers in the electric power industry, in conditions in the two-phase region near the critical point of water. As we shall see, this seems to be because it is currently quite impossible, on a realistic timescale, to interpret (validly) any experimental results where electrostriction plays an important part.

Currently, most studies of high-temperature electrochemistry now concentrate on solutions at far higher pressures than those of concern in the power industry (e.g., Palmer, 2004). The very slight disadvantages of working at higher pressures than those of saturated steam easily outweigh the interpretational problems that arise when there is no valid theory with which to interpret the experimental results obtainable. Some practical consequences of these facts are illustrated in Appendix A (https://naturalplasmas.com/files/VPE1_AppendixA).

It has *never* been realistically possible to claim a return on investment in less than two or three decades for the kind of work that used to be supported by, among others, the electric power industry in the UK. This fact also applied to the kind of basic stress-corrosion work once undertaken by corrosion scientists all over the world (Staehle, 1977). Under present conditions, almost any proposal for basic studies that cannot rapidly lead to obvious economies or profits for engineering companies would seem doomed to fail.

However, the situation was very different when I, together with other more experienced colleagues in several different countries, started to identify some of the more fundamental problems discussed in this paper. This century, many experimental studies of equilibria in high-temperature water have been published (e.g., Tremaine et al., eds., 2000; Palmer, 2004; Tremaine, Zhang, Bénézeth & Xiao, 2004; Fernandez-Prini, Japas & Marceca, 2010) and the systems are by now fairly well understood up to about 300^0 C. However, this is by no means true for conditions within 50^0 C of the critical point of water (at 374^0 C) or under any conditions at all in steam.

In what follows, a wide variety of evidence will be drawn together showing why it is currently impossible (validly) to use any normally successful kind of modeling for predicting the behavior of electrolytes in the steam-water circuits of *high-efficiency* power stations (those that operate at or above about 350 ^{0} C). Hardly any experimental study at high temperatures and pressures can produce results quickly. Despite this, there have been many revealing studies from several research groups. Some of these results were used in one very revealing analysis by Wood et al. (1994) - a study that is discussed later. Troubling though some of the problems are, our ignorance concerning electrolytes in moist air systems is even more limiting.

The ignorance to be described seems to have resulted from forces that are more societal than scientific. When anomalous observations are made, a valid explanation is unlikely to result unless a scientist can see a feasible path to making some progress and unless some funding agency is willing to support the work that has been identified as necessary. This does not need to be a serious limitation, even in very challenging areas of work, if the problems are *only* technological or financial. However, the situation can be very different if the problems arise at a very basic level, are generally considered boring, and are likely *only to be solvable on an extremely long timescale*.

Current Knowledge and Ignorance Concerning Electrostriction by Ions

Fundamental science can be thought of as an organized way to replace erroneous concepts with better ones. Physics, because of its dependence on centuries of work by mathematicians, has developed in the most fundamental ways. The result is the amazingly precise predictions that this combination of expertise can sometimes make (e.g., Penrose, 2005; Farmelo, 2019). However, very basic science can be expensive, and if it is both expensive and uninspiring to most people, it will receive little support *unless the needed work directly benefits some industry*. Commonly this will be a manufacturing or construction industry.

A very successful example of support by manufacturing industries was that aimed at understanding most aspects of *inorganic* chemistry during the 19th century. Apparently, most of our early knowledge of inorganic chemistry resulted from satisfying the specific needs of manufacturing industries (Mellor, 1928). Far less successful have been applications of the concepts of *solution chemistry* in an equally important industry: the electric power industry. One difficulty now is a general reluctance of most senior engineers in the industry to be at all concerned when, under specific conditions, computer models are demonstrated to be based on totally invalid science *but it would be far too expensive to do anything about it* (see Appendix A https://naturalplasmas.com/files/VPE1_AppendixA).

Specialization has obviously proved essential in advancing all of science. As implied earlier, the most fundamental advances have been in physics. General relativity and quantum mechanics are fields that best illustrate this, while studies in chemical thermodynamics have suffered from four major difficulties. 1: the field has never been fashionable. 2: the rates at which chemical changes proceed are often considered far more important than thermodynamics. 3: to be successful, assumptions need to be made and then tested and 4: the thermodynamic properties of only a tiny fraction of the compounds that exist have ever been measured. In this respect, chemical thermodynamics differs enormously from nuclear and particle physics.

Before the specific limitations of *vapor phase* electrochemistry are discussed, some much longer-known problems in treating ordinary, liquid-phase solutions of electrolytes need to be mentioned. Chemical thermodynamics controls most of the processes that occur in fluids, but the discipline has never been popular. Its unpopularity with research scientists is not difficult to understand if only because a single precise measurement of one thermodynamic property provides so little information compared with the normally relatively simple measurement of *changes* in solution compositions as a function of time.

Rates of chemical change (kinetic studies) fit easily into the normal three-year length of a Ph.D. research project, but most thermodynamic studies do not. Additionally, thermochemical properties of solutions are of little practical value unless a range of related properties *for other solutions* is also available. A typical chemical reaction in solution involves at least three or four chemical species, and appropriate data on *all* of them must be available before *anything of practical value* can be calculated. Worse still, solution properties vary with concentration, so to be useful, it is necessary to provide some concentration-independent definition of a standard state for each electrolyte of interest.

With mixtures of liquid phase *non-electrolytes*, there are natural standard states: the pure fluids. For electrolyte solutions, however, one of the pure substances is normally a solid, so quantifying their standard state properties requires the extrapolation of experimental measurements on a number of solutions of different concentrations to infinite dilution rather than simply obtaining the properties of pure liquids. To be of practical use, the standard state for an electrolyte solution is taken to have the relevant properties of an infinitely dilute solution, but, *at the same time,* the solution is taken to be at a unit concentration. There is a related problem with electrolyte solutions that is, in some respects, only slightly less serious than the fact that their standard states are unreal. This is the tendency of solutions to change their degree of dissociation as they are diluted, becoming completely dissociated at infinite dilution (Arrhenius, 1887; 1903). Although the experiments leading to the discovery of this fact were much later described as "some of the most fruitful that have been advanced in the history of science" (MacInnes, 1961), this was not at all how the contemporaries of Arrhenius assessed his discoveries (Arrhenius, Caldwell & Wold, 2008). The complicated behaviors of electrolyte solutions on dilution still tend to be found unattractive to most chemists.

More importantly, compared with mixtures of non-electrolytes, electrolyte solutions have the obvious disadvantage of employing *standard states* that are *not physically real*. Only an industry feeling the need to plan many decades ahead would support work addressing the kind of uninspiring science that results from the above facts.

The electricity supply industry in the UK, along with a few companies in other countries, was once run purely as a public service - that is *basically in the public interest.* Thus the engineers and physicists who ran these companies once felt pressured to support clearly needed thermodynamic studies - *even if progress would inevitably be extremely slow*. This is no longer the case.

We shall see that the fact that the standard states of electrolytes are not physically real can result in serious conceptual difficulties. Decades of testing the utility of electrolyte standard states had been summarized by the mid-20th century (e.g., Harned & Owen, 1950; Robinson & Stokes, 1955). Among the practical problems in *obtaining these standard state properties* were some long-known mathematical limitations of the basic Debye-Hückel model for ionic interactions, but these are not always the most serious difficulties.

Guggenheim (1929) early discussed some very basic electrostatic problems that are unavoidably involved in treating the thermodynamics of electrolyte solutions. One of them is the fact that *individual* ion activities cannot be measured - because they do not exist. Activities *only exist as real thermodynamic quantities* for complete electrolytes. The most frequently needed property of a solution is its pH which is nominally the logarithm of the hydrogen ion *activity* with its sign reversed. A pH informs us how acidic a solution is, and its knowledge can be important in assessing many systems, both biological and industrial.

Because a pH is only a property of convenience (not a real thermodynamic property) internationally agreed conventions are now used to define exactly what it means and how measured properties can be made to satisfy the needs of those scientists who study solutions, while still being reasonably consistent with the laws of thermodynamics. These conventions are periodically updated (Bates & Guggenheim, 1960; Covington, Bates, & Durst, 1985; Buck, 2002). Measurements of pH can be made in a variety of ways, the most precise of which measures the activities of electrolytes. In principle, pH values provide an unusually clear example of the differences between concentrations and activities, but frequently the differences are ignored.

These difficulties may have contributed to a long-standing antagonism between two eminent authorities on chemical thermodynamics: E.A. Guggenheim and G. Scatchard. In 1950, according to Edsall and Stockmayer (1980), Scatchard reviewed the first edition of Guggenheim's textbook on the subject and remarked that it might well have been subtitled "Pride and Prejudice". To many currently practicing chemists, Guggenheim's concerns still seem excessively pedantic, but they are valid and can be important. The disagreements just referred to might possibly have resulted from the main interests of the two men and their students.

The majority of scientists who deal with solution properties, such as analytical chemists, environmentalists, bio-chemists, and biologists, tend to favor the less pedantic views of Scatchard, where such problems as the difference between a concentration and an activity are frequently ignored. This is probably because solution chemists normally only study systems fairly close to room temperature. However, those in other areas of science can be concerned with systems over a much wider range of temperatures - where the difference between a proton's concentration and its activity can be considerable.

The Thermodynamic Properties of Aqueous Electrolyte Solutions

For a century, it has been generally accepted that, at least in sufficiently dilute solutions of electrolytes, the differences between thermodynamic activities and concentrations can be dealt with very easily, if only approximately, by using extended forms of the Debye-Hückel limiting law. So long as standard state Gibbs free energies of formation for all the components in a solution phase reaction are available, the pH of the solution can be estimated using such theories. Unfortunately, the vast majority of thermodynamic data on solutions has only been obtained at 25^0 C, so it is usually necessary (e.g., in geochemistry and the electric power industry) to *estimate* any free energies needed when data at other temperatures are required.

In estimating the free energy change of a reaction involving electrolytic solutions, it is usual to first calculate the standard state free energy change and then correct it for the non-ideal behavior of real solutions.

Because any errors introduced by faulty activity coefficient relations are normally far smaller than errors in the standard state properties, problems with the latter quantities are usually far more important than the effects of activity coefficients. Nevertheless, both types of contribution to a free energy change can be influenced by electrostriction.

The only simple approach known for estimating the standard state properties of ions in a solution is the use of the Born equation:

$$\Delta G = -\frac{(ze)^2 N}{8\pi\varepsilon_0 r}\left(1-\frac{1}{D}\right)$$

Here, ΔG is the change in Gibbs free energy for the transfer of a charged sphere from the gas phase to a solution whose dielectric constant (relative permittivity) is D. An ion is taken to have a radius r and a charge of ze (z being the number of electric charges on the ion and e is the charge on an electron), while *N* is Avogadro's number.

The right-hand side of the above equation was originally derived by Born (1920), and it has been discussed in numerous subsequent treatments of electrolyte solutions. A major problem with using this equation is that, although it is now usually *assumed* to apply to Gibbs free energies (as indicated in the above equation), this assumption has little to justify it. It is now generally taken to be a reasonable assumption (Atkins & MacDermott, 1982), although there are still doubters over this point. When Born first developed his relationship, it seems he thought he was calculating internal energy, but it was later concluded that what he had actually calculated was a free energy change (Bjerrum & Larson, 1927). For decades, this energy was *assumed* to be the Gibbs free energy change for the relevant process.

Later, Frank (1955) used the differential equations that govern thermodynamics and electrostatics to study the free energy density in an idealized thought experiment. This employed a parallel plate capacitor filled with a liquid and fitted with devices for measuring pressures. He used the model to derive and discuss many equations that are obtainable from these basic laws. His study implied that neither of the above conclusions regarding the Born equation is correct. One implied conclusion was that the expression on the right-hand side of the above equation is more like a Helmholtz free energy than a Gibbs free energy.

Many unquantifiable terms are present in Frank's equations and presumably this is why his work is now largely ignored. At CERL, Peters (1984, 1985, 1987a,b) did begin a study of whether it is possible to make practical use of his equations, but the privatization of the CEGB and the closure of CERL put an end to this program before much progress had been made. Other related long-term projects, discussed later, were also abandoned. For two concerned opinions, by academics, over the closure of CERL - see Fells (1992) and Atiyah (1994). The latter's comments on the politics involved seem particularly relevant in the context of this paper and are briefly referred to in Appendix A.

In practice, many poorly understood contributions to the energies involved have to be accommodated when attempts to use the Born equation are made, and there are many ways of doing this. In the absence of better approaches, the equation's use has continued to this day despite its known limitations. An extensive summary of its uses and limitations in understanding the properties of electrolyte solutions at 25^0 C was given by Conway (1981). As previously mentioned, this temperature is important because it is *the only one* at which large quantities of really reliable aqueous phase data are available.

At 25^0 C, a wide variety of structural factors in an aqueous solvent contribute to the problems with the Born equation. They have been discussed and studied almost continuously for many decades (see, e.g., Harned & Owen, 1950; Roux, Yu, & Karplus, 1990; Yang & Lim, 2008; Izadi & Onufriev, 2016). The conclusion is still that all hydration models require empirical fitting parameters in order to enable over-simplified models (such as the Born equation) to account for the properties of real ions of different sizes.

It was once hoped that, near the critical point of water, a simple electrostatic model, like the Born equation, might come into its own - because the huge effects of electrostriction would swamp any local structural influences. However, the difference between the Gibbs and Helmholtz free energies is a compressibility (PV) term, so it is arguable that serious problems could have been anticipated in any attempt to modify a Gibbs energy relationship by the addition of ad hoc parameters to account for local structural effects including electrostriction.

An idea of the magnitude of the problems near the critical point of water can be seen by comparing partial molar volumes obtained theoretically and experimentally. These are the thermodynamic quantities that are most obviously influenced by compressibility. An appropriate theoretical prediction for aqueous NaCl was that of Quint and Wood (1985), while an extensive set of experimental data on apparent molar volumes for the electrolyte had been made in the 1950s (Benson, Copeland, & Pearson, 1954; Copeland, Silverman, & Benson, 1954). A more recent and more extensive set of data has since been obtained. These densities, which were mostly obtained well above the critical point of water, in terms of both temperature and pressure (Majer, Hui, Crovetto, & Wood, 1991), will be discussed shortly.

Figure. 1 shows the earlier (1954) measurements of apparent molar volumes for NaCl solutions in water at 385 ^{0} C and at a pressure of 243 bar. An apparent molar volume of - 24 l mol^{-1} (for the lowest concentration studied) obviously represents a very high degree of electrostriction. Nearer room temperature, a similar plot would have been hard to distinguish from the x-axis of the graph. At 25^0 C, the apparent molar volume is roughly +17 ml. mol^{-1} (Harned & Owen, 1950). This is a little over half the value calculable from the density of solid NaCl (+27 ml. mol $^{-1}$). Thus electrostriction is actually significant even near 25^0 C. The significance of these findings is discussed a little more fully in Appendix B (https://naturalplasmas.com/files/VPE1_AppendixB)

The data represented in Fig. 1 were for solutions roughly 11^0 C and 43 bar pressure above their critical points so that sedimentation effects will be far smaller than they would have been at the critical point - since electrostriction is limited by compressibility and this is infinite only at the critical point itself. We will proceed by temporarily ignoring any effects of sedimentation in order to compare these measured values with those predicted by the thermodynamic model of Quint and Wood (1985).

From the apparent molar volumes of Fig 1, we can obtain partial molar volumes (the graph's slopes). This exercise yields partial molar volumes close to - 41 l.mol $^{-1}$ for the two most dilute solutions. (It is not obvious that the results are of sufficient accuracy to allow this similarity to be considered significant). The model of Quint and Wood finds that, for a temperature 0.5^0 C (compared with the experimental 11^0 C) above the critical temperature and at a pressure about 0.7 bar (compared with the experimental 43 bar) away from the critical pressure, the predicted partial molar volume was - 31 l.mol $^{-1}$ (Quint & Wood, 1985).

The modeled value for infinite dilution was for a solution *far closer* to the critical point than the measured ones so that a prediction of -31 l.mol $^{-1}$ represents a *very considerable* under-estimate of the real degree of electrostriction. On the basis of the NIST (2021) density data, the compressibility of water 0.5^0 C above the critical point is about 6.6 times greater than that where the experimental data had been obtained. Because the measured values refer to finite concentrations, which are much higher than for the standard state, the real discrepancy between the model and experimental results is far larger than between -31 l.mol $^{-1}$ and - 41 l.mol $^{-1}$.

To what extent sedimentation in the 1950s experimental study is responsible for the discrepancy is not known. It so happens that Wood et al. (1994) later concluded that the earlier estimate (Quint & Wood, 1985) might be unreliable. Hence sedimentation might not be the main cause of the discrepancy. However, the newer model of Wood et al. (1994) led to a *qualitatively more significant prediction*: that ions would *be more strongly paired* near the critical point than under conditions where the compressibility is neglected. This conclusion is the *exact opposite* of one drawn previously by Pearson, Copeland & Benson (1963) and of Monte-Carlo simulations by Peters (1987b) at CERL (see Turner, 1990a). Both these studies provide evidence supporting a *lower* degree of ion pairing as a consequence of high compressibility.

As we shall see later, in some of the experiments of Pearson, et al. (1963, p. 1049), conductances of NaCl solutions, unusually near to their critical points, had been measured. The authors' final conclusion was as follows: "In this region of high solvent compressibility, the attraction of ions for water molecules appears to exceed greatly the attraction of ion pairs". (Author, YR, Pg no) Similar conclusions seem also to be implied by the findings of Marshall and Quist (1967) and of Marshall (1969). This all casts doubt on the basis for the conclusions of Wood et al. (1994). The crucial importance of their results seems to be in clearly illustrating the complete inadequacy of normal methods of data treatment whenever compressibilities are high.

Clearly, our quantitative knowledge of electrostric-

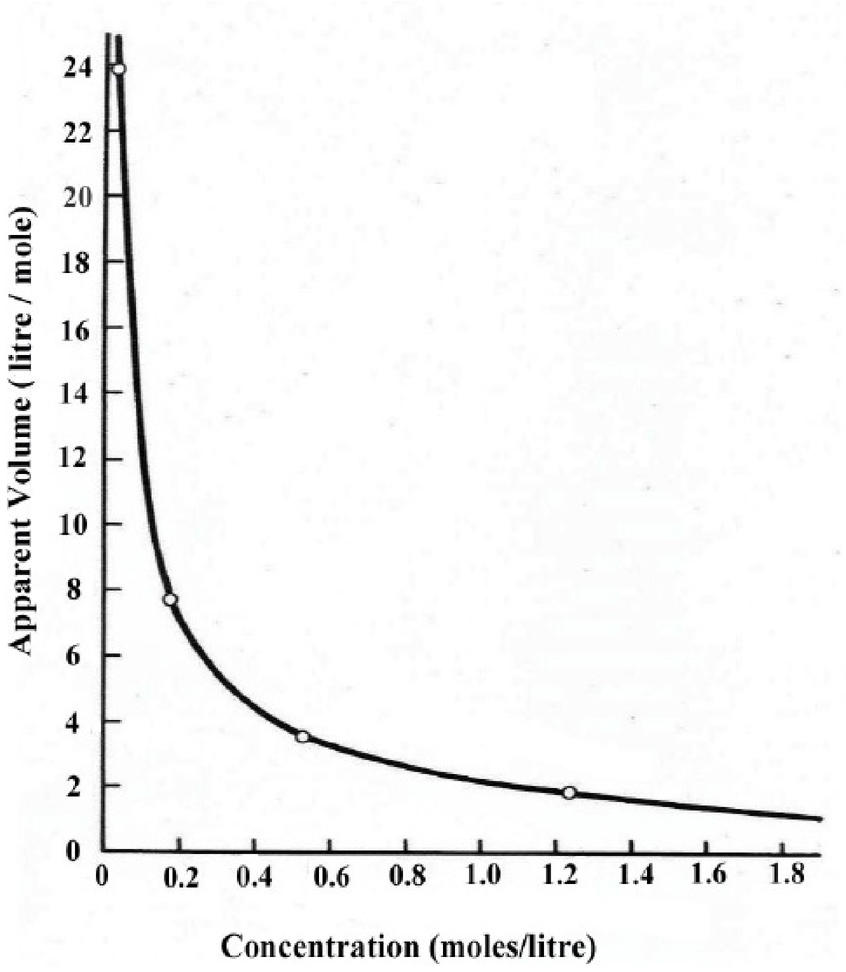

Figure 1 : Apparent molar volumes of aqueous supercritical NaCl solutions (Turner,1983). The actual results were reported in two separate papers by Benson, Copeland, and Pearson (1954) and by Copeland, Silverman, and Benson, (1954).

tion is still grossly inadequate, although it seems almost certain that the conclusions of Pearson et al. (1963) and of Peters (1987b) are correct concerning how easy it is for a water molecule to replace a counter-ion close to the central ion in a very compressible solution.

At the very much lower solvent densities of moist air, the favoring of hydration over charge neutralization proved to be one of the key ingredients in the author's electrochemical model for ball lightning (Turner, 1994, 1998, 2002, 2003).

THE USE OF WATER IN ELECTRICITY GENERATION

In an operating power station boiler, whose temperature might be 350⁰ C, understanding the degree of hydrolysis of salts in the water can obviously be important because hydrolysis reactions control the pH and because solutions of either very low or very high pH can significantly increase corrosion rates. The need to quantify quite different kinds of hydrolysis reactions can also be important when nuclear power problems are involved. Both the reliability of the regulations imposed on the industry and their degree of conservatism clearly require testing. This can apply both to normal running conditions of the plant and to conditions under the kind of plausible accident scenarios that are needed in making safety cases for a new nuclear plant.

Two quite different kinds of problems that involve iodine chemistry will be illustrated here, the first relating to the solvent properties of *liquid water* and the second to those in *steam*. Detailed models for the release of radioactivity from different parts of a water reactor circuit need to take into account the fact that droplets are far more easily contained than volatile species. In a boiling water reactor (BWR), the most volatile of the radioactive species is molecular iodine, I_2, while in a pressurized water reactor (PWR), HI would be the volatile iodine species initially released from any leak (though it could then be oxidized in the air to I_2).One of the most important equilibria, governing how much iodine can be in the gas phase is the hydrolysis of iodine according to the liquid phase reaction:

$$3\,I_2 + 3\,H_2O = 5\,I^- + IO_3^- + 6\,H^+ \qquad (1)$$

The main concern is, of course, how much of the iodine present can enter the gas phase. Unless the equilibrium constant for this reaction is known, the only safe assumption is that all the iodine released during the leak is in the gas phase (as molecular iodine) so that radioactive iodine can escape easily. For a PWR, this assumption is likely to be unnecessarily pessimistic, and, in the case of one of the most serious real accidents with a PWR, the predicted radioactivity release had indeed been greatly overestimated (Rogovin, 1979).

Unfortunately, the only data on Reaction 1, when the CEGB needed an assessment, were thermodynamic data at 25^0 C, which could be used in combination with methods for estimating high-temperature equilibrium constants from those at 25^0 C. Two such procedures were known: those of Cobble (1964) and of Helgeson (1967). Each is based on slightly different principles, the first being purely thermodynamic and the second explicitly allowing for some of the electrostatic forces. From what had already been learned about the properties of electrolyte solutions, Reaction 1 appeared likely to provide a very severe challenge for any estimation procedure because dissolved *ions* are far less well characterized than are uncharged molecules. In Reaction 1, twelve poorly characterized ions are obviously produced from six comparatively well-characterized neutral molecules.

When the estimation procedures were applied, a huge spread in predicted values for the equilibrium constant was found. By 90^0 C, the ignorance represented an uncertainty of *three orders of magnitude,* and by 150^0 C the uncertainty was *10 orders of magnitude* (Turner, 1978,1980). In other words, the available data were totally useless. Later experimental studies (Ashton, Corti, & Turner, 1986) greatly improved the situation. The main difficulty in addressing problems like this is that industrial *users* of the information tend to be far more concerned over such ignorance than are most academics - but industrialists can be unwilling to fund the necessary research if it is expensive and slow.

Around the same time, data on Reaction 1 were needed in trying to understand some very strange observations made in a Swedish BWR (Lindén & Turner, 1983). A BWR employs high-purity water in a single fluid circuit so that any chemicals leaked from a fuel can have direct access to the turbines. On a few occasions, unexpectedly high fractions of the iodine present in the circuit had been carried over from the boiler to the turbine. Normally the fraction carried over was between 3 and 8%. On one occasion, however, the highest carryover was 65%. In American BWRs, values between 0.2 and 2.5 % were more typical. It was eventually concluded that the very high levels of carryover arose *only after prolonged operation with water of unusually high purity*. This kind of finding indicates how very poor can be our current understanding of the solution chemistry of boiler water.

RELEVANT THERMODYNAMIC PROBLEMS

The matter of excessive specialization needs to be raised again here. In universities, the problems can often be minimized because of the frequent need for academics to lecture on a variety of subjects. Hence it is normally *assumed* that academia is the best place to minimize limitations due to over-specialization. One problem with this assumption is that lecturers usually have to rely, at least to some extent, on textbooks. As we shall see, it is all too easy for significant facts to be ignored in textbooks. If there are serious problem areas in basic science, an industrial laboratory could sometimes be the best place to discover them. However, when a company is run purely on a commercial basis, expensive attempts to avoid long-term problems by acquiring new basic information, are pointless - because all of a company's competitors are equally ignorant (see Appendix A).

The previously mentioned measurements of Majer et al. (1991) on the densities of aqueous NaCl solutions at high temperatures and high pressures used a completely new approach to density measurement under these conditions. It was a brilliant piece of innovation and proved to be a revelation. A vibrating-tube densitometer was used. This measures the masses of solutions (of known volume) that control the resonant frequencies of the tube containing them. The flow-through design of the system allowed measurements to be obtained at an unprecedented rate. This is a major advantage over traditional methods, and results were obtained over a wide range of conditions well above the critical point. Under the latter conditions, traditionally obtained data confirmed the reliability of the method, but *no results* could be obtained as close to the critical point as had been expected.

Most of the measurements were in excellent agreement with earlier measurements, but it was found that the resonant frequencies were so severely damped in the vicinity of the critical point of water that no densities in this region could be obtained. The failure was attributed by the authors to a phase change. Since a strongly sedimented solution can be considered to be an infinite number of slightly different phases, this explanation has to be correct, even if two distinct phases could never have been observed.

Comparisons with the results of earlier work revealed that the conditions where densities could *not* be obtained were far more restricting than when traditional methods for measuring densities had been used. It seems clear that the results of Majer et al. (1991) define, far more clearly than any other method, the region of phase space where sedimentation makes solutions *inhomogeneous at equilibrium*. In other words, the results clearly confirm that *the Earth's gravitational field significantly influences the physical properties of some salt solutions*. In an electric power station, far higher gravitational fields than the Earth's can be present where fast-flowing steam encounters sharp bends in the tubes containing it. Serious corrosion problems can and do result.

The routinely used assumption in the model of Wood et al. (1994), that any thermodynamic property *for an individual ion* has real significance, introduces its own limitations because of the unreality of the concept of an individual ion activity (see earlier). It seems likely, however, that most of the apparent discrepancies were due to the role of the Earth's gravitational field. That this can be important is also supported by a very much earlier study of Shröer (1927). Shröer used visual observations to measure the critical temperatures of pure water and of a number of electrolyte solutions, some of which were colored.

The significance of Shröer's (1927) observations on *colored* solutions seems to have been ignored by most subsequent investigators who have continued to ignore the obvious effects of sedimentation he reported. For pure water, his measurements show excellent agreement with the best currently accepted values of critical parameters, and his values for the apparent critical points for aqueous NaCl solutions mostly lie well within the (rather wide) range of values obtained in more recent studies. The agreement over the *pure water* data seems to be the only piece of evidence that has been used by later investigators (e.g., Marshall & Jones, 1974).

It should, perhaps, be noted that the effects just described are unrelated to the much-studied fields of near-critical study that discuss *critical exponents* and are common to all phase changes (Stanley, 1971). These effects are seen over a far smaller range of temperature and pressure than those that produce sedimentation. The neglected aspects of Shröer's work, with colored solutions, simply provide additional confirmation that the gravitational field of the Earth greatly complicates the physics involved. Such complications were, of course, what led the CEGB to support the collaborations with the ESA - the European Space Agency - (see Turner, 1983). The findings of Majer et al. (1991) clarify the range of parameters over which the problems are serious.

It took sixty years before Shröer's observations could be independently confirmed by simple removal of the Earth's gravitational field with near critical NaCl solutions (Turner, 1987,1988a). Unfortunately, support for the collaborations between the CEGB and ESA, which had produced this confirmation, ceased well before any really important results had been obtained. These results were, of course, needed to test any better theories whose development was, at that time, still being attempted.

The small autoclave developed for this work would also have allowed a variety of optical studies, such as holographic interferometry, to be used in an orbiting space vehicle (Turner et al., 1991; Tremaine & Turner, 1993). Such studies might well have been able to help address the problem referred to earlier of trying to use Frank's (1955) very complicated relationships to better understand the inter-ionic forces that control very compressible electrolyte systems. However, neither industrial nor governmental support was ever found, and both proposals had to be abandoned.

There is, unfortunately, another potential complication that would have needed addressing before any *definitive* tests of future theoretical models could have been made. It has long been a concern with engineers and corrosion scientists in the electricity supply industry. It relates to a potential hydrolysis reaction which is generally *assumed to be unimportant by almost all academics*. Its (qualitative) occurrence has, however, frequently been invoked by power station engineers to explain the specific locations of corrosion damage found in boiler tubes. The reaction can be written thus:

$$Na^+ + Cl^- + H_2O\,(l) = HCl\,(g) + Na^+ + OH^- \qquad (2)$$

The designations (l) and (g) refer to the liquid and gaseous phases. In this representation, the sodium ion is shown on both sides of the equation simply to indicate that the process considered occurs in a normal bulk liquid with *all the ions* assumed to inhabit the liquid phase - as they certainly do nearer to room temperature. If the reaction really does lie significantly to the right in high-temperature water, as it certainly seems to, then the reaction's occurrence would introduce a very significant difficulty in interpreting the properties of near-critical salt solutions.

If support for our micro-gravity studies had continued, the properties of aqueous HCl would have required study, ideally before those of NaCl. The need arises because HCl cannot possibly hydrolyze, while Reaction 2 is at least possible in principle. The autoclave system which had successfully been used in the preliminary micro-gravity studies (Turner, 1988a) would have required much-improved seals because those employed in all the studies of NaCl solutions routinely failed when the much more corrosive HCl was substituted for NaCl. It is easy to see why support for this kind of experimental work could only come from an industry that clearly saw the need for solving the relevant theoretical problems and was prepared to plan seriously for the future.

AN INDUSTRIAL PROBLEM INVOLVING STEAM

The inadequacies of available estimation procedures referred to in connection with Reaction 1, reflect changes in the *solvating properties* of liquid water as temperatures increase. Our ignorance is much more serious when it comes to the solvent properties of *steam*. Experimental studies undertaken in the context of the operation of PWRs (Clinton & Simmons, 1987) demonstrated this fact very clearly. Unlike BWRs, PWRs normally operate under chemically reducing conditions, so the covalent form of HI was expected to be the only volatile iodine species present in the liquid phase under normal operating conditions.

The results of Clinton and Simmons (1987) were the only *directly* relevant data on iodine volatility that were available for use in PWR safety cases. The authors employed iodine concentrations close to 6.10^{-11} mol/liter in the liquid phase, using the radioactive isotope ^{131}I to determine the iodine fraction in each phase. Such levels (realistic in practice) represent a sensitivity many orders of magnitude greater than conventional methods for chemical analysis could possibly achieve. Because of the low iodine levels and because temperature gradients in the experimental system could not be avoided, it seemed fairly easy to understand why the reproducibility was much lower than the authors must have expected. Far less easy to explain was the *complete* lack of dependence of iodine volatility on pH and its *very clear* dependence on borate concentration (Turner, 1989). When the results were first reported, none of the groups of scientists wishing to use the data in safety cases could make any sense at all of either of these facts.

At the time, reasonably precise estimates of the dissociation constant of HI were available at the relevant temperature (285^0 C). On this basis, no suitably qualified person (of dozens pondering the problem) could explain why a change of 5 orders of magnitude in hydrogen ion concentration forced *no change whatsoever* in the iodine volatility. Even more strange was the matter of how boric acid could so systematically increase the iodine volatility. The basic question raised was this: what is preventing the oppositely charged ions from annihilating each other's charges at low pH values, thus making HI behave like a normal acid?

A possible explanation for the lack of dependence on pH is that the ions are all present in a form that solution chemists refer to as solvent-separated ion-pairs. Ion hydration in such ion pairs can, it seems, prevent the process of *complete* charge neutralization of HI. However, this still leaves the clear dependence of the iodide on borate concentration unexplained. To the best of my knowledge, the only explanation for the findings ever offered depended on our almost total ignorance of what I now refer to as vapor phase electrochemistry. It seems that nearly all the iodine must have entered the vapor phase as an *ion pair* in which the iodide anion is *stabilized by the presence of boric acid* - through a fairly well-understood entropy effect (Turner, 1989).

This evidence was our first hint that solvent-separated ion pairs can exist *at equilibrium* in the gas phase at a moderately low temperature. Ionization in a dry gas (where there can be no such ion pairs) normally requires thousands of degrees Celsius. This ion pair explanation appeared to be the only reasonable (if surprising) one for the findings of Clinton and Simmons (1987). The explanation can be compared with the comment of Pearson, et al. (1963), quoted earlier, that high compressibility in an aqueous solvent causes the attraction of ions for water molecules to exceed the attraction of oppositely charged ions. The findings seem significant because the compressibility of steam is so very much lower at 285^0 C than it is near 374^0 C.

Later, the existence of solvent separated ion pairs in the gas phase was also supported by the behavior of a different pair of ions: those providing stability to ball lightning (Turner, 1994). Here there are additional reasons for believing that there need be *no driving force at all for complete charge neutralization* when ions are sufficiently heavily hydrated in the gas phase. It is the Gibbs free energy change on charge neutralization that determines whether or not a process can occur, and, *in the gas phase*, the entropy contribution to a free energy change can swamp that of the enthalpy change (Turner, 1994).

Attempts at Quantitative Studies of Ion-Water Interactions

There are many plausible explanations for the failure of simple relationships to permit satisfactory estimates of equilibrium constants in high-temperature water. Most can be seen to result from the still poor state of our understanding of ion hydration (e.g., Friedman & Krishnan, 1973; Vlcek & Chialvo, 2016). This field of study is still extremely active, but remarkably few new experimental data above 50^0 C become available each year, and even fewer in the two-phase region above 100^0 C, so there has been little incentive to investigate the kind of compressibility effects that seem to control processes at significantly higher temperatures.

It gradually became clear to those at CERL that, in a boiler at 350^0 C, ion pairing is controlled at least as much by the effects of electrostriction and compressibility of the solvent as by electrostatic relationships (Turner, 1988a). In fact, Tremaine and Goldman (1978) had much earlier recognized that our poor understanding of electrolyte solutions in high-temperature water was a direct consequence of solution compressibility. Later, the problem was also recognized by scientists at the National Institute of Standards and Technology (NIST) (Levelt-Sengers et al.,1992), but their proposals for new studies to investigate the problem came to nothing - presumably due to a lack of support.

A slightly later proposal (Tremaine & Turner, 1993) *definitely* failed for this reason (see Appendix A). As this Appendix seems to show, the political philosophy that drove the privatization of the CEGB, and the consequent closure of CERL, also led to the abandonment of most of the other work that had once been devoted (worldwide) to the study of aqueous systems that are highly compressible and strongly influenced by electrostriction and therefore by sedimentation. *I am not aware that anyone is currently studying systems in which gravitational sedimentation, of the kind referred to above, is considered to be important*.

It is now clear that very basic limitations apply to our understanding of the thermodynamic properties of all electrolytes in water in the two-phase region above about $250\ ^0$C (Cobble & Murray, 1977), to their conductances at temperatures above $300\ ^0$ C (Turner, 1983) and to both these properties *in steam and moist air at all normal temperatures* (Turner, 1990a,b., 1998, 2003). Conventional treatments of *real* solutions (at finite concentrations) become *invalid* in any sufficiently compressible solution (Turner, 1983, 1990a). One of the *simplest* ways of seeing the nature of the basic problems relates to the use of any version of the Debye-Hückel theory (which *assumes* the solvent to be incompressible) in obtaining standard state properties from the measured properties of real solutions. As we have seen, the effects of compressibility can be huge. This problem is discussed in Appendix B (https://naturalplasmas.com/files/VPE1_AppendixB).

Based mainly on the relationships found by Frank (1955), the earlier mentioned modeling studies at CERL (Peters, 1984, 1985, 1987a,b) were begun. The last of these studies involved a re-assessment of previous approximations for the radial distribution of charge in dilute, moderately compressible solutions of electrolytes at $325\ ^0$C. A linear approximation for the dependence of dielectric constant on solvent density, used previously by Wood, Quint, and Grolier (1981), was employed together with other approximations used by these authors. Although these frequently used assumptions were found to be consistent with the Debye-Hückel theory when applied to normal aqueous solutions, it later became clear that there seemed to be much more serious problems in significantly more compressible solutions (Turner, 1990a).

There are two other modeling studies showing that the problems are serious. One comes from an earlier review of failures of the Debye-Hückel theory by Morrison (1988), and the second from much later studies using molecular simulations (Reif & Hünenberger, 2011). The limitations were again attributed to compressibility effects. It now seems very clear, from an uncompleted study of Peters (1990), that so many currently unquantifiable terms are involved in Frank's (1955) relationships that it is quite impossible to estimate any practically useful standard state-free energies for electrolytes anywhere near the critical point of water - at least if reliable conclusions are required.

If obtainable, only experimentally determined free energy changes would currently have *any* practical value at all. Unfortunately, even if reliable *experimental* data of this kind were to be available, there is still the problem of how to extrapolate the data obtained experimentally to infinite dilution using estimated activity coefficient relationships that are unavoidably invalid. Being able to relate measurements on real solutions to standard state properties is essential if experimental data are to be of any practical use. Usable knowledge concerning ionic equilibria within about 50^0 C of the critical point of water is almost completely lacking.

In the present context, the most instructive of the findings at CERL came from Monte Carlo simulations which were undertaken for a 10^{-2} molar NaCl aqueous solution at $325\ ^0$ C (Peters, 1987b). A brief summary of the main conclusions was later discussed in an externally published paper (Turner, 1990a). As we have seen, comparison of these predictions with those of the Debye-Hückel theory showed that electrostrictive forces produce a major *reduction*, very near the central ion, of the concentration of the counter-ions that surround the central ion. This conclusion directly contradicts the conclusion of Wood et al. (1994) which was based on a conventional use of the Debye-Hückel theory so that the precise significance of the disagreements discussed earlier remains somewhat unclear.

Conductance Studies

Much of what is known about electrolyte solutions have resulted from measuring conductances as a function of concentration and interpreting the results as deviations from theoretical predictions. The theories used are normally modifications of the basic Debye-Hückel model as they apply to transport properties. Fortunately, conductance results can also be used in far simpler, though normally far less informative, ways. If solution conductances as a function of concentration are simply extrapolated to infinite dilution, without any attempt at interpretation, a *theory-free* property for the solution, known as the Walden product, can be obtained. This is the product of the limiting conductance (an extrapolation of the measurements to infinite dilution) and the viscosity of the solvent. Decades ago, Harned and Owen (1950) argued that, in an ideal *structure-free* solution, Walden products would be independent of temperature.

However, all aqueous solutions near room temperature are well known to be highly structured as a result of the strongly hydrogen-bonded nature of liquid water. Fig 2 illustrates this evidence in a revealing way. The lower temperature deviations from constancy arise from the structural effects of liquid water. As expected, these structural effects decrease with temperature. Above 300° C, the deviations are equally revealing - but in a totally different way. The critical temperature of water is close to 374° C. Significantly, the Walden products above 300° C seem to be heading for infinity - as they should be since water, like any other fluid, is infinitely compressible at its critical point.

The roughly horizontal portion of the line in Fig. 2 clearly implies a temperature-independent Walden product, as would be the case in any *ideal* solution. It certainly appears that the well-known abnormal structural effects of liquid water have been largely eliminated by about 100° C but a horizontal line between about 150° and 300° C is unlikely to be really justified because the arguments did not allow for electrostriction. It was mentioned in Section 2.1 that electrostriction is, in fact, significant in water even at room temperature, so there was really no justification for having believed that a horizontal line between 200 and 300° C should have been drawn. The results of Noyes (1907) were actually of very high precision, so it now seems that much greater weight should have been given to them than indicated by the line. Hence line should really have a negative slope over the whole temperature range between 100° and 200° C

It was partly on the basis of the data in Fig. 2 that our earliest experimental studies at CERL were justified. The original hope was that extrapolations of thermodynamic data would be most reliable if they were to be made, both up and down in temperature, from new measurements obtained between about 200 and 300° C (Turner, 1977). Conductance methods would not, in practice, have been used since our need was for thermodynamic data, and the use of this method would have depended on the development of a far more reliable theory than those based on any simple Debye-Hückel model (see Turner, 1983). This planned approach had barely begun when a catastrophic accident with one of several recently purchased designs of steam turbines directed our attention, for several years, to steam phase problems rather than those in the boiler water.

At the critical point of any electrolyte solution, but also in steam, which is also highly compressible, very serious theoretical problems are to be expected. This is partly because a standard state is defined to be a solution of unit concentration but possessing the thermodynamic properties of one that is *infinitely compressible*. This would appear to make the appropriate standard state a totally meaningless concept since a real salt, in its standard state of zero concentration, must be attracting the *infinite* number of water molecules nominally present into the electric fields of its component ions and *not* the quantity of water present in a real solution of unit concentration. As we shall see in the following sub-section, this seems not to be the case.

Some Unexpected Characterstics of Moist Gases

A strong electrolyte in a moist gas represents a somewhat similar problem to those just discussed since it might also be expected to invalidate the use of a conventional standard state. In the air, no related problems have ever been observed since no directly relevant experimental tests have probably ever been devised. A reason for suspecting that this problem *might not be real* is that all standard state thermodynamic properties are *functions of state* that, in principle, do not depend on the path through which they were obtained. It has long been known that the non-existence of a physically achievable standard state *does not matter in practice*. Such states possess perfectly well-defined and practically useful values - provided only that consistent conventions are followed when they are used (e.g., Wagman et al., 1982).

One such convention, used in tables like those of Wagman, et al. (1982) and of Chase et al. (1985), is that the enthalpies and Gibbs free energies of formation for the *chemical elements in their stablest forms* are all zero. The tabulated properties of individual gaseous ions also use the additional convention that the electron is in thermal equilibrium and has an enthalpy and Gibbs free energy of zero. A mole of dissolved ions, *all of the same charge,* is obviously not a physically attainable state, but the standard state thermodynamic properties of *separate* ions have long proved valuable despite representing totally unreal states. By analogy, the fact that solutions are highly compressible would not necessarily invalidate the use of standard states either.

The electrochemical model for ball lightning (Turner, 1994) was based on this expectation (questionable hope would have been a more accurate description at the time). Its ultimate success (Turner, 2002, 2003) supports the claim that consistently defined standard state properties of very compressible solutions and in moist air are indeed meaningful and very valuable quantities.

A fundamental problem in understanding many of the chemical reactions that occur with ions in moist air is a general belief, among both chemists and physicists, that solute activities and solute concentrations can be treated as more or less identical and that, where differences are significant, an activity coefficient can always be used to estimate the really important *thermodynamic activities* from the concentrations which can always be reliably known - at least in principle. Concentration gradients are, in fact, *not directly* relevant in determining rate processes. The fact that no change of any kind can occur unless it *lowers some clearly defined energy* is *far more important* than any estimate of a collision frequency (which can normally be obtained from a concentration). This fact is almost always ignored in considerations of chemical reaction rates.

It should be stressed here that most of the important problems raised earlier apply only to real *electrically neutral solutions*. Such problems do not apply to the many fruitful thermodynamic studies that have been undertaken inside mass spectrometers (see Keesee and Castleman, 1986). In such studies, charge neutrality is obviously not constrained in any remotely similar way to that in a

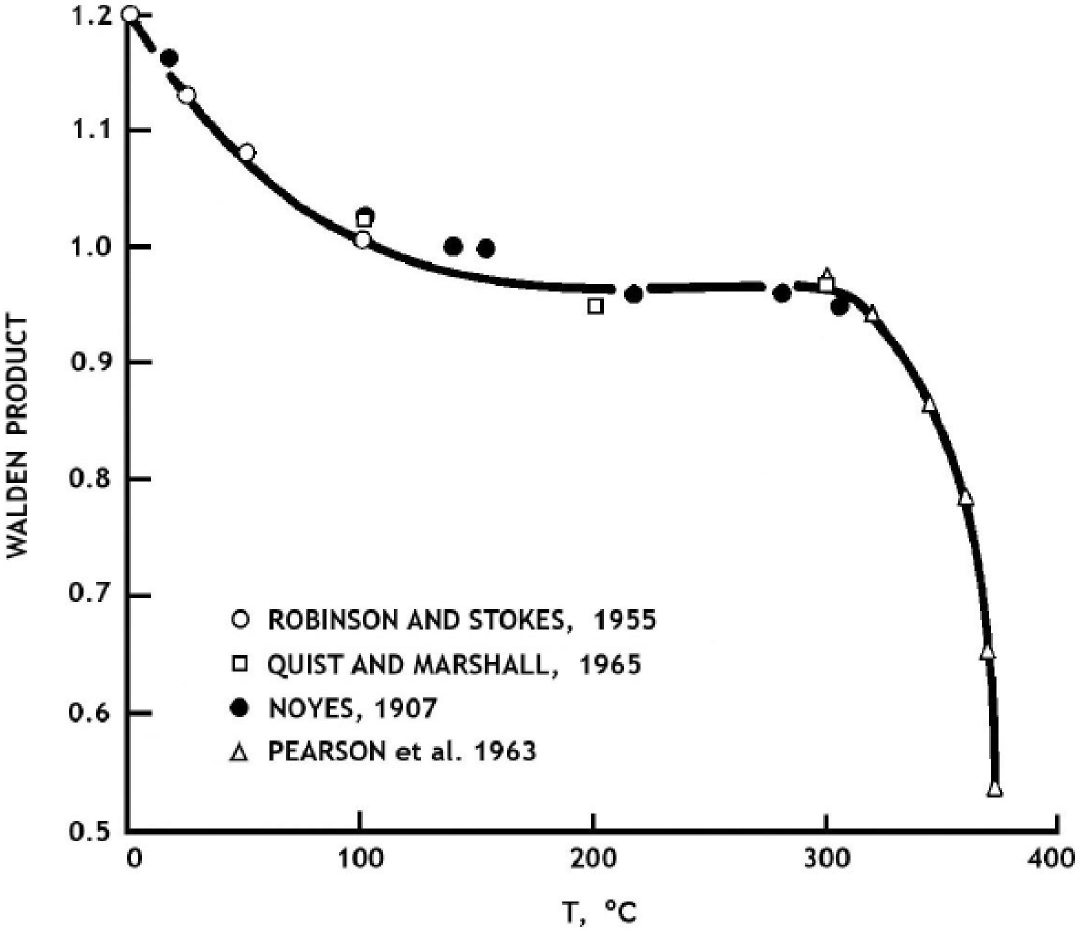

Figure. 2: Walden products for aqueous solutions of NaCl (Turner, 1983). Their units are those of the original investigators (cgs units). If the solutions were behaving ideally (no structural effects), the curve would consist of a horizontal line at a Walden product near 1.0. At best, this might be reasonably true for temperatures between 100 and 300^0 C

solution since no cloud of oppositely charged ions surrounds an isolated ion in a near vacuum. At first sight, it may seem surprising that standard state thermodynamic properties of hydrated gas phase ions correlate so well with their values in solution (Kebarle, et.al., 1967, Kebarle, 1974) but, as these authors have shown, they certainly do. Although standard states represent obviously unreal states, they are still, as we have seen, well-defined quantities. Such considerations were crucial in developing the basic electrochemical model for ball lightning (Turner, 1994).

In many other areas of study where charged species are involved, for example, in particle and stellar physics or in dealing with the mechanical forces produced by rocket engines, there is never any need at all to consider that concentrations and activities differ. In all these cases, if the fluid energies or momenta resulting from chemical or nuclear reactions need to be considered, the temperatures involved are always so high that hydration effects could never lead to detectable differences between concentrations and activities. It is obviously very convenient to be able to ignore these differences, and ignoring them has become almost universal. The problems discussed here *only* arise because *temperatures are so low that electrostriction is unavoidably huge.*

Some of the more successful kinds of study, for example, on formation paths of the elements in supernovae (Arnett, 1996), the aging of stars, or the pre-history of the solar system (e.g., Lugaro et al. 2014), are only possible because of the huge quantities of data that are available on *nuclear* processes *at extremely high energies (temperatures).* In such cases, detailed arguments can be made perfectly validly. By comparison, our knowledge concerning the behavior of ions in real moist air (or in any other moist gas, such as the hydrogen from which stars are born) is comparable to that of a hypothetical eighteenth-century chemist who still believes in the reality of phlogiston and who tries to use the concept to make quantitative predictions.

At low temperatures, almost no one ever considers that there are, in principle, electrolytes *at equilibrium* in the air, or in steam at normal air temperatures. Such concentrations are always far too low to measure. But even if measurements were to be possible, the solutions would be so strongly sedimented on Earth that it would be nearly impossible to obtain direct information on the true equilibrium state for comparison with a conceivably valid new theory that realistically takes compressibility into account. The data illustrated in Figs. 1 and 2 were originally used to explain the need for new experimental studies as the CEGB's part in the so-called micro-gravity program of ESA (Turner, 1983).

The results of our first two experiments in sounding rockets (Turner, 1988a) merely confirmed that de-sedimentation does occur when the Earth's gravitational field is removed from supercritical steam solutions of common salt. They also showed that the rate of de-sedimentation was far too slow for any sounding rocket flight to reveal anything useful about the equilibrium state. Experiments in orbiting craft were obviously needed. Our third and final low gravity experiment measured near critical pressures (Turner, 1993) - in anticipation of such flights. However, by 1993, CERL had been closed, and no alternative source of support was found. Thus no *useful quantitative* data were ever obtained from the brief collaboration with ESA.

While the evidence from the work of Copeland, Silverman, and Benson (1954) and of Benson, Copeland, and Pearson (1954), as displayed in Fig 1, concerns the equilibrium state, other kinds of evidence that involved electrostriction had also been reported in much earlier investigations of ions in moist gases (Townsend, 1897a,b 1898; Thomson, 1906). By 1960, extremely large hydration numbers for atmospheric ions had been calculated from the transport properties of ions (Loeb, 1958). For example, ions classified in meteorological studies as "large" (of the order of 0.1 ìm in diameter) can have hydration numbers up to 3.10^8.

Clues From Studies on Moist Ions

This crude separation of atmospheric ions into large and small have proved essential in most attempts to describe the electrical state of the atmosphere up to and into the stratosphere (Beard & Ochs, 1986; Levin & Tzur, 1986; Roble & Tzur, 1986). Naturally, several of these authors (among others) have understood the limited value of such approximations. It is obvious that most of what happens *chemically* with real atmospheric ions, whose hydration numbers lie between about 6 (where a few measurements have been made) and 10^9, is *completely unknown*. It is in the context of this problem that several much earlier studies than those just mentioned are so revealing. Among the most important were those reported by von Helmholtz (1887), Planté (1888), von Helmholtz and Richarz (1890), and Townsend (1898), together with studies of Tyndall (1868), of Wilson (1897, 1899a, 1899b) and of Vincent 1904.

The much earlier experiments of Arden and Constable, described in the books of Priestley (1781) and Cavallo (1782), are also of considerable importance. However, many prominent physicists of the late 18th century tried, but totally failed, to reproduce these findings. A few other physicists later concluded that chemistry must be important in systems like these, but only the studies of von Helmholtz (1887) and von Helmholtz and Richarz (1890) *directly* demonstrated chemical effects due to the presence of ions. By the 1990s, it was becoming increasingly obvious that the missing science described here is largely responsible for our poor understanding of such rare natural plasmas as ball lightning (Turner, 1994, 2002). Similar conclusions were drawn for the larger relatives of ball lightning that include earth lights, tornadic lights, and UFOs (Turner, 1998, 2003; Teodorani, 2004). In the commonly used acronym, UFO, the word "unpredictable" now seems more appropriate than " unidentified" (Turner, 2023a).

My interest in the observations of Arden and Constable began to increase following a realization that our longstanding failures to address the problems of electrochemistry in the vapor phase might be responsible for their findings and for the total failures of others to reproduce them. The *most significant fact* is that Arden and Constable produced *the only two fully realistic simulations of ball lightning ever to have been created*. Crucial progress for me resulted when advice was sought from the Royal Society enquiring whether Constable had been a Fellow of the Society. In fact, he was, but it so happened that plans for opening his family home to the public were being made at the time of my inquiry. As a part of this project, Constable's collection of science-related equipment was prepared for public display. I later learned (from Elizabeth Hall, who was researching the life of John Arden) that receipts for virtually all of Constable's equipment had also survived.

The Deputy Librarian at the Royal Society, Alan Clark, kindly arranged for me to visit Constable's home (Burton-Constable Hall in east Yorkshire) to see the collection. This seems to have included all the undamaged items that he (with Arden) would have been using when they produced their simulations of ball lightning. It appears that, in December 1757, Arden and Constable had performed two experiments, each of which they accidentally created a single, small, glowing ball of plasma (Priestley, 1781; Cavallo, 1782). The full account given in these books is now more readily available elsewhere (Turner, 2002).

Over the last three decades, I have spent thousands of hours conducting experiments that, in effect, were attempts to understand why it has proved so difficult to repeat the findings of Arden and Constable. These have employed experiments with different objectives, with systems of very different scales and designs, different materials of construction (and therefore different potential causes of chemical contamination), and employing different electric field strengths to produce sparks. Several of them taught me what seemed important lessons, but none produced a simulation of ball lightning. The most important conclusion was that the observations of Arden and Constable were probably genuine and might eventually be repeatable and understandable. I also demonstrated that short-lived *spherical* plasma balls, with diameters as large as 1 cm, could be produced extremely rarely but *always unpredictably*.

Such balls were formed only three times out of many thousands of brief tests. They probably all had lifetimes of less than 0.02 sec., although this was only proved true (by cine-photography) in one case. Smaller *hemi- spherical* discharges could, however, be produced fairly *reproducibly* when air of very high humidity was maintained by arranging that the cathode comprised a vertical bras rod surrounded by wet filter paper. A coil of copper wire provided the anode, and it had a diameter somewhere between 20 and 30 mm. The copper wire itself had a diameter of 2 mm, and the anode that it surrounded was pointed with its tip roughly in the plane of the anode coil. Three examples of the short-duration hemispheres around the anode are shown in Fig, 3.

Because the voltages supplied by a van der Graaf generator are so high, no commercially available switches are available. Thus the sparks in all the tests had to be generated by bringing a large hollow metal sphere into contact with the sphere at the top of the van der Graaf generator. This process could not be replicated at all well. Consequently, the energy deposited during none of the tests is known. The brightness (and, to some extent, the shapes) of the discharges varied considerably, most having been considerably less bright and rather less symmetrical than those illustrated. The red color on the first spark illustrated is presumably a consequence of some contaminant on the cathode ring.

Apart from their short lives, the larger discharges of this kind resemble approximately half of the kind of lightning ball that typically seems to have formed in fairly clean environments. I was, therefore, somewhat surprised to discover that a lightning ball that had been recently witnessed by my mother looked, to her, very similar to the sort of spark shown in Fig 3. My initial surprise was caused by evidence that this ball had like many other reported lightning balls, been formed when a normal form of lightning hits some part of a tree. I later realized that because a lightning strike is so brief, there was probably too little time available for much apart from the surface moisture to combine with the components of the air and thus create the ball.

In the experiments of Arden and Constable, two plasma balls were formed during successive experiments inside large open-topped Leyden jars of nearly identical size, shape, and materials of construction. The tests were being made to ensure that Constable's latest purchases operated satisfactorily. During the experiments, the balls destroyed the Leyden jars in which they had been formed, and they did this in very significant ways: circular holes were made in the glass jars, and they appeared to have had exactly the same diameter as the plasma balls. Unsurprisingly, the damaged jars are not in the collection but the machine used to charge them almost certainly is. This was only described in Arden's letter to Priestley as "a very good electrical machine". (technically needs citation and page number) Constable had possessed several of these. In fact, the actual device used in the experiments does not matter.

The detailed records of Constable's purchases might possibly clarify which of the machines could have been used in the experiments, but this is immaterial to the following arguments since the ways in which the machines were connected to the Leyden jar would have been virtually identical. Smaller items from the collection that date from the same period also still exist. Importantly, these include chains of the type that would have been used to connect any of the electrical machines to the inside of the Leyden jars inside which the air plasma balls were produced. The most noteworthy aspect of the two preparations was that they *immediately* followed one another and that preparations could not be repeated after that.

Simply seeing the actual objects that must have been used made it clear that it would have been very easy to replace the first damaged jar with the second one *without any disturbance to most of the heavy brass chain*. Its thick links would likely have been covered with a layer of oxide (naturally much thinner than they are now). If there had been some thin solid (possibly an oxide or sulfide) holding two links very slightly apart, and if the relevant part of the chain was not disturbed when the first jar was replaced, it seems likely that the spacing between the two links of the chain was identical for the two successive experiments. It may also be that the composition of the very thin solid separating them and the chemical composition and humidity of the air inside the jars happened to be optimal for the formation of lightning balls. I have assumed this to be the case ever since the equipment that Arden and Constable actually used was examined.

I never found any means for consistently increasing the size or duration of the small discharges shown in Fig 3, or of causing them to move away from where they were formed. The reason that any experiments of this kind were performed was that they seemed directly relevant to one of the ways in which lightning balls have been reliably observed to form. Once a spherical form of corona discharge, usually identified as St. Elmo's fire, has become reasonably stable, it has repeatedly, though very rarely, been reported suddenly to free itself from the electrical conductor to which it was attached. Only a very small fraction of the sightings of ball lightning have described its actual birth, and among the clearest of these was the conversion of a spherical form of St Elmo's fire into lightning balls. These spherical forms of the "fire" can be thought of as tethered lightning balls.

On the Creation of Lightning Balls

So far, attention has concentrated on those areas of neglected science, whose neglect seems to be responsible for our long-term difficulties in understanding the strange characteristics of ball lightning. As will be shown in detail elsewhere (Turner, 2023a), lightning balls seem to be the building blocks of air plasmas with even more extraordinary characteristics than those of ball lightning itself. My basic ball lightning model (Turner, 1994) resulted mainly from improvements to Stakhanov's (1979) basically electrochemical model, This was the first model that seriously attempted to explain *all* of the confusing properties of lightning balls. The improvements also required a slowly increasing appreciation of problems raised by the limitations of the missing science referred to earlier.

One of the most detailed examples of the formation of lightning balls was described by Mattétal (1895). It will be briefly summarized once an important matter concerning St Elmo's fire has been addressed. Originally, the name was given to a phenomenon that used to be fairly commonly reported on the wooden masts and rigging of sailing ships (during thunderstorms) *before* the invention of lightning rods in the 18th century. Apart from one engraving in a popular meteorology book (Flammarion, 1888), I have rarely seen a picture purporting to be of St. Elmo's fire that does *not* show a thin electrical discharge pointing vertically upwards into the air.

However, a picture of what may have been more typical on very early ships can also be found on the website of ScienceFacts (2021,https://www.sciencefacts.net/st-elmos-fire.html). The difference in shape presumably arises from very different current flow.

It is difficult to believe that anyone would ever have referred to thin vertical corona discharges either as "fire" or used the alternative name of "corposant", which means *body of a saint*. Most current illustrations of the phenomenon show these thin pointed discharges, and they seem to have been first published in the mid-19th century. By this time, most ships would have been fitted with lightning rods of some kind. The point of these comments is that nearly all books on ball lightning state *categorically* that St Elmo's fire and ball lightning are quite different phenomena. Some of my reasons for believing otherwise

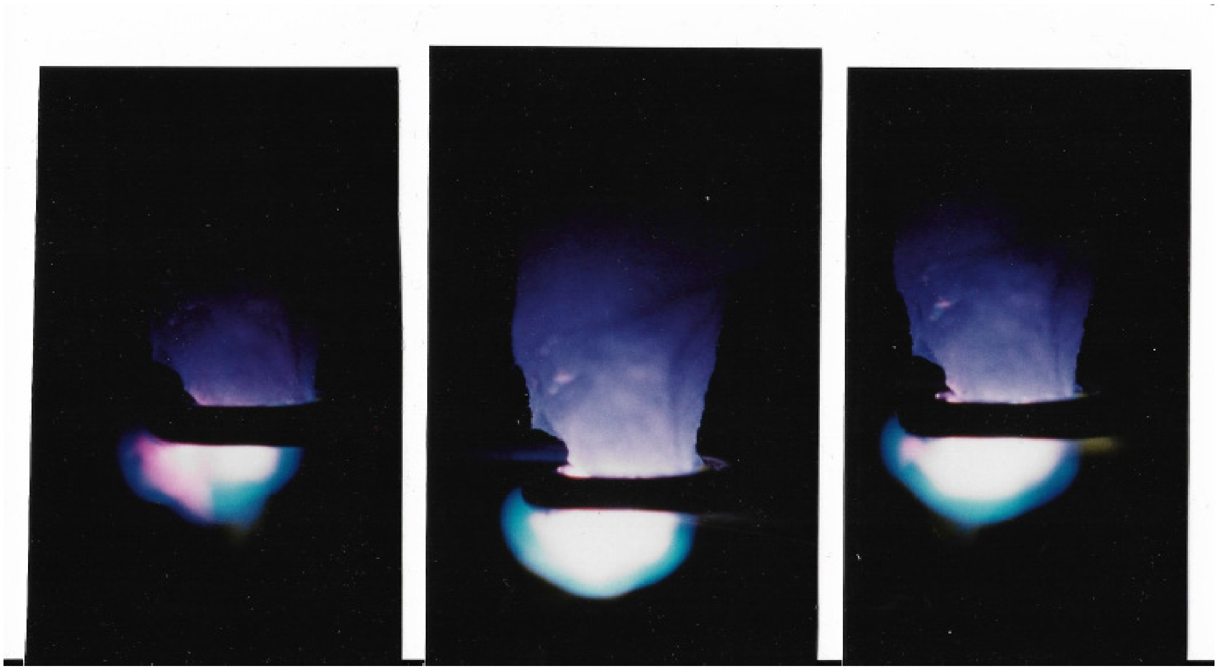

Figure 3: Three hemispherical discharges in very humid air. The sparks were produced using a small van der Graaf generator whose energy was discharged as efficiently as possible through the spark gap. This comprised a vertical anode and a horizontal copper coil surrounding it. The examples are three of the most powerful sparks obtained.

will now be illustrated.

The transformation witnessed by Mattétal (1895) occurred on the rooftop of a house, easily seen from the upper story window through which he was watching a prolonged and violent thunderstorm. He saw a "ball of fire" attached to an iron rod that supported a telegraph cable. The ball was expelling sparks downwards that resembled those produced when a power hammer is shaping a lump of white-hot steel. After about 40 to 50 seconds, the ball suddenly split into three smaller balls (each about the size of a child's balloon) which left the iron rod, fell to the roof, and then rolled down it. They produced no sparks until just before their demise when they had reached the gutter and, a few moments later, vanished (without exploding). Almost immediately, a second plasma ball formed in the same way at the end of the same rod. It seemed to behave similarly at first but only lasted two or three seconds before it simply disappeared without leaving the rod.

The characteristics described for these plasma balls leave little doubt that the ones which rolled down the roof were typical lightning balls or that the large corona discharges at the top of the iron rod would have been called St. Elmo's fire (though in a roughly spherical form) by many current physicists.

Mainly on the basis of this clear description, and similar less detailed ones, provisional approval, at CERL, was given for an attempt to reproduce the phenomena that Mattétal had observed. It was agreed that there were to be at least two days of experiments and that they would be carried out at the facilities of the High Voltage Laboratory. This was, at the time of the proposal, still part of CERL. However, when the time came for the tests, the company was in the process of being split up in preparation for privatization, and I, having been "allowed" to retire early, was in the process of moving temporarily to Bristol University to complete the collaboration with ESA.

Obtaining approval for the proposal (Turner, 1988b) and assembling the required hardware took several months. By the time of the planned experiments, the High Voltage Laboratory (recently transferred to the National Grid Company) was owned by a different company from CERL (then a part of National Power). However, relations between the two companies were becoming increasingly complicated, and I was about to leave for Bristol. For these reasons, and for others to be described shortly, only one day of experiments was ever actually conducted. It should be explained that some lightning engineers have long been interested in ball lightning (e.g., Uman, 1984).

These balls have been reported ever since they were claimed to be thrown by the gods (Singer, 1971), but the main concern of physicists and engineers now is the connection between the *physics* of normal lightning and ball lightning - not the relatively minor damage that lightning balls normally inflict. Although it is very rare for lightning balls to do serious harm to electric power transmission systems, damage has occasionally been reported, and several individuals transferred to the new National Grid Company were already interested in ball lightning.

When studies on ball lightning were first proposed (Turner, 1988b), the main justification had been in terms of what could be learned about the interactions between ions and water molecules. Although it was obvious that ball lightning studies might *eventually* lead to a new, plentiful source of carbon-free energy, it was equally clear - *from centuries of failed attempts to create artificial ball lightning* - that numerous questions needed answering if practical use of air plasmas was ever to be made.

A brief summary of the experiments needs to be provided here because the outcome influenced most of my interests after the collaboration with ESA came to an end, along with all hope for support for the basic electrochemical studies. The power supply used at the High Voltage Laboratory was a Cockroft-Walton four-stage voltage multiplier. For our experiments, it was decided to use a potential difference of up to 543 kV d.c. across a 1-meter spark gap. The current (of a few mA) was controlled by a large, high-purity water resistor that had much earlier been constructed in-house. The voltage could be varied during an experiment, as could the electrode separation.

The cathode consisted of a smooth hemispherical conductor suspended directly over an anode assembly that comprised two parts. In most experiments, a pointed central steel rod was surrounded by, and electrically connected to, a circular dish-shaped mesh of steel having a diameter of 1.2 m. The anode assembly was located partly in, but mostly above, a pool of warm, temperature-controlled, water through which a rapid flow of air could be bubbled through multiple nozzles. The purpose of the dish-shaped mesh was mainly to provide a healthy positive space charge between the electrodes before air breakdown was initiated (by increasing the field) but also to provide electrostatic stability to any ball that might be released from the anode tip.

High humidity in the air between the electrodes was maintained by enclosing the whole assembly within a humidified, wood-framed, chamber that was cube-shaped (with 4 m edges) and covered with sheets of polyethylene. This provided a relative humidity close to 100 % at the anode level. The relative humidity was probably also close to 100 % over much of the volume between the anode and cathode. The containment chamber had been constructed for and was kindly loaned by Dr. N.L. Allan of Leeds University. The mesh position was fixed, but the height of the central rod was remotely controlled hydraulically. Video cameras, operating at different wavelengths, recorded events near the anode and were placed inside the humidified enclosure. The voltages and hydraulics etc. were controlled from different positions, but it so happened that no one could see the cathode region during an experiment.

The most informative test was the 9th of 10 experiments performed that day and was the only one which did not use a steel rod as part of the anode. The first eight tests showed normal coronal glows and discharges at the tip of the pointed steel anode just prior to air breakdown, as the field was slowly increased. These glows were only a few mm in diameter, but their size depended reproducibly on the mean field strength. For the 9th experiment, a thick-walled, porous ceramic tube was substituted for the steel rod, and, on top of it was placed a piece of wet paper towel (roughly 12 mm per side) draped over the top of the tube. It was hoped that this might simulate the moist wood that is believed to be one of the most common supports for St. Elmo's fire in its spherical form.

The behavior in experiment 9 was totally different from all those observed with the metal rod. As the field was gradually increased, two bright spots were first observed on the paper and then what looked exactly like flames started to lap the whole length (about 15 cm) of the ceramic tube. My immediate reaction was that this behavior was clearly responsible for the name St. Elmo's fire and that, under slightly different conditions, a spherical plasma might well form at the top of the ceramic tube. However, the engineers in charge had become very concerned over some large and *completely unexpected* changes in voltage which could not immediately be explained. Nothing like them had ever been observed in years of previous experimentation.

As a result, it was decided to give the engineers running the experiment a little more time to consider the possible causes of the strange voltage behavior and that we should therefore delay further experiments with the ceramic tube until the following day. Since there was still time for one more test, the last one reverted to the use of a steel anode. There were two main differences from experiments 1 to 8. One was that, instead of using a sharp tip, a smooth metal ball was fixed to the top of the rod. The other was that the probably over-cautious limit of 543 kV was relaxed somewhat. Although it was clear that the quantity of water condensed on the polyethylene inside the enclosure had been increasing all day, no new risk from that cause was foreseen.

As the voltage was increased between 180 and 200 kV, a brush discharge started to surround the ball, the origins of the separate discharges being droplets of water on the ball. This is apparently normal in the period before a smooth metal surface has "conditioned itself". By the time the voltage had reached 543 kV the discharges had become much larger, but they were still nothing like those witnessed by Mattétal (1895). It was then decided to apply a voltage a little above the pre-agreed maximum, in practice to a little above 600 kV. The electrical breakdown between the *cathode and the containment* chamber occurred almost immediately, and the latter burnt down. No one could explain exactly what happened since, during the test, no one present could see the cathode region where the breakdown occurred.

The breakdown probably resulted from the presence of a much larger than normal space charge, consisting of heavily hydrated protons, that had formed between the electrodes. Townsend (1897a,b,1898) had, nearly a century earlier, showed how very easy it is to move very large hydrated ions in a flow of moist gas. Later it was realized that the accident was probably somehow the result of forming the large space charge. The ions present were carried upwards with the water-saturated air (delivered through the anode mesh).

This positive charge would have slowly moved upwards and could have helped cause the breakdown (as well as the voltage anomalies of the previous experiment). The breakdown does not, of course, mean that the discharge resembled a short-lived lightning ball - although this might have been the case. We had such possibilities in mind for the next day's experiments but, clearly, the destruction of the containment chamber would cause delays.

The long-term objective had obviously been to learn how to simulate ball lightning. Clearly, the electrical breakdown at the cathode *might* have resulted from an early stage of forming a lightning ball. Hence the delay made necessary by the accident was initially seen as a potential *advantage* in that we had time to revise our detailed plans for the second day's experiments. Unfortunately, although the next few months were used to prepare a variety of new anode designs, it never proved possible to arrange the implementation of the revised plans.

This was partly due to the very preliminary status of our results on the first day of experimentation and partly to the ongoing management changes arising in the two companies involved. My absence in Bristol and at the launch site of the sounding rocket clearly made matters worse. Nevertheless, what was learned during that single day of high-voltage experiments largely determined my later scientific interests - once it had become clear that gravity-free studies of the missing electrochemistry were unlikely to be supported.

These experiments had obviously been a digression from our main concerns which were the studies we had begun in collaboration with ESA. This work appeared to be needed by the industry, but it was unavoidably slow and boringly mundane in its objectives - at least compared with speculations on how to prepare artificial lightning balls. It was fully realized that anyone attempting such a preparation would be defying 240 years of failed attempts (see e.g. Singer, 1971; Barry, 1980). Thus, only attempts to *understand* a little more about the processes that can stabilize lightning balls seemed worth pursuing.

In this connection, a great deal was learned while at Bristol through reading some of the neglected 19th-century physics literature and from simple experiments I was encouraged to undertake during vacation periods in a teaching laboratory of the Physics Department. These experiments were designed to follow up on those that had been conducted in the High Voltage Laboratory at CERL. One important hint, obtained during the tests at CERL, implied that the large currents provided at any high-voltage testing facility might not be needed; in fact, they could be a disadvantage - in addition to the very constraining safety issues involved.

At this time, there seemed to be strongly conflicting evidence on how much current is needed to form a lighting ball. The birth witnessed by Mattétal (1895) was at one extreme while at the other was a case where a much more feeble ball was produced in the air immediately below the downward pointing finger of someone who was indoors and standing on a rug (Humphreys, 1937). Humphreys was, like many other physicists, very skeptical of even the existence of ball lightning, but he included this example in his summary of some of the 280 replies he had received in response to his request for claimed ball lightning sightings. He also referred to a much more typical account provided by the eminent physicist Leonard Loeb. It now seems clear that vastly different currents can feed a lightning ball because most of the energy needed *to support such a plasma,* once it has formed, is *chemical* and not electrical. In principle, ball lightning initiation resembles the lighting of a flame in that the process of igniting the flame has nothing to do with the chemistry of the fuel-burning processes that support it once it has formed.

Although it was not clear, at the time I left CERL for Bristol, that further experiments at the High Voltage Laboratory would prove impossible, from that time on, I started to take advantage of any available opportunity to work with very much smaller currents. Many hundreds of tests were carried out in the Physics teaching laboratory at Bristol (including those that produced discharges shown in Fig.3). Later on, hundreds more simple tests were undertaken at two different homes in the USA. These tests made use of a gradually increasing collection of instruments, tools, and materials.

OTHER STUDIES AND SOME IMPLICATIONS FROM THEM

Experiments from the 19th Century

Mention should be made of a set of completely different kinds of experiments, the first ones having been undertaken at the end of the 19th century. Any of them might be worth following up using more modern techniques than were available at that time. These were some of the early experiments of Townsend (1897a,b, 1898) in which he reported on the electrical properties of the gases released during the electrolysis of solutions of H_2SO_4 and KOH. In the second paper, he also reported briefly on the electrolysis of HCl solutions, but the results were so greatly complicated by the presence of chlorine gas that no useful conclusions could be drawn. The electrolysis cell normally reached temperatures in excess of 40^0 C by the end of an experiment. In his first two papers, Townsend (1897a,b) established that many of the gases produced by electrolysis carry with them significant electric charges. Most of the charge is maintained within these gases even after passing them through glass wool to remove any liquid spray carried with the gases and then bubbling them through a series of flasks containing various solutions - or pure water. For these experiments, short "tunnels" of paraffin wax were provided to insulate the electrolysis cell from the electric charge measuring region. In this region, the flasks were insulated from their surroundings using blocks of paraffin, and an earthed metal screen was provided.

The vessels could be weighed before and after the passage of known quantities of charged gas so that the water content of the clouds and the charges on them could be determined. The temperature of the first vessel, through which the gases passed, could be cooled to temperatures between 0 and 15 ^{0} C (Townsend, 1898). It was found that any hydrated ions carried with the gases could be *rapidly and reversibly* de-hydrated and re-hydrated and that in some experiments, *but not all*, the gases released by electrolysis rapidly formed clouds when they were bubbled through pure water. Condensation was found to be possible *only* if the gases were electrically charged (not all were). In other words, the electrolytically produced gases must have contained the kinds of aerosol that meteorologists now usually refer to either as charged Aitken nuclei or large ions.

One important implication of the last paragraph is that at least some of Townsend's experiments had *failed* to produce ions in the gases released during electrolysis. No result for the electrolysis of *nitric* acid was reported. Both Townsend and Wilson shared an interest in atmospheric processes. It was therefore surprising to note that the electrolysis of nitric acid was not even mentioned in any of Townsend's studies. It is probable that the electrolysis of nitric acid *was in fact* studied but that it failed to produce charged clouds. Such a failure would not now be thought surprising since we now know that nitric acid *in the gas phase* is thermodynamically unstable (see Fig.4) with respect to the components of the air at the temperatures rapidly reached in Townsend's electrolysis cell.

This can be seen using available thermodynamic data on nitric acid formation from the principal components of the air. Fig. 4 illustrates the three most favorable Gibbs free energies of formation, for these reactions, as a function of temperature.

Since nitric acid might be formed from water in either the gas phase (g) or in an aerosol (liq) and the product can be either gaseous (g) nitric acid or an aerosol (aq) containing the acid, there are four reactions which, in principle, can lead to its production in the air. The Gibbs free energies of the three most favorable of these reactions are shown in Fig 4, the necessary data having been obtained from the tables of Wagman et al. (1982). The three lines in the figure refer to the following reactions:

$$N_2\,(g) + 2.5\,O_2\,(g) + H_2O\,(g) = 2\,HNO_3\,(aq) \qquad (3)$$

$$N_2\,(g) + 2.5\,O_2\,(g) + H_2O\,(liq) = 2\,HNO_3\,(aq) \qquad (4)$$

$$N_2\,(g) + 2.5\,O_2\,(g) + H_2O\,(g) = 2\,HNO_3\,(g) \qquad (5)$$

Since these reactions could only proceed if they were to lower the Gibbs free energy of the system, it is clear from Fig. 4 that neither Reactions 4 nor 5 can produce nitric acid at any temperature. Very significantly, even Reaction 3 (which forms the aqueous acid from the three gaseous reactants in the air) is thermodynamically possible only at temperatures *below* 15^0 C.

Each of the reactions whose free energies are represented in Fig. 4 has an associated enthalpy which is given by the identity

$$\Delta G_0 = \Delta H_0 - T\,\Delta S_0$$

Here ΔG_0, ΔH_0, and ΔS_0 are, respectively, the standard Gibbs free energy, enthalpy, and entropy of the process, and T is the temperature. The enthalpies represent the quantities of heat that would be released *if* the reactions could be made to occur with each component in its standard state. They are somewhat temperature dependent but, for example at 10^0 C, they would be -168.2, -123.6, and -27.9 $kJ.mol^{-1}$ for Reactions 3, 4, and 5, respectively - again based on the NBS tables (Wagman et al., 1982). In other words, the major chemical components of the air contain energy, but only Reaction 3 *can* proceed and release it.

It is clear that the above arguments refer to the reactions proceeding from left to right. At first sight, they say nothing about the reverse reactions, which would be the ones of practical importance in Townsend's electrolysis experiments. However, the energies involved do seem to be relevant even in this case. This is because, in an electrolysis cell that has a tendency to produce ions in the gases released at the electrodes, any ions formed will have very high energies and so would normally lead to a fairly *rapid approach to the equilibrium state.* Clearly, this does *not* favor the formation of nitric acid. In fact, Reaction 3 is very much more important in the context of ball lightning stability than it is in explaining why Townsend probably failed to obtain charged gases in his electrolysis experiments. Reaction 3 is only able to proceed because it can liberate heat (locally), and this heat is, in principle, capable of being transformed into more useful forms of energy, such as electrical energy or mechanical work. As was shown in my first paper on ball lightning (Turner, 1994), the air surface next to an air plasma needs to be initially refrigerated through the formation of a different oxyacid of nitrogen, nitrous acid which has to occur first. Part of the difficulty in producing long-lived lightning balls undoubtedly results from the need to establish a region around the plasma in which a strongly endothermic (heat removing) reaction, producing nitrous acid, is in very close proximity to an exothermic one producing nitric acid (Turner, 1997).

Whether or not the electrolysis of nitric acid was actually undertaken in Townsend's studies, a repeat and extension of his work should at least confirm that no charges are produced during the electrolysis of nitric acid solutions. It might also provide a way of discovering a little more about vapor phase electrochemistry - though vastly less than would have been likely from experiments on the International Space Station - as had once been expected. New studies like Townsend's are, however, unlikely to reveal very much more about nitrogen chemistry except, possibly, to confirm that the electrolysis of nitric acid liberates no charged gases.

More Recent Meteorological Studies

With respect to the ball lightning study, there are three very important implications from the data displayed in Fig. 4 and from the reactions which they represent. One concerns the fact that the oxidation of N_2 to nitric acid can only arise through Reaction 3; the second is that this reaction is only possible if the temperature is below about 15^0 C; the third is that this reaction results in a significant *reduction in the number of particles* when it occurs (making 2 moles of the acid from 4.5 moles of the reactant gases). The reaction thus produces an inflow of air toward the reaction site at the surface of the plasma (Turner, 1994).

It should be noted that sites where Reaction 3 is possible *are not limited* to the surfaces of air plasmas. It is well known that nitric acid is present in clouds (Seinfeld & Pandis, 2006) and, as suggested decades ago (Turner, 1998), what might distinguish cumulus clouds, with their sharply defined edges, from other clouds is that, in them, there could be a more than usually rapid inflow of air - producing nitric acid through Reaction 3.

In principle, Reaction 3 can occur anywhere in the atmosphere where the temperature is below about 15^0 C, and this is true of practically all of the air in the troposphere above the Earth's surface (Seinfeld & Pandis, 2006). The endothermic (cooling) reactions that produce nitrous acid (Turner, 1994) can, probably only occur in the presence of sufficiently energetic electromagnetic radiation, or where population inversions are present. One cannot help wondering whether it is only a coincidence that the mean temperature of the Earth is so close to 15^0 C. Over the last 150 years, it had been close to 14^0 C (Jones et al., 1999), while it was already about 0.5^0 C above this by 2006 (Seinfeld & Pandis, 2006). Could it be that there is a direct connection between the thermodynamics of Reaction 3 and the much-feared tipping point for the climate? If air temperatures on Earth rise much above the current estimate for the maximum safe value, we might well be closer than we thought to beginning an *unstoppable* change towards an almost totally ice-free world.

Investigations of a Tornadic Storm

Shortly after arriving in the USA, I was invited to give a talk on ball lightning at the Naval Research Laboratory (NRL) in Washington, DC. A few days later, Graham Hubler, who had long been interested in ball lightning, but who was unable to attend my talk, began to plan for a collaboration with me on the subject. Unfortunately, a few months after that, the terrorist attack of September 11th took place. As a consequence, the NRL formally decided that it would only support new projects if they were terrorism-related. Thus our plan was never implemented. However, an event intervened before this decision had been made, which resulted in a single measurement being obtained at NRL that I firmly believed (and still do) was directly related to air plasma chemistry.

The measurement made at the NRL was of the mean concentration of nitric acid in a single large hailstone. This hailstone was one of many I had collected when a tornadic storm passed fairly close to our house. The residents who had collected the hailstones were only too happy to offer them when they were assured (mistakenly, as it transpired) that they would be used in a detailed research project of the NRL.

The hailstones were obtained in the first place because I had previously found evidence (Turner, 1998) that some tornadic storms contain glowing air plasmas and because this particular storm appeared to be one of them. More details of the event and its study are described at https://naturalplasmas.com/.

The most important findings, summarized below, resulted from gradually melting three of the largest stones, as symmetrically as possible, from the outside toward the center and collecting samples of the melt-water during the process. The samples were then taken to the Chesapeake Biological Laboratory for chemical analysis of the anions present. Apart from the first few and the very last samples collected (where contamination from contact with the ground and from the initial hailstone nucleus might be expected), the analyses showed a remarkably consistent pattern of nitrate concentrations. They also showed the complete absence of nitrites, while chloride and sulfate concentrations varied greatly (*over many orders of magnitude*) with radius.

Large oxidation potentials were also observed, and they were found to be almost totally uncorrelated with nitrate levels. Apart from one fraction, taken from the center of one hailstone, all the potentials were very high. These results are summarized in Table 1. The table shows the nitrate concentrations and oxidation potentials found in the seven hailstones examined, together with similar results for distilled water and one nitrate analysis (HW) of rain which had accompanied the remnants of a hurricane. This had passed through the local area a few months after the tornadic storm.

The three samples identified as average (av) in Table 1 were those whose nitrate dependence on radial distance from the center is illustrated in Fig 5. The information on the locations from which the hailstones had been collected is only approximate, but it seems clear that the largest came from nearest to the center of the storm's path. This is to be expected from the findings of Browning and Foote (1976) on an apparently very similar supercell storm.

Much debris is always present in very large hailstones (see, e.g., Mason, 1971), and in our samples, grass was a major component. By the time the first hailstone was melted, the color of the grass had faded somewhat. It was distributed randomly through the hailstones so that the absence of a correlation between oxidation potential and nitrate levels is readily understood, with most organic materials (and any ammonium salts) being easily oxidized. It may be that the similarity in structure between water and hydrogen peroxide allowed a considerable quantity of this oxidizing agent to form a solid solution.

That slow reactions were occurring in the solid ice was confirmed 44 months after the first analyses, when two hitherto unexamined hailstones (MJ and SM3) were found to possess significantly reduced oxidation potentials. Also, the grass had lost even more of its color. Clearly, no correlation between nitrate levels and oxidation potentials should have been expected. The one exceptionally low oxidation potential was for the sample that had the atypically high nitrate concentration. This hailstone presumably had a particularly contaminated nucleus - possibly due to the presence in it of some originally solid ammonium salt (whose dissolution and oxidation would have reduced the sample's oxidation potential).

An important point, shown in Fig. 5, concerns the remarkably similar nitrate levels found throughout most of each hailstone. When hailstones are sliced and examined, it seems they always possess a clearly banded structure in which clear ice and cloudy ice alternate. This is believed to result from freezing at two very different temperatures (see, e.g., Mason, 1971). Presumably, the hailstones under consideration had passed through air that differed considerably in temperature but not very much in nitric acid concentration. In other words, the temperature gradient around the group of plasma balls was probably larger than the concentration gradient.

If, as is believed to be the case, the banded structures of our large hailstones were formed by the stones' passage through air close to a group of plasmas, the structures would have been the result of some kind of elliptical motion around the plasmas that had a significant component of their axes in the horizontal plane (Browning & Foote, 1976). If, as was also probably the case, the hailstones did not rotate very rapidly in the air near the plasmas, it would be expected that each spherical shell of melted ice would contain different levels of nitric acid around its circumference. For this reason, even if each pass of a hailstone near the plasmas was at an identical distance from them, the nitrate levels would not be expected to be identical. Clearly, they were not identical though they were very similar.

It is obviously very significant that *only* nitrates showed a smooth dependence on sample number (which represents the inverse of the radius), while chloride and sulfate varied by orders of magnitude. Taken together, the results imply that the nitric acid had formed from the air. The finding that all the samples were strongly oxidizing strongly supports the expectation (Turner, 1998) that some oxidizing agent was being produced just outside an air plasma. Only oxidation reactions are likely to be induced by UV radiation in the air.

The only cation present in the cleaner parts of the ice will have been the H_3O^+ ion since no other cations can be formed from the air under oxidizing conditions. The absence of nitrites is, of course, fully consistent with the strongly oxidizing environment indicated by the oxidation potentials. In more usual kinds of meteorological investigations, low levels of nitrates, at roughly half the concentration listed for HW, are nearly always detected in rain and snow (Mason, 1971). In the samples from the three largest hailstones examined, the nitrate levels were at least twice as high as those in the hurricane sample (HW in Table 1).

The high levels of oxidizing agents support the claim that the stones were produced close to the plasma or plasmas that were known to be present (from several sightings of the huge supercell cloud) somewhere deep inside the cloud. There is no obvious alternative to oxidation induced by the UV from an air plasma that can explain such high oxidation potentials or the surprisingly unchanging nitrate levels as a function of radius. It seems (Turner, 2023a) that the hailstones had been circulating around the plasma, their centripetal force being largely balanced by an inflowing wind. It is difficult to think of any explanation for the results provided in Fig 5 and Table 1 other than that oxidation of nitrogen to nitric acid was occurring somewhere close to an air plasma. This plasma would have been producing high-energy UV as a result of charge neutralization within the plasma.

Experiments on UV Produced Oxidation

A likely role for nitrogen oxidation by the kind of high energy UV that can be emitted from an air plasma has been

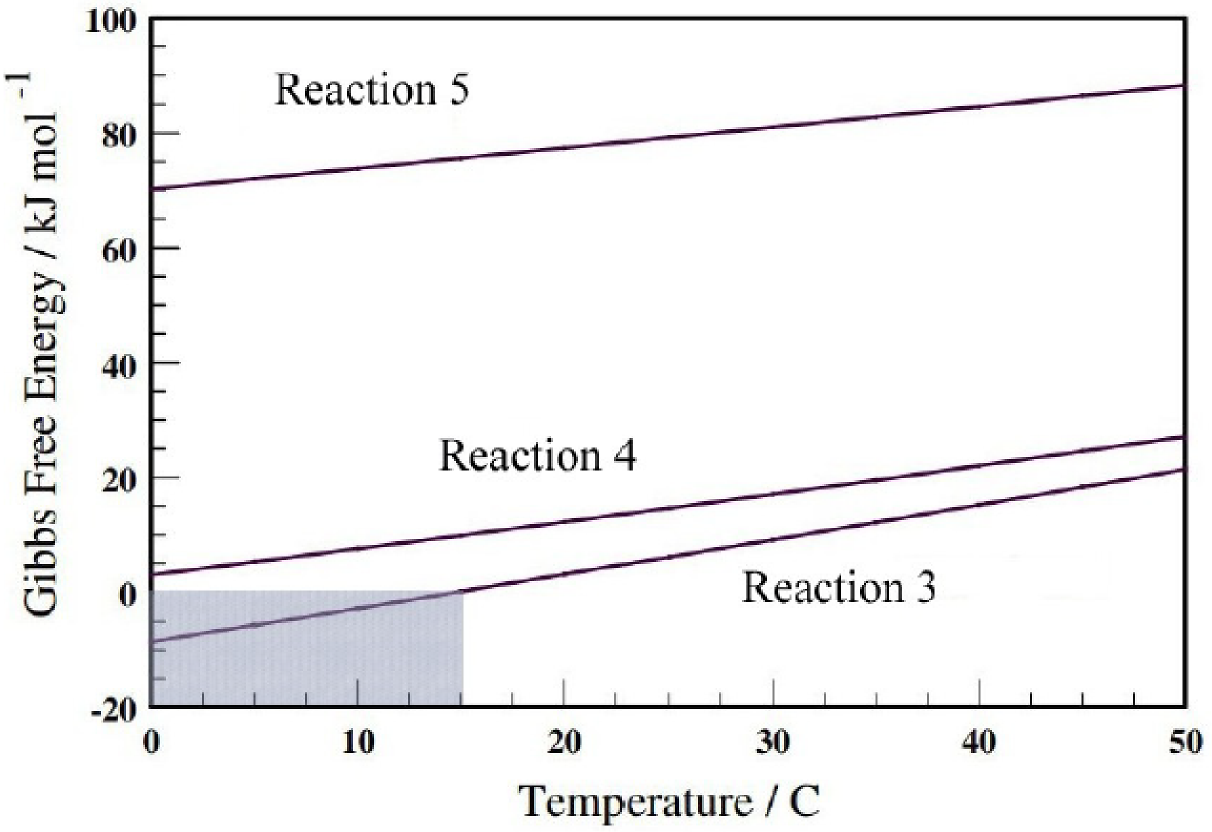

Figure. 4: Standard free energies for the formation of nitric acid from the components of the air. The reaction numbers close to the three lines refer to the reactions listed in the text. Since reaction-free energy needs to be negative for the reaction to be possible, the only reaction of the three possibly concerned is Reaction 3, and even this one is only possible at temperatures below 15^0 C. Only reactions with free energies within the shaded area are thermodynamically possible.

investigated much more recently. Here, only conclusions relevant to the present context will be discussed. We were attempting to repeat some findings of C.T.R. Wilson (1899a) that have been almost completely neglected for over a century. They involved the irradiation, by UV light, of water-saturated air that had been completely freed from dust particles.

Among these long-forgotten observations was a finding that condensation can be produced following prolonged exposure to UV radiation *at relative humidities near 90%*. This finding contradicts a *claimed fact* that is assumed in all current condensation models and meteorology textbooks: that *at least* 100% relative humidity is required before condensation is possible. Wilson had used zinc and cadmium arcs as sources of UV, and the aerosols produced had been shown to take approximately half an hour of exposure to grow to a size that was detectable by light scattering. However, our experiments with zinc arcs all failed completely to produce condensation in air at even 100% relative humidity and even if exposed to UV for an hour. The many possible reasons for this failure are not relevant here, but an accidental consequence of our attempts to understand the failure certainly is.

During these investigations, a miniature mercury vapor lamp was placed very close to the silica lens we were using to admit the UV to our cell. The electric power driving this lamp is minute compared with that driving the zinc arcs; thus we were amazed when the lamp was accidentally switched on and clouds were formed in the cell within minutes. Confusion reigned for several months since there seemed to be no combination of components or their relative positions that consistently predicted whether or not mists would form.

It was eventually noticed that a significant fraction of the anti-reflection coating on *one* lens had disappeared, and it became clear that this was the *only* component that had allowed mists to form. The coating had been partially removed in an earlier experiment where dilute hydrochloric acid had replaced the distilled water normally used. The coatings permit very low reflection losses above a wavelength of 200 nm, and I purchased only lenses and windows that were coated. The only *specified* wavelength of the mercury vapor lamp was 253.6 nm, so there seemed no obvious explanation for why this line produced mists so rarely.

It was only when it was realized that mercury also possesses an emission line at 185 nm that any sense could be made of our accumulated observations. Once this had been appreciated, all the experiments made perfect sense. Removal of the coatings on the other components and the purchase of new uncoated ones demonstrated that, while some "pure" silica absorbs some of the 185 nm line, fairly thin silica components do not usually absorb very much. Significantly, we easily confirmed condensation at relative humidities below 90 % - in confirmation of what Wilson (1899a) had claimed. This 185 nm line of mercury lies well into the so-called UVC region of the spectrum, where air absorbs virtually all of the radiation. Hence this line could not have produced the mists that Wilson observed, fairly long path lengths having been used in his experiments.

The only stable ions in any experiment *before hydration* are likely to be NO^+ and NO_2-(see Appendix C: https://naturalplasmas.com/files/VPE1_AppendixC). As we shall see, there is every reason to believe that these ions were formed in air that had been irradiated using the mercury vapor lamp. Of course, the detailed ion-forming *processes* in our experiments can hardly be the same as those that produced ions in Wilson's experiments or presumably those that can form near the surface of a lightning ball. Nevertheless, the dry ions formed will be the same in all three cases because they are believed to be easily the most stable ones that are at all likely to be present (very briefly before hydration) in the air.

In cool, moist air, long-lived molecules of increased energy content, such as ozone, nitrogen oxides, and active nitrogen, are all likely intermediates in forming the ions that would have been responsible for Wilson's findings. Very many lines in the UV will have been present in these experiments, and, almost certainly, some extremely complex chemistry must have been involved.

Fortunately, with mercury vapor emission, the system is much simpler, there being only two high-energy emission lines that could be important. The use of thermodynamic tables and conversion of wavelengths of these two lines into energy units readily shows that neither line of mercury can produce ionization in air from a *single* photon. However, among the likely intermediates involved, ozone is known to have a particularly long lifetime and it is also well known (by those dealing with health matters) to be produced from the 185 nm line of mercury. This suggested that the reaction:

$$\gamma + N_2 + O_3 = NO^+ + NO_2- \tag{6}$$

could be important in ionizing the air. Here ã formally represents a mole of photons, and all the chemical species are taken to be in the gas phase. As previously mentioned (and shown in Appendix C) NO^+ and NO_2- are the only really likely ions to be formed from any of the main components of dry air. Reaction 6 is, of course, a more than usually symbolic process because the photon is traveling at the speed of light and so cannot be at equilibrium. Free energies clearly cannot be usefully compared, but enthal-

Table 1. Mean Properties and Locations of Hailstones from the La Plata Storm.

Hailstone Identifier	Hailstone Mass/g	Mean $[NO^{3-}]$ ng N. g^{-1}	Oxid'n Potential mV	Distance from La Plata / km.	Distance from storm path / km.
SS4b	5.63	72	232	-3.9	9.2
SS5b	10.61	77	213	-3.9	9.2
MJ (av.)	48.85	87.4	207	-1.9	2.7
JA4b	10.43	62	232	5.5	9.0
MO1b	13.28	65	197	8.7	8.5
SM2 (av.)	52.04	106.9	234	21.1	2.6
SM3 (av.)	44-97	86.7	205	21.1	2.6
Water	-	0	168	-	-
HW	-	40	-	-	-

pies can.

Both ions produced will rapidly become hydrated, but NO^+ will be changed to H_3O^+ during the process of hydration (Turner, 1994). However, the dry ions would need to be formed first. Reaction 6 appears to be uniquely important. This can be seen by adding (algebraically) the standard enthalpies of formation for the chemical species involved in the reaction. These values are 0, +142.674, +990.185, and - 202.715, respectively, for N_2, O_3, NO^+, and N_2O^- according to the JANAF tables (Chase et al., 1985). The algebraic sum of these formation enthalpies is 644.8 $kJmol^{-1}$.

When converted to a wavelength, this energy is 185.5nm which is remarkably close to the wavelength of the more energetic mercury lines (184.9 nm). In all probability, the uncertainties in the tabulated data mean that Reaction 6 could equally well have indicated that the reaction was supplied with just too little energy.

Nevertheless, in view of the huge spread of the input enthalpies in the calculation of the energy needed, it is almost impossible to believe that the close similarity in the two wavelengths is a coincidence.

In providing photons of a single very high energy, we seem to have been extremely fortunate, not only in that the energies involved were so revealing but also that *our initial efforts to form mists all failed* and that a mercury vapor lamp happened to be at hand and then inadvertently switched on. This precise matching of the required energy to that from the mercury arc is presumably why, despite the low electrical power needed to run the mercury lamp and the low intrinsic power of the 185nm line (compared with that specified at 253.6nm), the mercury lamp still produced clouds significantly more rapidly than did Wilson's arcs.

IMPLICATIONS AND APPLICATIONS

Historical Matters

Possibly the most important general conclusions, from the evidence assembled here, concern the *reasons* for our current, very limited, understanding of vapor phase electrochemistry. The reasons do not seem to be primarily scientific. In part, they have resulted from the order in which important discoveries happened to be made. One important matter arising from several of the studies discussed is why it has taken so long for some 19th-century findings to be repeated. A number of practical difficulties in repeating Wilson's experiments (on mist formation using UV irradiation) might provide a partial explanation. However, the main reasons are probably that most of those interested in the studies, being physicists, were not very interested in the chemical aspects. Wilson's later development of the cloud chambers that bear his name, plus the major discoveries that followed from them, would have seemed far more interesting than understanding how cloud condensation can possibly arise at a relative humidity of 90%.

At the time of Wilson's experiments, the difference between concentrations and activities had still to be demonstrated because the crucial contributions of Gibbs (1878, 1928) to thermodynamics had still not been definitively proved by quantitative evidence. The fact that Faraday's (1839) studies preceded those of Gibbs by nearly four decades explains why Faraday was unavoidably mistaken when he expressed the view that ball lightning, although real, is not an electrical phenomenon. In 1839, there was no reason whatever for believing that oppositely charged ions in real (moist) air could avoid their charges rapidly annihilating one other. No strong evidence was found until 1994 that oppositely charged ions in the air do not need to annihilate each other's charges rapidly - if at all (Turner, 1994).

Attitudes to very basic science like this were much more positive toward the end of the 19th century than they are now. The question arises of how different the present perilous state of the Earth (through global warming) might be had Gibbs been born decades earlier and had more scientists realized the importance of his work. Of his famous contemporaries, only Maxwell seems to have fully appreciated his contributions to science. In this context, it is of interest to note that, according to the records of the Sloane Physics Laboratory, where Gibbs had worked, it seems that Einstein once described Gibbs as "the greatest mind in American history" (Panek, 2017, p. 5). Einstein's view would clearly have been justified on the basis of the latter's rarely consulted works (Gibbs, 1878, 1928). Very few currently active scientists would probably agree with this view, although those interested in black hole thermodynamics (e.g., Jacobson, 1995; Penrose, 2005) might at least include him as *one* of the greatest minds in American history.

Specialization

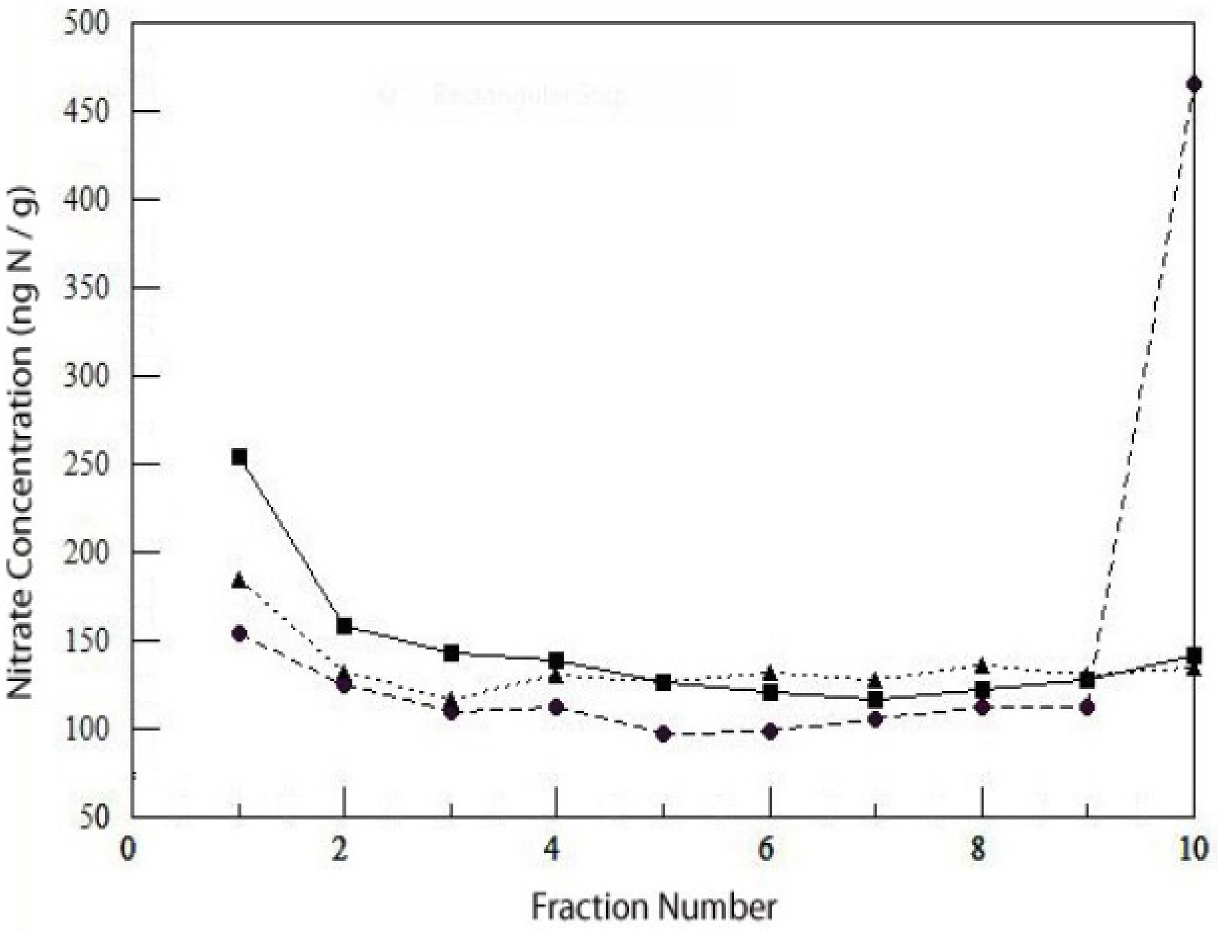

Figure 5: Nitrate concentrations of melted samples. Large hailstones are only approximately spherically symmetrical, although this symmetry can be achieved roughly by melting away the crystals of ice that protrude and so spoil the symmetry. The volumes of ice melted from the protruding crystals in fraction 1 were just sufficient to leave good approximations of spheres for the remaining samples taken. Nitrate levels are fairly similar for fractions 2 to 9, but for one of the fraction 10 samples, the nucleus must have been contaminated.

Specialization is another problem. It has proved invaluable in advancing science but, in excess, it can greatly inhibit progress. There are aspects of astrophysics, such as the formation of electric double layers in space, which attract little interest and are, in principle, closely associated with vapor phase electrochemistry (Turner, 2023c). They illustrate how very serious the problem of over-specialization can be. For decades, many such problems were repeatedly stressed by Alfvén, most of these concerns having been outlined in his book Cosmic Plasma (Alfvén, 1981).

A very obvious cause of surprise, encountered by any non-specialist who has read this book as well as a significant number of papers by conventional astrophysicists, is that, with the exception of so-called “Alfvén waves” and of “Alfvén critical surfaces” (the latter used in connection with the surface of the Sun), the role of plasmas in space itself is *completely ignored* by almost all conventional cosmologists - even though the Universe consists mainly of plasma (Uman, 1984).

Only electrical engineers (e.g., Peratt, 2015) and lightning specialists (e.g., Uman, 1984) seem to accept that plasma physics has importance in astrophysics. The basic problem for those studying the relevant science is, of course, that it is impossible to construct models that can make testable predictions without knowing details of the *distributions of electric charges and currents*. These cannot be measured remotely (only magnetic fields can), so models directly involving electrical influences are only ever used to describe processes fairly close to the Earth, for example, in studies of the behavior of solar wind particles.

One of the most frequently repeated claims of conventional astrophysicists is the need to invoke the existence of an unidentified substance known as dark matter. Little expense seems to have been spared over the years in trying to discover the nature of this hypothetical substance. The earliest and most convincing evidence for the existence of dark matter was the shape of spiral galaxies, but there are also several less convincing *claims* for evidence in the much more speculative field of cosmology.

These include explaining the expansion of the Universe and the web-like structures that are known to connect galaxies together. The latter studies usually make use of the extraordinarily precise data that are available on the cosmic microwave background. Clearly, such exercises need to involve assumptions, many of which are implicit and untestable. Once one accepts that most of the Universe actually consists of plasma (Alfvén, 1981; Uman, 1984) and that electrostatic forces are immensely stronger than gravitational forces, the ignoring of plasma physics should seem absurd to far more scientists than Alfvén and other plasma physicists who accept the importance of electrical effects in space.

It must surely be highly relevant that *even explanations of the shapes of galaxies do not need to invoke dark matter*: they can be explained perfectly rationally using the concepts of plasma physics (Snell & Peratt, 1995; Peratt, 2015). Similar arguments apply to other concepts claimed to be necessary by cosmologists - even such unconventional ones as Hoyle, Burbridge, and Narlikar (2000).

Aside from the arguments used by Peratt, which mostly appear only in electrical engineering journals, other arguments (based on measurements of plasma density) have been made and have appeared in at least one scientific journal, Nature (The COSINE-100 Collaboration, 2018). These measurements also imply that there is no need to invoke mysterious dark matter in order to explain the shapes of spiral galaxies. To many scientists working in more mundane fields, the speculative interpretations of the fine detail in the cosmic microwave background can look like little more than interesting mathematical games.

Political and Societal Influences

There are also adverse societal and political influences that have magnified the historical influences. Of these, the most important ones were the political changes that resulted from the rise of neoliberalism following what has been called the Thatcher-Reagan revolution. This began in the 1980s. These influences seem irreversible because they are now strongly favored by the rich and powerful in every country. Thus any suggestions on how to solve the basic problem of the absence of valid theories are inevitably going to be limited in extent. This conclusion seems unavoidable and must be borne in mind if proposals to study the associated problems are to have any hope of being implemented in time to help solve the problem of global warming.

If we consider how scientific research is currently supported, it is clear that some areas receive very much more support than others. This disparity began to increase greatly following the prolonged competition that once existed between the USSR and the West. This led to competition in the fields of rocket engineering and to the enormous advances in space science that have followed from them. One very positive consequence has been the inspiring research now carried out by the world’s space agencies in astronomy and in planetary science.

However, governments tend to be far less interested in advancing science than in the economic advantages to large construction companies that can be gained through such work (see Appendix A).If there is to be any hope for future progress in the field of vapor phase electrochemistry, acknowledging this kind of reality is crucial. As seems clear from Appendix A, vapor phase electrochemistry is a sub-discipline of science whose advancement is now of *no perceived advantage to any individual or industry*. Fortunately, this does not necessarily imply that no scientists at all are likely to be interested in advancing specific aspects of the missing science.

The most obvious specific conclusions from the variety of studies discussed concern the extremely limited progress that has been made, over more than a century, in understanding vapor phase electrochemistry. The inevitable limitations have resulted in inadequate or invalid approaches to the following: the processes that lead to cloud formation and to charge separation in moist gases; also to our almost complete ignorance concerning exactly how air plasmas form and sometimes seem to survive for several hours.

On the basis of the findings represented in Fig 5 and Table 1, there seems to be strong evidence that either one large air plasma or, more likely, on the evidence discussed elsewhere (Turner, 2023b), there was an assembly of air plasmas present inside the La Plata supercell (NOAA, 2002) which was producing occasional tornadoes for an hour and a half. Long-lived air plasmas almost certainly need to use chemical energy in the air. In principle, this energy could be extracted and used. If, as seems to be the case, basic vapor phase electrochemistry is unable to advance at all rapidly, it would seem desirable, in the future, to investigate all the various *qualitative clues* available much more thoroughly than has proved possible so far.

A quite different problem is the need to accept that thermodynamics is a branch of science that is, and has always has been, very unfashionable. In addition, it now seems clear that studies in the field of vapor phase electrochemistry that existed until the 1980s were abandoned purely for political reasons (see Appendix A). If more is to be learned about the role of electrostriction in compressible solvents, it seems clear that the *only real hope* for this generally boring subject is through new meteorological studies such as those suggested earlier regarding air plasmas in supercells. The need to quantify the very basic science by avoiding gravitational fields in experimental studies appears to be far too slow, boring, and expensive to attract any support at present.

One would think that meteorologists should be interested in better models for cloud formation while engineers in the electric power industry, even if they ignore the invalidity of some theories associated with the models they use (see Appendix A), should value a completely new way of producing electricity. A fairly obvious method for extracting the energy in the air to make electricity would be to surround an air plasma with solar cells. It is clear that if such energy extraction were ever to be used commercially, there would be concerns over such matters as how to hold an air plasma safely in a fixed position.

This should not be a serious problem assuming that the electrochemical explanation (Turner, 1998) for what used to be called "electrostatic guidance" provides the correct explanation for it. If the electrochemical model for ball lightning is basically correct and if air plasmas could ever be produced at will, the provision of a strong dc field should be able to hold such a plasma in a fixed position. There is clear observational evidence that this is possible (Turner, 1996, 1998). Producing electricity from air plasmas need have no harmful environmental consequences since the only chemical inevitably produced is dilute nitric acid.

Scientifically and Technologically Relevant Proposals

It is quite possible that all of the supercells that produce tornadoes contain large assemblies of air plasmas (which are normally hidden far too well to be observed) and that their presence is crucial to the development of the supercells themselves as well as of the tornadoes that can form within them. A fairly economical set of experiments would involve sending specially designed heat-seeking drones into a few large supercells to investigate the possibility that they all contain plasmas. Initially, an even more economical approach would be to investigate the likelihood that the very large hailstones expelled from large supercell storms *always* contain similarly smooth nitrate distributions and variable oxidation potentials to those shown in Fig. 5.

The large *power density*, implied by the measurements of Teodorani (2004) on one of the earth lights he studied, appears to be far greater than that available from arrays of solar cells or wind turbines. This would be very advantageous with respect to land usage. Unfortunately, although some details have been confirmed fairly recently concerning how air plasmas are stabilized and provided with their occasionally long lives, there are still numerous important questions to which answers are needed before it could be claimed that we know how to create them artificially or how to ensure long lives for such air plasmas once they have formed. Fortunately, any potential safety problems, in using air plasmas for producing electricity, should not be too serious because, if we could apply well-arranged electric fields of sufficient strength across any air plasma ball we might make, the ball would not move (Turner, 1996, 1998).

Concerning one of the experiments of Arden and Constable during which air plasmas were formed, Priestley wrote the following in 1781, "Could we repeat this experiment, there would not, I think, be any natural phenomenon, in which the electric fluid is concerned, that we could not imitate at pleasure." (Priestly, 1781, p. 383) The numerous failed attempts to achieve this objective have long acted as a warning that we do not yet know anything like enough to guarantee success in this field of study on any given timescale. Surely, however, *we should not give up on Priestley's perfectly valid hope*.

In this connection, an important point made earlier is that we are almost totally ignorant of the *chemistry* that occurs in those aerosols in which a central ion is surrounded by between about 5 and 10^9 water molecules. Recent molecular dynamics studies of intermediates in the reactions of organic compounds at water surfaces can usefully be mentioned here. They showed surprisingly large influences on reaction rates that clearly depend on the size and orientation of rather small organic molecules passing through the water surface (Zhang et al. 2018). In principle, similar kinds of modeling might begin to indicate at least how many water molecules need to surround an ion before the chemistry in an electrostatically charged aerosol starts to resemble that in a bulk water phase.

Going much further than this, using *molecular dynamics* simulations for any bulk solution would seem impractical. This is because of the large-scale non-homogeneity in any very compressible electrolyte solution and, consequently, the very large number of particles that would need to be tracked during a molecular simulation. Monte Carlo simulations would be much more efficient, but they cannot avoid the well-known limitations associated with the Debye-Hückel ion distribution function (see Appendix B) that we wish to understand much better - or somehow manage to avoid. It was these problems that limited what Peters (1987b) was able to demonstrate concerning the compressibility effects discussed in the earlier section entitled "Attempts at Quantitative Studies of Ion-water Interactions. Computer speeds have obviously increased enormously since the 1990s, but it is difficult to believe they are yet able to probe the properties of solutions that are very much more dilute and very much more compressible than those studied by Peters.

If the various non-technical problems, which seem to have led to the present issue with the basic science, have been correctly identified, then it might still be possible at least to resume some studies of the theoretical problems that limit our understanding of electrolyte solutions in water near to its critical point. At least a few theoreticians might be willing to address this problem since the costs of any time needed on high-speed computers are likely to be small compared with those of long-term experiments carried out on orbiting space vehicles. Much could probably be learned by the (careful) use of Monte Carlo simulations.

A possibly important incentive to work on this problem is that there is one specific question that it might be possible to address using molecular dynamics simulations *without the need for any new experimental study*. This is to investigate the extent to which the apparent molar volume measurements near the critical point of water (Benson, Copeland, and Pearson, 1954; Copeland, Silverman, and Benson 1954) were influenced by gravitational forces.

It is also possible there might be a way in which valuable lessons could be learned about the weaknesses of the Born equation as it is normally used. It seems likely that some of Frank's (1955) thought experiments on the influences of electrostatic fields on liquids might well be amenable to *experimental* investigation. A sapphire windowed autoclave, possibly similar to those previously used in sounding rocket experiments (Turner, 1988a), could be used to study near-critical water at the tip of a sharply pointed metal electrode using Shlieren photography to investigate the density field near the tip. The proposal would be similar to that made by Tremaine and Turner (1993) for work under microgravity conditions, but *all measurements could be made on Earth* since no *solution* (complicating matters through sedimentation) would need to be studied - at least initially. This would make the experiments vastly less expensive than those originally proposed.

Finally, there are the previously mentioned proposals for studying the air plasmas that seem to reside in supercells. The most instructive investigations would use drones to locate and study such plasmas. Related studies could prove even more instructive if the (plasma-related) forces that seem to hold hurricane "hot towers" together could be investigated (Turner, 2023d). Several of the observed characteristics of hurricanes imply that they also contain powerful air plasmas, and seeking and studying them might be well worth the extra difficulties (compared with the tornado study) involved in working far from land.

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most clearly defined. His crucial contribution was planning the way in which research was carried out at CERL. One aspect was his encouragement of interdisciplinary approaches to all research whenever this was possible. In the present context, however, the most significant feature was the very unusual way research projects were authorized and carried out. Details of this feature are outlined in Appendix A.

Much advice and encouragement from the second individual also proved essential. It came from Sir Brian Pippard. He first became interested in the missing science when the UK government asked him to interview all UK scientists who were collaborating with the European Space Agency (ESA) as part of the Agency's Microgravity Program. Following lengthy discussions on our collaborative work with ESA, he agreed to read a draft paper of mine on ball lightning, a subject seemingly only remotely connected with power station chemistry.

This draft paper was far too long for publication in most journals. Sir Brian promised that if he could find nothing wrong with it, he would ensure it was published by the Royal Society - in Philosophical Transactions (where very long papers had once been accepted). He found he had to overcome several unjustified criticisms of the paper, but, in abbreviated form, it was eventually published - in 1994. He also tried to help me over the following few years and provided much-needed encouragement after CERL had been closed.

The third individual, Olga Martynova (of the Moscow Power Engineering Institute), also provided prolonged encouragement over the need to study vapor phase electrochemistry. She and I were regularly on the same side of arguments at the International Association for the Properties of Water and Steam (IAPWS). Early on, these discussions seemed to be very fruitful - but only while the secretariat of the Association was still in the hands of the (USA-based) National Institute for Standards and Technology (NIST). Some of the adverse consequences of the eventual change of secretariat are described in Appendix A.

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