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Vapor Phase Electrochemistry 3: Preparation of Metastable Nitrous Acid

Viv Bartlett
jse@tumblewood.co.uk

David Turner
condphys@frontiernet.net
orcid.org/0009-0003-9245-1844

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HIGHLIGHTS

Ball lightning can be formed when an air plasma cools through a chemical process, creating a stable outer layer that contains the plasma and gives it a defined shape.

ABSTRACT

A qualitative electrochemical model for ball lightning was developed during the 1990's (Turner, 2002). The key requirement was electrochemical refrigeration at the surface of an air plasma. The cooling was shown to result from the conversion of metastable, fully ionized, gas-phase nitrous acid to its stable molecular form. If the refrigeration cools the plasma surface to below 15^0 C, aerosols of nitric acid can be produced in subsequent oxidation processes. These particles restrict the inflow of air toward the plasma and provide the ball with a very effective surface tension. This helps explain several unusual characteristics of lightning balls and also their close relatives, such as earth-lights and Unpredictable Flying Objects. The experiments to be described were undertaken because of their relevance to ball lightning stability, but they also have relevance in other fields of meteorology. They were attempts to reproduce several early observations by C.T.R Wilson that have been largely neglected ever since they were first reported. He irradiated moist, dust-free air with focused beams of ultraviolet light. Using the emission from zinc or cadmium arcs, mists were produced after about 30 minutes of exposure. All our nominally similar experiments failed to produce mists. However, UV radiation from a mercury vapor lamp produced them after a few minutes. The mists contained both nitrous and nitric acid. We also confirmed Wilson's observations that these mists could be produced at relative humidities slightly below 90%. This is considered impossible according to all models of cloud formation.

KEYWORDS

Air plasmas, ball lightning, earth lights, UFOs, vapor phase electrochemistry.

INTRODUCTION

This study can best be seen as an unexpected outcome of the identification of a small area of physical chemistry that has never been developed. The very basic nature of the missing science gradually became clear to one of us (DJT) through attempts to understand several industrial problems associated with impurities in high-density steam. The studies had been conducted at the Central Electricity Research Laboratory (CERL), which was one of the laboratories of the former Central Electricity Generating Board (CEGB) in the UK - see Chown (1993).

By 2003, several different ways of describing the most basic problems had been employed (Beysens et al., 1987; Gates et al., 1982; Turner, 1983; Turner, 1980, 1987, 1988, 1990, 1998, 2003; Wood et al., 1983). Unfortunately, the same political forces as those that forced the privatization of the UK's electric power industry seem to have ensured that it is currently in no one's financial interest even to acknowledge that these very basic scientific problems exist (Turner, 2023).

A serious consequence of the missing science is that no *quantitative* explanation for the properties of ball lightning or of any other air plasma is currently available. This situation is likely to remain the same unless current ways of supporting certain very basic areas of science change (Turner, 2023). This seems very unlikely. Fortunately, it has proved possible to make some progress in understanding naturally contained air plasmas using arguments that are almost completely qualitative. For the systems considered here, the missing science can conveniently be referred to as vapor phase electrochemistry.

The most basic problem in understanding contained air plasmas is the electrostriction of water molecules in the very high electric fields close to any ion. The consequences are mainly thermodynamic, but they also make it impossible to develop valid kinetic arguments (Turner, 2023). There are several reasons for this situation, the most significant relating to the properties of metastable nitrous acid and its subsequent oxidation to nitric acid. Those relevant to the matters considered here are summarized in Section 2.

Since very diverse arguments are employed, it is desirable to summarize their basis at this point. The arguments all stem from experiments, dating from the 1890's and conducted by C.T.R. Wilson, *a few of which* were never replicated. There were two main consequences of Wilson's findings. Decades later, he developed the cloud chamber that is named for him. The other consequence was a general acceptance by meteorologists and others that condensation of water vapor into droplets of liquid water *always* requires that the degree of saturation of the air be greater than 100% relative humidity. Nearly all of the experiments that Wilson conducted in the late 19th century supported the now accepted view, but some clearly did not.

They showed that, when very clean air was irradiated with UV radiation spark gaps, made of either zinc or cadmium, condensation was obtained at about 90% relative humidity. It seems that other investigators must have failed to replicate these particular findings and they have been ignored until fairly recently.

By the last decade of the nineteenth century, many experiments on moist air had been described, some of which were attempts to understand the role of ions in cloud condensation. Three of the most informative studies were by C.T.R Wilson (1897, 1899a,b). All three studies were mainly concerned with the *physical* process of condensation, but many of the findings appeared to be *influenced by chemistry*. These studies, and more recent ones with similar histories, imply that our current understanding of basic cloud condensation is very far from complete (Turner, 1998, 2003). It is now clear that, for over a century, very few scientists have felt the need to address the subject of vapor phase electrochemistry.

Our final choice of experimental approach was based on two considerations. The first was financial since, for decades, support for this kind of work had been unavailable. The second was the hope that confirmations of some of Wilson's findings might prove instructive. The limited nature of the study resulted from the UK's privatization of electricity generation in 1989. Gradual changes in political thinking, in both the UK and elsewhere, have resulted in the abandonment of all of the relevant electrochemical research that had once been supported by the electric power industries in several industrialized countries (Turner, 2023).

Beginning in the 1990s, hints of mistakes apparently related to those of concern here, but in scientific and technological areas *other than electricity generation*, began to be collected. Diverse reports in the literature seemed to result from the same missing science (Turner, 1998, 2003). This realization followed an earlier, very unexpected conclusion: that none of the well-established properties of ball lightning violates any known law of physics (Turner, 1994). This is also true of the real objects (as opposed to psychologically produced effects) that are usually referred to as unidentified flying objects, or UFOs. The name preferred here is *Unpredictable* Flying Objects since the objects will have been identified. It also seems that air plasmas can have several other manifestations. These include the plasmas occasionally observed inside tornadic super-cells and those that might well contribute to holding hurricane clouds together (Turner, 2003, 2023).

All the more obvious anomalies in the reported behavior of ball lightning (Arago, 1855; Barry, 1980; Brand, 1923; Charman, 1979; Flammarion, 1888; Singer, 1971; Stakhanov, 1979; 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 and approximations are not always appropriate.

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

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

A more general problem in understanding vapor phase electrochemistry arises from the differences that exist in the ways in which quantum mechanics treats nuclear and chemical energy levels. Nuclear properties can be predicted precisely, and the result is that the theory and experiment have progressed extremely well. This is not the case for chemical properties. Hence, the largely qualitative rationalizations of properties provided by the Periodic Table are still vital to chemists. More importantly, in the present context, these limitations define the kinds of problems that most physicists *choose not to study*.

Specialization has obviously proved essential in advancing all of science, but most of the dramatic advances in physics have resulted from its reliance on mathematics. The limitations of prediction in chemistry arise from the fact that quantum mechanics can provide little more than qualitative guidance on such matters as the shapes of molecules and the thermodynamic properties of chemical species - whether these are stable molecules, radicals, or ions. Consequently, most thermodynamic properties of such species need to be measured experimentally, and obtaining all the data needed for every chemical entity would require a totally unrealistic research program. In practice, very few molecules have been characterized thermodynamically, and even fewer molecular ions.

2. SOME THERMODYNAMIC CONSEQUENCES OF NITROGEN OXIDATION IN MOIST AIR.

Because of the well-known health risks associated with the presence of nitrogen oxides in the air, large numbers of rate constants for reactions involving these oxides have been measured over many decades (Seinfeld & Pandis, 2006). Carbon and nitrogen are elements of the periodic table that are among the most plentiful and whose chemistry is far more complicated than that of any of the earlier elements in the periodic table - i.e., those with lower atomic weights.

As is well known, the complications with carbon chemistry result from the huge number of kinetically stable compounds that are based on long chains of carbon atoms. However, nitrogen chemistry is complicated by an entirely different characteristic: nitrogen compounds exhibit far more stable *oxidation states* than is the case with any earlier element in the periodic table. As a consequence of this fact, many simple nitrogen compounds are well-characterized thermodynamically. This applies to some stable ions that contain nitrogen, but, for fairly obvious practical reasons, it does not apply to unstable ions.

Most of the data we possess on nitrogen oxidation processes tacitly assume the air to be dry (Seinfeld & Pandis, 2006). It has long been realized that this can seriously limit the models. The potential existence of water (and solutions) in two phases adds so greatly to the complications (both thermodynamically and kinetically) that realistic attempts to deal with the chemistry (in the actual two-phase systems) have never been made. Clearly, the existing literature on air pollution can offer little help in understanding the matters of concern here - where the presence of water vapor is crucial. The situation is serious because ions are always present in the air, and they inevitably attract huge numbers of water molecules into their electric fields (Turner, 2023).

In the 1930s, Loeb (1934) showed the great importance of electrostriction in gases, and by the 1950s (Loeb, 1958), he had calculated extremely large hydration numbers for atmospheric ions from their transport properties. For example, ions classified in meteorological studies as "large" (though invisible) can have hydration numbers up to $3x10^8$. Effectively, this means that we know nothing at all about electrochemical processes that occur in aerosols whose solute-to-solvent molar ratios vary over eight orders of magnitude (Turner, 2023). The experiments to be described here attempt to obtain information on a few important chemical processes that can occur when aerosol chemistry seems to be very important.

The 19^{th}-century experiments we considered repeating were all chosen because ions and water vapor were both involved. The clearest *direct* evidence for unexpected chemical changes in water vapor when ions are present came from studies of von Helmholtz (1887) and von Helmholtz and Richarz (1890). They studied droplet growth at an electrified jet through which steam at atmospheric pressure was passing. Influences very specific to the identity of several nearby gases were found on droplet growth rates. The high energy content of ions will have been important because the presence of ions can catalyze otherwise very slow chemical reactions, such as

those involving any thermodynamically unstable gas that has drifted into the region of the electrified jet.

These chemical influences seemed very significant but no practical way was seen for learning much more than the qualitative facts that Helmholtz's studies had revealed. A serious additional problem was that there was no obvious way of learning anything about the electrochemistry that can take place *nearer to room temperature*. This is important because it is only at 25^0 C that enough relevant thermodynamic data are available to permit useful comparisons - assuming that such an attempt were to be made.

Townsend (1898) studied the electrical properties of the gases released during the electrolysis of HCl, H_2SO_4, and KOH solutions. He had earlier established (Townsend, 1897) that such gases carry with them a large percentage of the charge they hold even after passing them though glass wool, to remove liquid spray, and bubbling them through various solutions. The last few vessels were enclosed within an earthed metal screen and at least one of them normally contained concentrated sulfuric acid for drying the gases. The vessels were separated from the electrolysis cell by a short "tunnel" of paraffin wax and mounted on a block of the same material. They could thus be weighed before and after the passage of known quantities of the gases so that both the water content of the clouds and the charges on them could be determined.

It was found that the heavily hydrated ions carried with the gases from the electrolysis cell could be rapidly and reversibly de-hydrated and re-hydrated. However, *not all the gases released by electrolysis* formed clouds when bubbled through pure water. Condensation was found *only* to be possible if the gases were electrically charged. The *negatively* charged clusters that Townsend produced were found to be larger (and hence would fall faster) than those that were charged positively. Townsend noted that effects like this might explain the positive charge of the upper atmosphere (Townsend, 1897).

One seemingly important implication, from the description just given, is that, in some cases, electrolysis had failed to produce ions in the gases released during electrolysis. Both he and Wilson, his fellow student at the Cavendish Laboratory (whose early experiments will be discussed shortly), were very interested in atmospheric processes. It was, therefore, surprising to note that the electrolysis of nitric acid was not even mentioned in either of Townsend's papers. It seems most likely that the electrolysis of nitric acid *was, in fact*, studied, but it failed to produce charged clouds.

Such a failure would not now be considered surprising since we have subsequently learned (Turner, 1998) that *gas phase* HNO_3 is thermodynamically unstable (with respect to the components of the air) at the temperatures reached in Townsend's experiments. Only at temperatures below 15^0 C is gas-phase nitric acid stable in the air. All of Townsend's experiments rapidly reached far higher temperatures than this because he wished to produce his gases as rapidly as possible. In all his experiments, he first bubbled the gases released during electrolysis through temperature controlled, cool, water. This was presumably so that his method for measuring the charges on the gasses was not complicated by possible thermal effects .

Townsend's experiments showed clearly that electrostriction by ions is very important. However, any repeat and extension of Townsend's findings could only be improved at financial costs that would be economically unrealistic. The final conclusion, from all our early comparisons, was that one set of Wilson's earliest experiments was probably the most promising of all the neglected 19^{th} century studies.

Some of the facts discussed above are very relevant to the stability of ball lightning. If sufficient *metastable* nitrous acid were to be converted to its stable form *at the plasma surface*, a stable surface could form. The air temperature next to the plasma needs to be maintained below 15^0 C for the whole life of the plasma (Turner, 1998). Then nitric acid production, in parallel with the cooling processes close to the plasma, will be extracting *chemical energy* from the air. This easily explains the long lives of many lightning balls and the even longer lives of other air plasmas. The Sun's energy maintains the chemical composition of the air, so that (assuming the ball lightning model is correct) an air plasma is capable of extracting solar energy and converting it into another form of energy - such as tornadic energy (Turner, 2023) - or, far more usefully, into electricity.

Air plasmas are rare phenomena and, over the centuries, nearly all attempts to produce realistic simulations of the smallest of them, which are lightning balls, have failed. The last time anyone reported an adequate simulation of ball lightning was by accident in the mid 18^{th} century (Priestley, 1781; Cavallo, 1782; see Turner, 2002, for a complete but more readily accessible account).

The two matters over which we are most seriously ignorant are why it is so difficult to form an air plasma in the first place and why only the most powerful air plasmas seem able to survive for more than two or three minutes. It has long seemed clear that a major difficulty is maintaining the required delicate balance of physical and chemical forces that can provide structural stability at an air-plasma surface (Turner, 1994).

Currently, it seems we need most guidance on the processes involved during the *initial formation stages* of the plasma (Turner, 2002, 2024).

Because the sub-discipline of vapor phase electricity has never been developed, progress in understanding air plasmas has only proved possible using approximate thermodynamic arguments (Turner, 1994, 1998, 2023, 2024) In this context, it is worth noting that nitrogen oxidation reactions in moist air formally resemble the burning of a hydrocarbon *except* for one very significant fact: water, a very stable compound indeed, is a *reactant rather than a reaction product* in the "burning" of nitrogen. Energy contained in a highly stable compound, such as water, can only favor a process involving it if it is present as a *product* and not as a *reactant*. Entropy changes can sometimes, however, more than compensate for this fact. This is why the "burning" temperature of nitrogen (Turner, 1998) is so low.

The mechanism by which a plasma surface can be maintained below 15^0 C (and thus nitric acid formation can be possible) is clearly crucial to the stability of ball lightning (Turner, 1994). It would be expected that nitrous acid would form before nitric acid - although the production of this acid might be so fast that nitrous acid could never be detected. More importantly, it is now clear that *interference of any kind* in the production of either acid can prevent the formation of a long-lived air plasma. The experiments to be reported here relate mainly to the formation of metastable nitrous acid. Most consist of attempts to reproduce some early experiments of C.T.R. Wilson. Any failures to replicate his findings might well explain why some of his most important experiments have been neglected for over a century.

3. WILSON'S EARLY EXPERIMENTS ON CLOUD FORMATION AND SOME RELATED STUDIES.

Wilson is best known as the inventor of the cloud chamber, which, following developments he made years later, led to early discoveries in particle physics and to his Nobel prize in 1927. However, the experiments from which the device was developed were reported much earlier than this (one paper in 1897 and two in 1899). For convenience, these will be referred to as W1, W2 and W3. The earliest major paper of his (Wilson, 1897 or W1) described a very thorough study of condensation from contained volumes of dust-free gases that had been saturated with water vapor and then expanded adiabatically.

There is an obvious problem in studying systems that are saturated with water vapor: condensation on the walls of any containment vessel can sometimes be easier on such surfaces than in the gas itself. Wilson circumvented such problems, when necessary, in different ways depending on the details of his experiments. Efficient filtering of the gas was found to be absolutely essential if reproducible results were to be obtained.

Dust removal was also achieved by pre-expanding water-saturated gases and allowing the droplets so formed (on any dust particles) to settle before investigating how the degree of expansion influences the form of the condensate. In Wilson's study W1, radiation was employed in very few experiments. With the exception of these, the use of expansion ratios near 1.38 produced thick fog in the air at remarkably consistent ratios, while "rain-like" droplets were observed when the expansion ratios lay between this value and 1.25. No condensation was found to be possible at smaller expansion ratios than this. The degrees of super-saturation that produced fogs or droplets were calculated in nearly all cases.

The studies in W1, plus those described in Wilson's third major paper (W3) and later confirmations of many of his findings by others, have provided the basis for what meteorologists now believe to be true about all cloud condensation (Mason, 1971). In W3, Wilson employed the same pre-cleaning methods to water- saturated air as in W1 but this time the air was irradiated with X-rays before its final expansion.

Both these and gamma-rays had previously been shown (in W2) to ionize the air very easily so that ions were assumed to be responsible for the condensation. W3 was undertaken *primarily* to investigate a suggestion of Thomson (1898) that Earth maintains its negative charge because, in the air, condensation around anions occurs more rapidly than it does around cations. This possibility was also hinted at in Townsend's experiments (see Section 2).

The experiments proved clearly that Thomson's (1898) suggestion was correct: the anions present in the air do produce condensation considerably more rapidly than the cations. *Despite this finding*, however, Thomson's original explanation for the electrical charging of the Earth is *still ignored* in textbooks on the relevant aspects of cloud physics (e.g., Mason, 1971; Rakov & Uman, 2003). Strangely, Mason (1971) discusses several details of Wilson's other early findings (in W1 and W3) but completely ignores W2. Nor does he mention the main *reason* the W3 study was undertaken: to test Thomson's (1898) suggestion for how the Earth maintains its negative charge. The *inability to quantify* this idea seems to have left physicists and meteorologists uninterested in either the evidence itself or the very significant suggestion.

No explanation for the different condensation rates around anions and cations was available at the time, and this may partly explain why Wilson's *justification* for the study W3 was subsequently ignored. A qualitative explanation for Wilson's findings, based on chemical thermodynamics, was eventually provided (Turner, 1998), but

as far as can be learned from current meteorology textbooks, *Thomson's proposed explanation for charging the Earth is still completely ignored*. Collisions between raindrops and/or ice particles during thunderstorms are still the only charge separation mechanisms that are considered to be at all relevant (Mason, 1971; Rakov & Uman, 2003). *No study has been found that attempts to justify what seems the complete neglect of Thomson's (1898) idea or of Wilson's proof that he was correct*.

Wilson's second paper (Wilson, 1899a - or W2) has received almost no attention at all. His observations in W1 and W3, together with later confirmations of them by many others, are now routinely taken as evidence that the relative humidity of the air needs to be *at least 100%* if condensation is ever to occur.

However, this suggestion is *directly contradicted by evidence in Wilson's paper,* W2. This work clearly demonstrated condensation at relative humidities as low as 90%. Even before the results had been published in full, Rutherford (1898) had stressed their significance. This was a fully justified assessment if only because ultraviolet light, the form of radiation employed by Wilson in these studies, is far more plentiful near natural clouds than are the X-rays or gamma rays, which Wilson found made condensation very easy.

The only early investigation of the conclusions of W2 seems to have been by Vincent (1904). Guided by Thomson and Wilson, he employed equipment rather similar to some of Wilson's in an attempt to understand Wilson's puzzling finding that UV light was able to induce cloud formation in oxygen just as easily as it does in air. This objective was not achieved, but Vincent made two observations of potential interest. One led to doubts over Wilson's (W2) speculation that the presence of hydrogen peroxide (rather than nitric acid, his first assumption) was responsible for cloud formation in the air. Vincent found he could not detect any hydrogen peroxide chemically when he simulated Wilson's experiments. This could obviously have meant simply that the molecule's concentration was below the limit of detection. Arguments in the Appendix suggest otherwise.

The other point Vincent (1904) made was that, although most of the cloud particles were uncharged, small quantities of charged particles of both polarities could be detected when strong electric fields were applied. It seems that he (and Wilson) had been producing what those studying atmospheric electricity now refer to as "large ions". As we have seen, Loeb (1958) estimated that there can be thousands of millions of water molecules in these "large ions". It is, of course, most unlikely that the *chemical content of natural aerosols* would be identical to those produced under controlled laboratory conditions - the natural ones are almost certain to contain a wide range of other chemical species present as air contaminants. In fact, one possible reason for the rarity of ball lighting and other air plasmas is that these contaminants usually interfere with one or more of the chemical reactions needed to produce and maintain a stable plasma surface.

We decided to re-investigate W2 partly because condensation at less than 100 % relative humidity had been claimed but also because, with UV radiation, cloud formation had been found to be much slower than when either of the higher energy sources were used. This implied that differences in condensation rates might yield new information. Additionally, an *equilibrium state* seemed to be produced under irradiation by UV. We have found no modern meteorology textbook that refers either to these aspects of Wilson's work or to the findings of Tyndall (1870), which Wilson saw as closely related to his own. Even Mason's (1971) exceptionally well-documented book on cloud physics makes no mention of W2. Nor does the equally well-documented book of Rakov and Uman (2003) on lightning.

An additional fact, not discussed earlier, but implied in arguments that follow, is that UV light normally acts as an oxidizing agent in humid air. It can be helpful to think of high-energy photons as chemical species that can induce chemical reactions. It is then possible to assess the reactions they induce, using their energies in conjunction with ordinary estimates of reaction enthalpies. One reason UV photons usually act as oxidizing agents in real (moist) air is that they easily break up water into H atoms and OH radicals and that H atoms normally react very slowly in such systems, whereas OH radicals tend to react very rapidly.

For *really pure, really dry* gases (in which most detailed studies are made), it is usually found that UV photons lead to both oxidation and reduction at the same time. This is to be expected because the energy supplied can be easily sufficient to overcome any large energy barriers there may be in any of the relevant transition states. Such is the case, for example, with formic acid (Su et al., 2000), carbon dioxide (Schmidt et al., 2013), and nitric oxide (McGee & Heicklen, 1964). However, in moist air, the presence of oxygen and the great thermodynamic stability of water, normally mean that UV exposure can lead only to oxidation.

It has long been obvious that, under natural conditions, concentrations of trace contaminants in real air vary enormously in space and time (e.g., Wallace & Hobbs, 1977). This is less likely to be the case in air that has spent a long time away from continental contamination. Fairly recent measurements from an exceptionally

clean region of maritime air (taken on a coastal cliff top in Tasmania), support this claim and imply that exposure to low energy UV in very clean air yields mainly the radicals HO_2 and OH. This is the case provided that NO levels are low (Creasey et al., 2003). In our experiments, HO_2 and OH were probably the main long-lived, nitrogen-free, oxidizing radicals involved as reaction intermediates.

In the main part of W1, Wilson described experiments that had been conducted in several dust-free gases in which condensation was produced by their rapid expansion, and no source of ionizing radiation was provided. He found distinctly different condensation behavior from the observations of all of the earlier investigators. The reason was that they had not pre-treated their gases by thoroughly removing all dust particles from them prior to the adiabatic expansion. It seems clear that processes occurring in dust-free air are quite different from those that occur if condensation nuclei are already present. The water-saturated gases that Wilson studied included air, oxygen, nitrogen, carbon dioxide, and hydrogen.

Expansion ratios that were just high enough to produce condensation in all the clean gases were found to possess two different, but well-defined, critical values of v_2/v_1, where v_1 is the initial gas volume and v_2 the final one. For all the gases except hydrogen, these values were fairly close to 1.252 and 1.379 (the values for air). Below expansion ratios of 1.252 with air, no condensation occurred, but, between these two limits, "rain-like water droplets" would appear. Above the higher limit, fogs formed very rapidly. The higher value corresponds to air super-saturated by a factor of nearly 8 (based on calculated temperatures for adiabatically cooled gases). Just above a ratio of 1.408 with air, the clouds produced were green, followed, as v_2/v_1 was increased by other colors. The colors were clearly produced by optical interference in the clouds.

Wilson had shown that, in air at and above an expansion ratio of 1.38, no pre-existing condensation nuclei were needed for condensation. Later (in W3), Wilson measured the conductance of mist-containing air and concluded that, by $v_2/v_1 = 1.25$, condensation around anions is complete, but condensation around cations is only complete at $v_2/v_1 = 1.38$. It also seemed from the earlier studies that, between the two expansion ratios, condensation nuclei can be produced by cosmic rays or by high energy emissions from radioactive elements in the surroundings nearby.

On the basis of his W2 experiments in dust-free air that had been irradiated with UV, Wilson initially assumed, quite reasonably at that time, that condensation nuclei at expansion ratios above 1.25 but below 1.38 must have formed around protons and nitrate ions. However, his finding that pure oxygen required almost identical expansion ratios to those in the air convinced him that this was impossible. He thus argued that the only relevant chemistry must involve the formation of hydrogen peroxide. Three possible reasons for doubting this conclusion, including the findings of Vincent (1904), are provided in the Appendix. As will be demonstrated later, it now seems clear that Wilson's first thoughts concerning condensation from moist air (nitric acid formation) were correct.

There were three quite different kinds of unusual observations in W2. One was that condensation could be produced in the air *without applying any adiabatic expansion*. The second was that condensation from *dust-free* air in the presence of UV was observed to occur at *less than* the saturation vapor pressure of pure water (as opposed to the 790% of it when UV was absent). The third was the production of unusual patterns in some of the clouds and even stranger temperature-induced motions in them when a finger was applied to the bottom of the vessels near to where the light had been focused. These patterns mainly involved near-vertical motions in freshly produced clouds.

Both of the solutions used by Wilson to depress the vapor pressure of water (potassium hydroxide and sulfuric acid) were found to produce condensation at 90% of the saturation vapor pressure. This would occur *even in the absence of air expansion*. In much more concentrated solutions of either electrolytes, no clouds or fogs could be formed under UV irradiation (with no expansion). Clearly, one of the questions of interest is how it is possible, using UV radiation (with no expansion), to produce clouds at such low relative humidities while high degrees of expansion were needed to form clouds when radiation of much higher energy was used.

A possible *justification* for the subsequent neglect of W2 may have been the very reason the work was undertaken in the first place. This had initially been to *disprove* an earlier claim by Lenard that fogs produced in this way were a consequence of the interaction of UV radiation with the surfaces of *the silica windows* used to admit it. Wilson conducted numerous experiments that disproved this claim. Another possible reason for neglect was that later parts of the paper used a corona discharge instead of radiation as the source of ions. These findings might well have been thought to be more important than the earlier parts of the paper since they were, in effect, early contributions to the study of chemically related aspects of coronas. This subject would probably not have interested most meteorologists of the day.

Ions can be introduced into a moist gas during the electrolysis of electrolyte solutions (Townsend, 1897,

1898) by electromagnetic radiation of sufficiently high energy or from a corona discharge in the air.

Obviously, the *motions* of the charged chemical species produced will be very different in the different cases, but much of the underlying chemistry is likely to be the same. Subsequent work on electrical coronas has produced a truly immense quantity of experimental data but virtually no general principles that can provide the field with predictive power (Loeb, 1965).

The early experiments described in W2 showed clearly that the growth of new condensation nuclei produced by UV radiation is very slow compared with their initiation by higher energy radiation and subsequent expansion of the air. Later experiments using UV seemed to show that an equilibrium state is attained - usually on time-scales of a few minutes and apparently in both particle size and particle concentration.

As mentioned earlier, in all of Wilson's earliest experiments, visible evidence for the presence of condensation nuclei required a rapid (adiabatic) expansion of the humid air. Later, it was shown that *more powerful arcs* than those initially used could produce UV that formed clouds in humid air *without any need at all to expand it.* All our most informative experiments were of this type.

Two much more recent studies of the *chemical products* of corona discharges in water-saturated air are relevant when considering the nature of the condensation nuclei that Wilson must have produced. Peyrous and Lapeyre (1982) inferred, by measuring the influence of ozone and nitrogen oxides on the products of such discharges, that nitric acid was the likely source of condensation nuclei produced in their coronas.

Later, Pinart et al. (1996) showed, by direct analysis of an aqueous phase covering the lower electrode (in an investigation using a standard point-to-plane geometry), that both nitrous and nitric acids can be formed reproducibly in the air whose nominal humidity was 100%.

In the experiments of W2 that are of prime interest here, the source of ultraviolet light was an electric arc between either zinc or cadmium electrodes. This was energized by high voltage discharges from an induction coil plus capacitor combination, the component values being chosen so as to maximize the brightness of the arc. The UV light had been focused, using silica lenses of various focal lengths, into variously shaped vessels containing dust-free air that was saturated with water vapor.

These vessels were mostly horizontal tubes of several cm diameter. Perhaps the most encouraging aspect of Wilson's studies (to anyone attempting reproduce his findings) was that he used many different shapes of vessel, several different metal components in contact with the vapor and a variety of different materials for sealing the cells containing his water-saturated air.

The only apparent restriction was that the beam of UV should not be shone directly onto a metal surface inside the cell. Apart from this restriction, necessary to avoid complications from electron release at the metal surface, none of the materials chosen appeared to influence the conditions under which clouds were formed. For this reason, there appeared to be considerable freedom in the choice of the materials of construction and of those used as seals. We took full advantage of this fact.

Wilson did not explain his choice of zinc and cadmium for his arcs. It seems that a normal carbon arc must have failed to yield condensation in his experiments. This would probably have been the case because the emission is mainly thermal in a carbon arc but predominantly through spectral lines if the arc is metallic. Several years later, Vincent (1904) successfully used an aluminum arc to produce mists. All three metals produce numerous emission lines in the UV. It is worth considering *why* no independent confirmations of the most unusual of the W2 results ever seem to have been published.

Any early attempt to reproduce them is likely to have demanded, as in Wilson's own case, a basically trial and error approach that might well have proved far more time-consuming than was thought worth the effort. This could explain the lack of any supporting evidence by other physicists for the observations. Our early attempts to reproduce the findings of W2 certainly implied that if most of Wilson's unexplained findings were ever to be replicated, a largely trial-and-error approach would still be needed.

Most likely, this was because of the number of questions, the answers of which were unclear. The list includes the following:

(i) On what basis did Wilson choose to use zinc and cadmium electrodes to produce his arcs?
(ii) How pure would the two metals providing the arcs have been ?
(iii) Is it likely that multiple emission lines are needed, each facilitating a different reaction step?
(iv) How powerful and how thermally homogeneous would the arcs have been?
(v) How important might the focusing positions of the different wavelengths have been?
(vi) How certain is it that traces of volatile impurities in the water did not influence the observations?

4. OUR MORE RECENT EXPERIMENTS

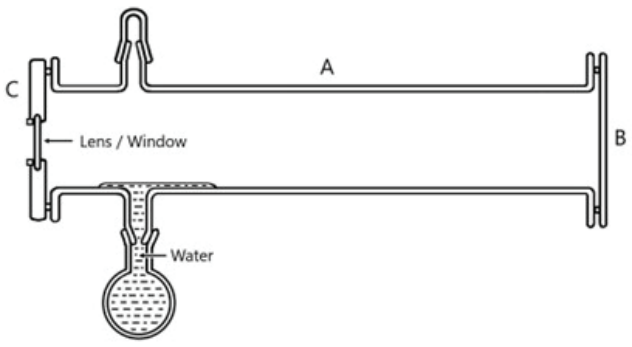
4.1 Experimental Details and Early Findings

Most of the above questions had not even been raised when our experiments were begun, but they very soon needed addressing since all our initial attempts to repeat the findings of W2 failed. It quickly became apparent that the above questions would not all be easy to answer. If attempts to reproduce all of Wilson's findings using UV light had been made soon after they were reported, there could still have been serious obstacles resulting from a lack of answers to one or more of these questions. The experiments of Vincent (1904) illustrated this problem. However, one simple point seemed clear: the strangest of Wilson's findings in W2 are unlikely to be explicable unless *ionization* was being produced by the UV radiation he used. All our experiments were conducted at temperatures close to 21^0 C. Most were conducted inside a glass cylinder 300 mm long with an internal diameter of 50 mm. Its ends comprised identical flat rings of glass (having 50 mm internal and 73 mm external diameters) with an o-ring groove incorporated, the outside diameter of which was 65 mm. Two tubes of 18 mm internal diameter were placed opposite one another and mounted normal to the axis. They were located 50 mm from one end of the cylinder. These allowed water in the cell to be adjusted to any required depth.

The cell was designed for flexibility. Its main features are shown in Fig.1. Component A represents the cylindrical glass vessel containing humid air while B normally consisted of an acrylic (Plexiglass) plate sealed, using o-rings, to one end of the vessel. With appropriately placed holes in it, B allowed a variety of inserts into the cell. Component C is a standard aluminum support for either lenses or windows (sold by Edmund Optics). The latter components were all made of pure silica, and they initially permitted radiation with wavelengths down to 200 nm to enter the cell.

Except in the very earliest tests, filtered water-saturated air was pumped into the vessel of Fig. 1 using a glass tube (sealed with epoxy) through B and out through the side tube at the top of the vessel. The process was normally continued for a minimum of 30 minutes at a rate of 2 to 3 liters per minute. Any residual gas motions in the vessel were then allowed to dissipate for at least 5 minutes before UV radiation was applied.

Figure 1. Sketch of the Basic UV Irradiation Cell.



Holes in item B of Fig.1 permitted introduction into the cell of filtered air plus components in the form of thin support rods, thermocouples, or thermistors. The end of the cell where these introductions were normally made will be referred to as the 'far end' while the UV admitting end, on the left, is called the 'near end'. The cell could be mounted with its 18 mm diameter side tubes near either end of the cylinder. All the early tests, plus a few of the later ones, used radiation from focused zinc arcs.

The vessel, and its associated components, were mounted on a metre length optical bench. The axes of the optical components, either lenses or windows, were normally aligned as closely as possible with the axis of the cylinder but the cell could be tilted to provide different depths of water along its length. It could also be moved transversely if the use of a rather large diameter insert was required.

UV light was always admitted at the near end of the cell and initially always through windows or lenses made from "UV grade" silica that had been coated for maximum transmission above a wavelength of 200 nm. In all the experiments from which significant conclusions were drawn, mists or clouds in the cell were identified through their scattering of light from the red beam of a helium-neon laser whose output had been expanded to provide a nearly parallel beam about 15 mm wide. It was necessary to undertake the testing for condensation in the dark, and digital images, either still or as movies, were made when appropriate.

The cell did not precisely duplicate any of the ones used by Wilson, but his work implied that this is unimportant. He used a wide variety of cells in his three papers. In W2, 18 different designs were employed, and still others were used in W1 and W3. A variety of metals and sealing methods was employed, but none appeared to influence whether or how fast mists formed. Slight differences in mist formation rate might have been present, but none were reported. In our first few experiments, Wilson's method of cleaning the air by forced condensation on dust in a preliminary near-adiabatic expansion was used. However, for our experiments, it was soon realized that commercially available filters effectively remove all traces of solid condensation nuclei. A very surprising observation Wilson made was that, with a UV source of sufficient power, in contrast with the use of X-rays and

gamma-rays, mists could be obtained using UV *without applying any adiabatic expansion at all* to the humid air. None of our experiments from which any conclusions are drawn employed such an expansion step.

Because arc lighting equipment is no longer commonly used, we initially formed our arcs using what is known as TIG welding equipment. This employs a thin, pointed electrode of tungsten held above the metal to be melted. When used on an easily oxidized metal like zinc, it is supplied with a flow of argon as close as possible to the metal being welded. In our arc source, the electrodes were mounted vertically, and the gas was supplied vertically from above. To keep the arc as cool as possible, the lower electrode, a 13 mm diameter zinc rod, was surrounded by a thick (35 mm outside diameter) copper cylinder. This rested on a square copper plate with four thick copper legs screwed to it. The whole assembly was cooled by forced air flow - at room temperature - underneath this copper "table".

Initially, the electrodes were supported inside a cube-shaped box (having 100 - mm sides) through holes in the box. The box was constructed from a building material sold as a substitute for asbestos. Two circular holes, opposite one another and at right angles to the axis of the electrodes, were provided. One was fitted with a short tube closed with a silica lens of 50.8 mm diameter. Another hole, on the opposite face of the box, allowed the extraction of any zinc oxidation products and the argon. The position of the arc relative to the lens was such that it allowed a 75 mm focal length lens to focus the parallel beam, leaving this lens, through silica components, into the glass cell. After a few minutes of operation, a small (3 mm dia.) puddle of liquid zinc would be established at the top of the zinc rod.

With this arrangement and modifications to the dc power supply of the welder - to reduce its power - a stable arc could be maintained for 30 minutes. This was the length of time that Wilson had found was quite sufficient for condensation to be produced in water-saturated air. All experiments prolonged much beyond 30 minutes resulted in obvious evidence for overheating inside the enclosure. The experiments all failed to produce mists. An obvious potential cause for our failure was that the ratio of IR to UV radiation was too high.

In the context of this failure, it is also relevant to refer briefly to some historical matters related to Wilson's findings in W2. Several physicists succeeded in following up on his earlier and later findings concerning condensation following the adiabatic expansion of water-saturated air (Mason, 1971). These studies have led to a general acceptance of the fact that air needs to be at a minimum of 100% saturation with water vapor before cloud formation is possible. However, Wilson's findings that this is not always the case (under UV irradiation) seem to have been completely ignored since about 1904.A point of potential relevance to our initial failures to produce mists seems relevant also to the matter of why these particular findings of Wilson were not duplicated soon after their first being reported. In Vincent's (1904) study, zinc electrodes were not used to produce the UV illumination; instead he used a spark between electrodes of aluminum. He did not explain this choice, but it might well have been that his zinc arcs had failed to produce mists just as ours did. If this is the case, it might well be that Wilson happened to have been very fortunate in the precise impurities (and their concentrations) in the zinc he had used (see later).

Vincent was a chemist at a far less prestigious laboratory than the Cavendish. This might help explain why his findings were neglected. Nevertheless, with the help of Wilson and Thomson, he did succeed in confirming condensation at 90% relative humidity. However, he failed completely to detect any hydrogen peroxide in the condensate. The latter evidence seemed to confirm Wilson's original assumption that his clouds had resulted as a consequence of nitric acid formation. This matter is discussed a little more fully in the Appendix.

One obvious potential cause of our failures to form clouds was that we had felt the need to use 21st century safety standards (by enclosing the arc in a box). Zinc was chosen since it is less poisonous than cadmium. A very plausible cause of the failure was that the ratio of IR to UV radiation was too high in our arcs. In order to investigate this possibility, a few attempts were made to measure internal temperatures, but it proved impractical to shield the sensing elements of the detectors from the IR radiation.

A more realistic approach was therefore tried. This was to remove the IR by means of a grating filter specifically designed for this purpose (Edmund Optics # 85-299). Again, no mists could be detected. It was clearly possible that the filter's inability to pass UV below a wavelength of 240 nm might be responsible for this failure. However, it seemed equally likely that the problem lay with the zinc.

It had originally been decided to use a commercial grade of zinc rather than a high-purity metal on the grounds that *impurities* in the zinc Wilson had used might have been responsible for the ionization his arcs had produced in the air. At this stage, multiple emission lines were thought more likely to aid condensation than to inhibit it. It also seemed possible that the pulse rate of the UV was important. Later experiments used the UV from a variable frequency pulsed power source that used an induction coil circuit. It was hoped that this would mimic (and be more flexible than) the circuit used by Wilson.

The electrodes used in these open-air arc experiments consisted of sharpened pairs of zinc rods. First, the old commercial-grade zinc was used with air extraction as close as possible to arcs. Then, 99.95% pure zinc was used. Neither kind of electrode succeeded in producing condensation in the cell. Wilson's success might have resulted because the precise impurity content happened to be optimal with the metals he had used. This suggestion seemed possible after consulting an old chemical encyclopedia (Mellor, 1928). It seems that trace impurities in any sample of zinc can differ surprisingly greatly depending on the *specific mine* from which the zinc ore was extracted.

For this reason, even the 0.05% of impurity in our "pure" zinc might have been significant. Alternatively, specific impurities might be needed. Emission line intensities for different lines differ enormously (Lide, 2003), so the impurity content of Wilson's zinc might well have been crucial. This seems to be the most likely reason we could not replicate Wilson's findings. Insufficient power seems a less likely cause of our failures. We never did succeed in discovering why we could not replicate Wilson's results with zinc electrodes. It is certainly possible that all early attempts by Wilson's contemporaries failed to replicate his findings for this reason.

Before describing our more significant experiments, it is convenient to mention some of our early ones which were only partial failures. They were conducted inside ordinary 2-litre glass flasks and in a 250 cm^3 Dreschel bottle, both vessels being open to the air. UV was admitted to the vessels using a miniature mercury vapor lamp whose emission tube was 50 mm long and 7 mm wide. It was made by Analyic Jena US and produced light intensities, at 254 nm, of a few mW cm^2. The use of this lamp failed to produce clouds over distilled water but succeeded, within a few minutes, above fairly dilute solutions of hydrochloric acid. This provided much-needed encouragement that it might still be possible to confirm at least some of Wilson's other findings.

Our most crucial experiment, using the cell of Fig. 1 and this miniature mercury vapor lamp, resulted from an accident. The lamp had been temporarily placed within a few mm of a silica lens that happened to be in use. While discussing many of our failures to produce mists (and the partial success using dilute hydrochloric acid), the lamp was accidentally switched on, and we were amazed to see that a mist was produced in the distilled water-containing cell within a few minutes. The focal length of the lens in use at the time happened to be 100 mm, and a lamp placed that close to the lens was obviously producing a hugely divergent beam within the cell. Using the mercury pen lamp, we then found it totally impossible to produce condensation in the cell when any of our other lenses or a silica window was employed - so this finding seemed incomprehensible.

No sense at all could be made of any of our numerous earlier results until the significance of two facts started to become clear. One was that the technology for producing low reflectivity coatings of optical components would not have been available to Wilson, and the other was that mercury possesses a much lower frequency emission line than the one specified by the manufacturer of the lamp. The specified line is at 254 nm but mercury also possesses a much weaker line at 185 nm. All our original lenses were rather thick and had multilayer coatings on them that passed very little energy at wavelengths below 200 nm. These coatings *should* have completely stopped mercury's 185 nm line - based on the curves in various manufacturers' literature.

The only possible explanation for our finding seemed to be that the more energetic line was the one producing condensation in our experiments - but how could the 100 mm focal length lens *and only that one* have passed radiation UV at 185 nm? This question was answered when our earliest records were consulted. These revealed that previously unobserved damage had been done to *part of* the anti-reflection *coating on one face of this particular lens*. The damage had occurred during the experiment *immediately prior* to the accidental production of our first cloud in the vessel of Fig.1. An area on one face of this lens (defined by a straight line that would have been horizontal when it formed) had *lost its coating*. The damage was only obvious when viewed very carefully in optimally directed light.

The partial removal of the anti-reflection coating occurred during what was the *only* early experiment in which the cell of Fig.1 contained dilute hydrochloric acid instead of distilled water. It had been noted at the time that the level of the acid in the cell was unusually high in this experiment, and this was consistent with the position of the line on the lens. It now seems clear that, during our first production of a mist in the cell of Fig.1, a little of the 185nm UV had penetrated one layer of the lens coating (on the outside), and then the portion of the lens that had been previously in contact with the UV-irradiated HCl, the accidental treatment having removed the submerged part of the coating. This explanation was confirmed by the intentional removal of the coatings on other lenses, using UV irradiated HCl solutions, and/or by gentle grinding of the lens surfaces, also when a new, un-coated window was used.

Because the 185 nm line is strongly absorbed by the air, we could not *focus* the light into our cell as Wilson had done. Fortunately, our *unfocused* 185 nm line of mercu-

ry produced mists much faster than Wilson's *focused* UV. However, because the beam was divergent inside the cell, and because it was clearly producing local refrigeration where the aerosols were forming, it was initially very difficult to avoid condensation on the inside of the glass vessel (component A of Fig. 1) in what would otherwise have been an optimum viewing position. Presumably, Wilson had been able to avoid this problem by using a focused beam, and nothing we found later contradicted this assumption.

Two reasonable expectations of the condensation behavior were soon established. One was that clouds would form more quickly the nearer they were to a water surface. Also, the presence of significant IR radiation does indeed inhibit cloud formation. With the exception of a few experiments in which a saturated solution of KCl replaced pure water, no effects from changing the water level or tilting the cell were observed - though more quantitative measurements might have revealed them. In a few experiments where changes were observed, a gradual separation of solid KCl from the surface of the solution was observed.

This was presumably caused by rapid surface evaporation of water as numerous invisibly small aerosols in the air grew in number and size.

The solid KCl caused an obvious change in the pattern of reflections within the cell, after which extremely thin mists were eventually detected - but only after prolonged UV exposure. It seems clear that Wilson's clouds could not have been produced by radiation at 185 nm because he had used focused beams requiring paths in the air that would have stopped all radiation much below 200 nm. The tests with KCl were made to check the effects Wilson found on relative humidity. He had only used an acid and a base to achieve this change, so we tried a salt whose solubility was high enough to reduce the relative humidity to below 90%. Condensation was easily detected with solutions slightly *below* KCl saturation, in which the relative humidity would have been about 86 %. The only reasonable explanation for mist production at relative humidities below 100 % is refrigeration close to small hydrated nitrite ions.

In our experiments, with both KCl solutions and distilled water, we eventually noticed that the pattern of condensation within the cell was not what would have been expected on the assumption that condensation would begin where the UV intensity is greatest. In some of our earliest experiments, this assumption appeared to be justified. In these experiments, component C of Fig.1 was replaced by an acrylic plate through which the mercury lamp was placed so that it was in direct contact with the air in the cell. In this case, condensation appeared to have first formed very close to the lamp. However, because of condensation on component A of the vessel, this was uncertain, and later experiments suggested that no condensation was likely to have occurred very close to the UV source. Shields for eye protection were always employed, and they could add to the difficulty of distinguishing condensation close to the lamp from that on the cylindrical glass of the cell.

Whenever cloud formation was observed *clearly*, which means that droplets were *not condensing locally on a surface in the viewing path*, the clouds would appear to fill the vessel in such a way that condensation was first observed a few cm from the lamp. Condensation would eventually be fairly uniform except close to solid surfaces and in regions that the cloud had yet to reach. We never managed to correlate the precise positions of the mercury lamp with the observed locations where water had condensed on the surfaces of the glass cylinder (A of Fig. 1). Multiple reflections inside the vessel, combined with the imprecise positioning of the lamp, seem to have been responsible for this. It was eventually concluded that a combination of slow aerosol growth and the diffusion of water vapor completely determined where mists would first be observed.

Had the accidental de-coating of one lens not occurred, we might never have learned enough to understand most of our earlier detailed findings. One thing seems very clear: Wilson's clouds could not have been produced by radiation at 185 nm because its absorption in the air would have stopped it completely. The clear evidence that Wilson's UV took longer to produce condensation than ours is fully consistent with the implication that it was the lower wavelength of the mercury radiation we used that was responsible for our eventual success.

Some Semi-quantitative Evidence

It seems obvious, based on earlier considerations (Turner, 1994, 1998), that the most likely cause of the unexpected condensation found by Wilson was that metastable nitrous acid is formed in experiments like his. It also seems obvious that any acids produced (nitrous or nitric acids) need only to have been present in very small quantities and that, quite possibly, insufficient material was present to permit either acid to be detected by any method that was both simple and reliable.

However, it so happened that some pond-water test papers had been purchased shortly before the experiments were begun, but none had been used, and all were still in their sealed can. These papers allow testing for pH, nitrates, and nitrites. Their normal use requires several ml of pond water to give reliable results. Nevertheless, it

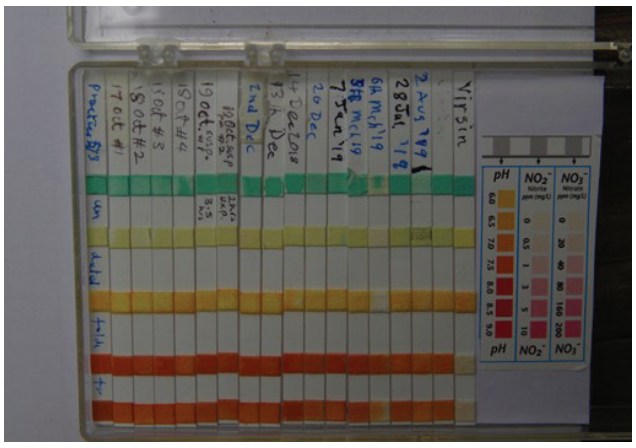
seemed just conceivable that something might be learned by testing the wet parts of the cylindrical glass vessel after the completion of an irradiation experiment. The test papers being to hand, a few tests were made using them. It is convenient to discuss here what was found with the test papers - before our more significant observations are described.

Plate 1 shows the results of 16 tests with the papers that were undertaken over a period of nine months. All the used papers were eventually stored together in a small transparent plastic box (visible in Plate 1), which was just wide enough to hold them. They represented a wide range of experiments, but no obvious relationship with the experimental type or detailed observations was found. The two top rows of colored squares in Plate 1 relate to pond chemicals of no current concern. The lower three represent pH, NO_2 and NO_3 respectively. A copy of the standard colors that permit estimates of concentration is provided to the right. The dates of the tests are indicated in the top row, with the oldest date on the left.

The last two papers on the right were never used in the irradiation cell, the one marked virgin having been placed with the others in the plastic box that held them all *just before* the photograph was taken. The other one, the unlabeled one, was put in the box at the same time as the last dated one. It is clear, from these two papers (never used in the cell), that slow changes in apparent nitrite and nitrate concentration had taken place *solely* as the result of being confined within the box. Obviously, *only freshly observed colors* have much value.

In some experiments, the papers were pre-positioned in the air near the cloud-forming region, while most simply tested the inner surface of the glass cylinder after the experiment had been completed. An important point concerns the pH values indicated. When the sealed can that originally contained the papers was first opened, the pH indicated on all the fresh dry papers was 7 - that is pH neutral. The first seven tests (up to the 19th of October, 2018) made inside the cell all indicated a pH at or below 6, while the dry, unused papers still indicated a pH of 7. By the time of the 2nd of December experiment, however, the unused, initially dry papers were all indicating a pH of 6 even *before* they had been used. This is quite normal due to the formation on the papers of carbonic acid from moisture and CO_2 in the air. The pH values of 6 or below in *all the earlier tests*, however, show clearly, that the aerosols formed were acidic. Since hydrated protons are the only cations likely to be present in the samples, this finding was to be expected in the presence of either of the nitrogen oxyacids.

Plate 1. Test Paper Results s for pH, Nitrite and Nitrate.



In Plate 1, the two papers that had never been in the cell (those on the right) show obvious evidence for color changes with time spent in the plastic box (for both acids). Presumably, these changes in color occurred in *all the anion-detecting strips* as a consequence of one or more volatile components (presumably nitrogen oxides) being released from other papers that had been stored together. Nitration of the aromatic rings of the dye used for detection is the probable cause of the color changes.

Whatever the cause, however, the papers used to test the droplets *immediately after* opening the cell (which were never photographed) were the *only ones* likely to be at all meaningful. It took several hours in the box before the fresh colors started to change noticeably, but even the fresh NO_2 and NO_3 tests are obviously of limited value *quantitatively* since they had probably started to change color while still in the cell (due to the presence of nitrogen oxides). Despite these problems, however, there is little doubt that, among the products of irradiation are nitrous and nitric acids or that more nitric acid than nitrous acid had been produced in all the aerosols (and in condensate on the cell walls). All the dated tests indicated in Plate 1 were made on samples that had been exposed to UV in the cell for longer than a quarter of an hour. No tests of shorter duration were made.

That the chemical reactions between nitrogen compounds in the air are very complex has been known for well over a century (Mellor, 1928), and because of their role in air pollution, huge numbers of relevant reaction rates have been measured over the last half-century. In the present context, such data cannot make any useful predictions concerning the important gas phase reactions because nearly all the rates available involve radical intermediates, and none of them have ionic intermediates. Of course, reactions mediated by radicals will still proceed and will occur in parallel with the more relevant ion-mediated reactions. For such reasons, some of the already known complications in air chemistry can usefully be mentioned.

One is an *equilibrium state* that has long been known to be attained fairly rapidly in a system that includes gas-phase nitrous acid and liquid water (Lewis & Edgar, 1911). It can be represented as Reaction 1. In this representation, *all the species, except for the ions, can be components of either phase*.

$$3\,HNO_2 = 2\,NO + H_2O + H^+(aq) + NO_3(aq) \quad (1)$$

Clearly, even if this reaction were to be the only one occurring in our experiments, data on at least the diffusion rates of HNO_2 and NO in both phases would be needed to quantify anything about the detailed mechanism of cloud formation. However, the real situation is far more complicated than this since other oxides of nitrogen will also be present. We can obviously only use detections of NO_2 and NO_3 as *qualitative indications* of the final products of some of the complex processes that must have occurred. However, this does not mean that the results are without value. None of the tests made immediately after exposure indicated a nitrate concentration of more than 60 ppm, but the aged ones *falsely* imply levels close to 200 ppm (if the obvious changes in color are ignored). Also, only three freshly indicated nitrite values were much above one ppm (compared with 10 implied from the papers later).

Despite these complications, it is virtually certain that nitrous acid was produced. The presence of ozone, which is a well-known product of UV irradiation of the air, suggests that nitrous acid was probably formed first, and most of it later oxidized, possibly by ozone, to nitric acid. Little more can be deduced. However, the stored papers do contain other information that is informative. It is obvious from Plate 1 that a few of the chemical test pads have been almost completely bleached while others are only partly faded. This implies that the chemicals formed by the photolysis were not uniformly distributed in the moist air of the cell. This is hardly surprising since the clouds were not uniformly distributed.

A likely bleach is ozone, since forming O atoms from oxygen does not require much energy, and these atoms can react fairly rapidly with oxygen molecules to yield O_3. Several test papers were supported inside the cell *during the experiments* (some were in contact with the cell surface and some were in positions where mist could form). There was no obvious correlation between any of the test results and where the papers had been placed. Bleaching of the papers occurred slowly and was not, in fact, noticed until they had been stored in the plastic box for several days.

The main conclusion from these crude experiments is that the production of mists, on irradiation with UV, almost certainly involves the formation, in the gas phase, of metastable nitrous acid and its subsequent oxidation to nitric acid. The formation of nitric acid could only have arisen either inside aerosols or very close to where the nitrous acid transformations were cooling the air. This is because nitric acid is stable *only* if the temperature is below 15^0 C (Turner, 1998) and the cell was at room temperature, which was close to 21^0 C.

In W2, Wilson reported producing very inhomogeneous clouds in some experiments, and we have clearly observed similar phenomena. The lack of homogeneity implied by the bleaching of the test papers implies that all the nitrogen-containing species present would also have been distributed non-homogeneously. Clearly, the processes involved in oxidizing nitrogen to oxyacids are very complicated. Despite this, it seems absolutely certain that both nitrous and nitric acids were produced in all successful tests and that much more nitrate than nitrite was eventually formed. Because of the lack of homogeneity, it is clear that far more detailed experimental studies (if possible at all) would be needed if we wish to use similar experiments to learn more about the *detailed processes* that produce *local refrigeration and cloud condensation* in moist air.

Comparisons with Wilson's Findings

After it became clear that we could not *precisely* duplicate any of Wilson's experiments, we tried to replicate them more closely by using a pulsed arc across a pair of zinc electrodes - instead of the continuous arcs produced by the TIG welding setup. It was speculated that a continuous and a pulsed arc might well lead to significantly different chemical outcomes in the two kinds of experiment.

Our pulsed arc was produced by driving the spark between zinc electrodes in the secondary circuit of a traditional motor car ignition system. The coil's primary circuit was fed with a current of rectangular wave- shape, the drive circuit allowing for control of the output pulse duration, frequency (in the range 40 -220 Hz), and polarity. The resulting 32 kV output pulses allowed us to generate arc-lengths of up to 8 mm.

Both the original zinc and a pure (99.95 %) variety were employed in the new experiments.

This method of energizing the zinc arc also failed to produce radiation that could induce condensation in our humid air. Following these tests, only the small mercury vapor lamp was used. Its use proved unexpectedly informative despite what turned out to be the impracticality of focusing its light into the cell. All attempts to focus our lamp's UV (using an evacuated focusing chamber fitted with CaF_2 windows) failed. CaF_2 transmits somewhat higher energy UV than does silica - but it seems not to be

available in lens form - only as windows. It should not be concluded from these failures that focusing the 185 nm line of mercury is impossible or even particularly difficult.

The reasons for believing this are twofold. Firstly, our lamps were not very powerful, and secondly, 185 nm is very close to the cutoff wavelength where silica loses its ability to transmit UV *even with the purest silica available*. Our experiences with a nominally identical mercury vapor lamp (from the same manufacturer) illustrated the second problem. A second lamp was purchased because of the possibility that the first one might be losing power. However, the new lamp turned out to produce mists considerably *more slowly* than the first one. Since we were using the lamps at a wavelength well below that specified by the manufacturer, we had no reason to believe that the new lamp was in any way substandard. It seems we had simply been very fortunate in the high degree of purity of the silica envelope that contained the mercury in our first purchase.

One of the most surprising findings that Wilson reported in W2 resulted from his placing a finger directly below one of his cylindrical glass vessels that contained a *freshly formed* mist. When UV light from his arc was focused into a cell containing only dust-free water-saturated air, mist eventually began to form at the precise location of the focus. It then slowly expanded in all directions from this initially small volume. The non-homogenous mists produced in this way would display totally random motions until a finger was placed underneath the cell near the position of the focused beam. Then, soon after heat from a finger was applied, the mists became organized into vertical patterns of scattered light. Localized thermal effects were implied.

Clearly, the mists produced by UV radiation are very sensitive to tiny temperature gradients. This is expected to result from the refrigerating gas phase reactions proposed in the original ball lightning model (Turner, 1994). Since we were unable to produce clouds using focused beams of UV, we were obviously unable to reproduce Wilson's findings precisely. Nevertheless, the unfocused UV beam from the mercury vapor lamp did display what appeared to be *closely related* motions of the clouds when a finger was placed for several seconds under the cell.

The 185 nm line of mercury is absorbed by silica and by air, so the thinnest available optical components were employed. Most used was a 1mm thick silica window close to which the mercury penlight was placed. Patchy clouds were produced that would sometimes display swirling motions. The swirls had curvature radii of a few cm. Their motions, not surprisingly, were very dependent on the precise positioning of the lamp.

This was mainly because of the finite length of the lamp discharge and multiple reflections inside the cell.

None of our original silica components could pass radiation at wavelengths below 200 nm. On the basis of the best thermodynamic data available, multiple UV photons would have been needed to promote ionization in the air. The need for more than one photon is presumably part of the reason Wilson found that ionization by UV is so much slower than by X-rays and why we found that condensation produced by the 185 nm line of mercury was significantly more rapid than that observed by Wilson.

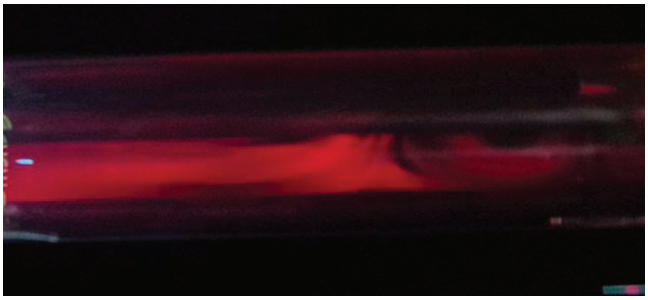
There have been numerous different chemical intermediates present in the UV-irradiated air, but these need not all be favorable for the ionization of the air. Extra emission lines in an arc are, in fact, just as likely to inhibit the overall ionization process as to enhance it. Any *essential* intermediate could easily fail to produce a specific intermediate that is crucial to ion production if it can more easily lose its energy through some alternative reaction path that might be facilitated by some specific spectral line. The differences between our results and Wilson's imply that this could have been the case.

Unfortunately, this is not the only possible reason for our earlier failures. Whether or not our difficulties resulted from different impurities in the various sources of our zinc, there is also the problem, raised at the end of Section 3, concerning the possible role of trace impurities in the air that might be introduced as the result of trace impurities in the water used. In all except our earliest experiments, the distilled water used was readily obtainable in supermarkets. This is provided in plastic containers, while Wilson will almost certainly have used water purified by distillation from a tin-lined still and then kept in glass. It is reasonable to assume that the oxidation state of any trace impurities in the water might differ between Wilson's experiments and ours.

For this reason, an opportunity was taken early to purchase a fairly old, tin-lined water still. In our earliest experiments, it was used to test whether there was any difference in the ease of producing mists using the two sources of water. There appeared to be no difference because, in these early tests, no condensation was induced. Thus, we did not investigate directly whether or not trace impurities in the water might have influenced the rates of mist development. Such an investigation might conceivably prove informative in future experiments, but simpler and more direct approaches seem preferable.

If we had later used water from the tin-lined still, the slow rate of water production would have significantly reduced our rate of experimentation. This was the main reason the use of the still was abandoned, but it already seemed probable that other causes of failure would present more serious problems. This assumption seems

Plate 2. A Single Frame from a Video Image of Cloud Motions.



to have been justified by our later experiments.

Plate 2 shows a single shot from a video image of mist formation. It is less clear than the original, but it still shows the mist in the expanded laser beam after a finger is placed repeatedly to the right of the swirls for between 1 and 3 seconds.

Plate 3 was obtained much earlier - before the initial problems of condensation and reflected light had been minimized. The colors in this image are by no means correctly reproduced but Plate 3 does show one type of swirl more clearly than do any of the later shots.

Many video images were obtained of the development of the clouds and of their responses to placing a finger underneath the cell. Condensation usually developed until thin mists covered most of the cell toward the far end and then they would thicken. Although thermally induced movements in these clouds could still be produced in the thick clouds formed after fairly long exposure, very much longer contact of the finger with the glass was required before any cloud motion could be detected. This is qualitatively to be expected on the basis of the *thermodynamics* of the ion re-combination reactions:

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

The reasons for this expectation have been discussed elsewhere (Turner, 2024).

The individual reactions represented by the generic one (Reaction 2) are believed to be largely responsible for the occasional stability of lightning balls since, when n rises above about 6, the reactions begin to extract heat from the local air rather than adding to it (Turner, 1994). However, once n exceeds about 25, the reactions become *thermodynamically impossible*. Thus the large ions are stable, there being no longer a driving force for charge neutralization.

This implies that it is only in the very early stages of aerosol growth that refrigeration of the air is possible. The restriction probably explains the fact that the clouds are most sensitive to the heat from a finger at the earliest stages of cloud formation. It also shows the vital importance of Reaction 2 in cooling the air close to an air plasma surface. One consequence of this very localized refrigeration process, when air is close to an extremely hot plasma, is that lightning balls occasionally crack circular holes (of apparently the same sizes as the balls themselves) in glass windows (Grigor'ev, Grigor'eva and Shiryaeva, 1992; Turner, 1997).

In later experiments, a somewhat more straightforward view of the condensation process was obtained when the lamp was inserted into a silica tube (wall thickness 1 mm) that was mounted between acrylic plates at each end of the cell. The lamp was supported inside this tube close to the end of the cell, and a continuous flow of air was maintained down the tube to cool the lamp. With this arrangement, a thin band of cloud would form not far from the lamp, and then it would slowly move to the far end of the cell, leaving a cloud-free region of air behind the advancing cloud. Again this behavior is consistent with the thermodynamics of the processes summarized by Reaction 2.

Thermal influences like these appear to be close analogs of the effects that Wilson reported in W2. However, they may have the potential to be more informative in the future. Local refrigeration seems the only reasonable explanation for the effects. These effects might be interpretable quantitatively in the future. They would need to be interpreted in terms of hydration rates, cluster sizes, diffusion rates, and the thermodynamics of Reaction 2 and other reactions. We have seen that refrigeration seems only to be possible when hydration numbers lie between about 5 and 25. However, these figures strictly apply *only to standard state conditions* and with identical hydration numbers for the two ions H_3O^+ and NO_2. More detailed studies would be needed if much more is to be learned. However, such studies might at least allow us to learn the real degrees of hydration that are needed to produce naturally contained air plasmas.

By the end of the 19th century, ionization in gases induced by X and gamma rays was well known. However, this was not the case when UV radiation was used. Nevertheless, Wilson was in a position to contrast his own

Plate 3. A Much Earlier Clip from a Video Record.

findings with measurements of ion recombination rates in various gases that had been blown past a source of X-rays (Rutherford, 1897). Rutherford had found that, in pure oxygen, the ions produced were small - having diameters representing a cluster of about 5.5 molecules. He pointed out that to explain the observed results, the carrier (of electricity) need not be greater than 5 times the radius of the molecule. In these experiments, the oxygen will presumably have been thoroughly dry, so *only O_2 clusters* were present.

On the other hand, in W3, Wilson showed that the ions produced in water-saturated, adiabatically-expanded air that had been exposed to X-rays were very much larger than this. Their velocities, under moderate electric fields, were several thousand times smaller than those produced by X-rays. In some ways, the most surprising of Wilson's observations in W3 was that, following irradiation, the two characteristic sets of values of v_2/v_1 (1.25 and 1.31) needed to begin producing clouds when the moist air was expanded were remarkably similar to those observed in the *absence* of ionizing radiation (1.25 and 1.38).

Wilson deduced that the ions producing condensation at the lower value of v_2/v_1 were anions, while expansion ratios of 1.31 were needed before any cations could begin acting as condensation nuclei. This is consistent with Thomson's (1898) inference that the Earth maintains its negative charge because the anions in the air fall faster than the cations present. This explanation *still seems to be ignored* by meteorologists and lightning engineers even though it had been demonstrated experimentally more than a century ago and had later been shown to be readily explicable electrochemically (Turner, 1998).

Assuming that Wilson's basic assessment of his data is correct, there seems to be a simple explanation for why X-rays and high-energy UV behave so differently in promoting condensation. A single photon of an X-ray (or gamma ray) could be sufficiently energetic to separate a pair of ions *and* impart sufficient *kinetic* energy to them to propel them to a distance where hydration is possible, but mutual charge annihilation is not. As a consequence, clouds form almost immediately. Under UV irradiation, however, little energy above that needed to produce ionization is available to separate the ions very far (through their kinetic energy).

Hence, aerosols formed by UV irradiation can take half an hour or so before becoming visible. The condensation nuclei that eventually form clouds will, in this case, consist of large (water-separated) *ion pairs* so that their local electric fields will have been far smaller than with the isolated ions. Condensation will inevitably be slower. It seems very unfortunate that it has taken so long to learn a little more than Wilson had demonstrated. It seems we might, by now, have had a much better understanding of the physical and chemical processes that occur in clouds if Wilson's early findings had been followed up by more than a single chemist (Vincent, 1904) or if his experiments had been *conducted a decade or so later*, by which time the importance of Gibbs' work on thermodynamics might have been applied to the problem.

Some Quantitative Considerations.

Our findings, on their own, imply that the only requirement for forming clouds in moist air is that very high energy UV (so-called UVC) radiation be present. However, Wilson's results show that very energetic UV is *not* necessary. It is clear (from W2) that a range of lower energy spectral lines can *sometimes* achieve the same crucial result: the production of metastable nitrous acid that is later oxidized to nitric acid. The differences in the two studies should not be too surprising since many plausible intermediates in the oxidation of nitrogen exist, and they possess a very wide range of lifetimes.

As we have seen, we possess far too little information to discuss possible reaction mechanisms, but we can consider any *thermodynamic* constraint that it is possible to apply. In this context, it is particularly informative to consider the energetics of Reaction 3:

$$\gamma + N_2 + O_3 \rightarrow NO^+ + NO_2^- \qquad (3)$$

because ozone is easily produced by low-energy UV, and it is known to have a long lifetime in the air. Here, ã formally represents a mole of photons. All the other species are considered to be in the gas phase and in their standard states. The reaction products are the lowest energy ions known that can be formed from the main components of completely dry air (Turner, 1994). The reaction can be taken to describe, symbolically, the uptake of a single photon per molecule of nitrogen *as if* the photon is in equilibrium with species in the air. The process is a purely symbolic one for several reasons, among them that the photon is traveling at the speed of light, and so can hardly be at equilibrium. However, the *enthalpy* needed to *permit* Reaction 3 to proceed can be very relevant because, in general, energy differences are always important and because both gas phase ions produced in Reaction 3 happen to be well characterized thermodynamically.

While the problems introduced by electrostriction in moist air are expected to be very serious *for the free energies of formation of hydrated ions* at equilibrium (Turner, 2023), there is no known reason to expect that *standard enthalpies* of formation of the *dry ions* (those formed ini-

tially), will behave in any way anomalously. Thus, the enthalpy values for the formation of the molecules and ions involved in Reaction 3 all have well-defined meanings. These values are 0 + 142.674, + 990.185 and -202.715 respectively for N_2, O_3, NO^+, and NO_2^- according to the JANAF tables (Chase et al. 1985). The appropriate sum is 644.80 kJ.mol $^{-1}$ for the photon energy needed to allow the reaction to proceed.

When converted to a wavelength, this energy is 185.5 nm, which is remarkably close to the wavelength of the 184.9 nm line of mercury. In all probability, the uncertainties in the enthalpies of formation as well as the fact that only standard state partial pressures are available, mean that Reaction 3 might equally well have predicted that the reaction was supplied with *just too little* energy rather than just too much - as happens to be the case. Nevertheless, in view of the huge spread of the input enthalpies in the sum, it is extremely difficult to believe that the close similarity in the two wavelengths is a coincidence. In having provided photons of that specific energy, we seem to have been extremely fortunate that our mercury lamp was accidentally switched on and that it rapidly produced a mist.

Clearly, a single mole of photons formally allows Reaction 3 to proceed. However, another mole of photons must also have been involved in allowing O_2 to be split and then to form O_3. On the basis of the available thermodynamic data, it is clear that most other reactions that can produce ions using photons equivalent in energy to a wavelength above 185.5nm would require a minimum of three photons to produce ions. This can explain why, despite the far lower power needed to run the mercury lamp and the low intrinsic power of the 185.5nm line compared with that at 253.6 nm, the mercury lamp still produced clouds considerably more rapidly than Wilson's arcs.

The ions produced in Reaction 3 are believed to be of crucial importance to the stability of ball lightning because they are the *most stable ions* known to form from the main components of an air plasma (Turner, 1994). This conclusion was reached mainly as a consequence of a 1969 spectroscopic study by Powell and Finkelstein (1969). They had exposed a variety of mixtures of nitrogen and oxygen to brief but powerful radio-frequency discharges. They thereby obtained spectra from the mobile plasma blobs they obtained. Their spectra covered wavelengths between 300 to 600 nm, and the radiant power emitted was up to 160 W (for oxygen). Their not very spherical plasmas had temperatures close to 2,500^0 C, and radiation was emitted over a wide range of frequencies for periods of up to one second.

The authors took their plasmas to be incipient lightning balls - and so did one of us when their findings were used in the thermodynamic assessment referred to above (Turner, 1994). The following chemical species were among those considered by Powell and Finkelstein (1969) in attempting to interpret their spectra: N_2^*, O_2^* (where * indicates a long-lived excited state), NO, NO_2, O, H, OH, N_2^+, O^+, O_2^+, NO^+, O^-, O_2^-, NO^-, H_2O^-, H^- and OH^-. Once all the high-energy ions had reacted with other components of the mixture, only the most stable ones would be expected to remain. In order to assess the thermodynamic consequences of the most likely reactions (Turner, 1994), reactions involving the following chemical species were also considered: O_2, N_2, H_2O, H^+, NO_2^+, O_3, HNO_2, HNO_3, N_2O_3, N_2O_4, N_2O_5, NO_3, NO_2^-, and NO_3^-.

At a sufficiently high temperature, many of the above species might be expected to form - if only for very brief periods of time. However, in the time taken for an air plasma to cool near its surface, the gas laws tell us that millions of collisions will have taken place, and the highest energy species would all be expected to decompose to lower energy species. It is thus extremely unlikely that any of the species with the highest free energies of formation would survive at temperatures much below 500 K or so. In order to identify the most stable ions that could form from an air plasma, it is simple to eliminate all the least stable species from the list above. For the remaining ions, however, it is necessary to consider the actual energies released during all such plausible processes as the following:

$$2\ O_2^+ + N_2 = 2\ NO^+ + O_2 \quad (4)$$

$$2\ H^+ + N_2 + 3/2\ O_2 = 2\ NO^+ + H_2O \quad (5)$$

$$2\ NO_2^+ = 2\ NO^+ + O_2 \quad (6)$$

$$O_2^- + NO_2 = NO_2^- + O_2 \quad (7)$$

$$OH^- + HNO_2 = NO_2^- + H_2O \quad (8)$$

The Gibbs free energy changes for all these reactions are strongly negative - in other words, favorable. The clear conclusion from all the possible reactions considered feasible is that the only ions left by the time an air plasma has cooled to room temperature are NO^+ and NO_2 (Turner, 1994). Of course, if the air is not pure, nothing at all can be concluded about the ions present because the thermodynamic properties of very few other gas-phase ions have ever been measured.

5 CONCLUSIONS.

The main long-neglected findings of Wilson in W2

have all been confirmed. However, the clouds he produced could not have been produced by radiation at 185 nm; the air would have stopped such radiation from reaching his cells. The fact that Wilson's UV took longer to produce condensation than ours is fully consistent with the fact that his source of UV would have required at least one more photon to oxidize nitrogen than ours. It also seems clear that the nitrous acid, whose presence was confirmed by the test paper results of Plate 1, must have been produced by a somewhat *different chemical mechanism* from that which produced Wilson's clouds. Only the *thermodynamic facts* will have been common to the two sets of experiments.

The new experiments support the claim (Turner, 1994) that gas phase transformations of metastable (fully ionized) nitrous acid to the stable (molecular) form of the acid are endothermic processes which refrigerate the surfaces of lightning balls. In principle, the formation of the two acids can occur anywhere in the atmosphere where UV radiation of sufficient energy is to be found and where the relative humidity and other local physical and chemical conditions happen to be *appropriate*.

Unfortunately, we still have little idea what "appropriate" actually means in the above context – either in the presence or absence of a visible air plasma. The rarity of air plasmas could easily result from the fact that we are totally ignorant of the role of common impurities in the air that can drastically alter the crucial ratio of nitrous to nitric acids produced in any specific location. To establish a stable air plasma surface, low levels of radioactive species, or species deposited by cosmic rays, might also need to be present at an early stage in the ignition of an air plasma. It is even possible that traces of a volatile mercury compound might prove to be essential at some stage of air plasma ignition.

Although the results obtained here tell us little regarding these problems, they confirm the general nature of the electrochemical processes that can, on rare occasions, provide structural stability to ball lightning (Turner, 1994) and it may now be somewhat easier to understand why ball lightning and other naturally contained air plasmas are so rare. This problem probably needs to be understood much better if useable contained air plasmas are ever to be created artificially and used for electricity production.

There is little doubt that both nitrous and nitric acids can be formed at specific locations in the air if enough of the conditions are appropriate. Almost the only parameters that are thought to be crucial in these oxidation reactions are the local relative humidity and humidity gradient very close to any plasma ball.

However, we do not even know what the optimum values actually are before a plasma ball becomes stable. Worse, the required humidity might need to change as a function of time during the stabilization of a plasma surface and so could the rate of nitrogen oxidation. In addition, we have almost no idea what are the roles of air contaminants. Far more detailed experimental studies than those described here are clearly needed.

APPENDIX: WILSON'S RATIONALIZATION OF ONE OF HIS FINDINGS.

In Wilson's paper W2, UV-induced condensation in a variety of moist gases was studied. He originally suspected that when clean air was used, the production of nitric acid was responsible for the condensation that was produced between expansion ratios of 1.25 and 1.38. This assumption seemed reasonable since nitric acid was the only strongly ionized compound known at the time that might have been formed by the UV irradiation of moist air. However, the experiments performed in moist oxygen showed that almost exactly the same expansion ratios were needed for condensation in this gas as those needed in the air. For this reason, Wilson discounted his original idea and concluded that hydrogen peroxide was probably the chemical agent responsible for the condensation.

Apart from the subsequent finding of Vincent (1904), that hydrogen peroxide was not detectable in simulations of Wilson's experiments, there are two reasons for doubting a role for this compound in modifying the vapor pressure of water. One is that its structure is so similar to that of water that any effect it has on the equilibrium vapor pressure of water at an aerosol surface, is likely to be extremely small.

Another is the fact that only a very small number of ions need be present to act as condensation nuclei, so traces of nitrogen in the "pure oxygen" used might have been quite sufficient to allow condensation.

However, the main reason for discounting the hydrogen peroxide explanation probably comes from more recent experiments on the material from which Wilson's "pure oxygen" was made. There is now evidence that the method he used for oxygen preparation might *never produce a gas completely free of ions*. This method involved heating potassium permanganate until much of it has been converted to manganese dioxide. This is still a recommended procedure for preparing very pure oxygen. However, the extremely low levels of ions needed to produce a fog are likely to be far too small ever to be detectable chemically.

Wilson could not possibly have known that the thermal decomposition of permanganate to form MnO_2 is not the simple reaction it was once assumed to be:

$$2\ KMnO_4\ (s) \rightarrow K_2MnO_4\ (s) + MnO_2\ (s) + O_2 \quad \text{(A1)}$$

If this were to be the relevant reaction, permanganate decomposition could not have produced any gas phase ions. However, Herbstein et al. (1971) have shown that the reaction is far more complicated than this. There still seems to be no agreement over exactly what the detailed mechanism is, but there is no doubt about the main fact: K_2MnO_4 , MnO_2, and O_2 are *not* the only products. Manganese can exist in five different oxidation states: 2,3,4,6, and 7 (e.g., Moeller, 1952), and few of its gas phase reactions have been studied in detail. As is the case with other metals in high oxidation states, the higher oxidation states of manganese could easily include volatile oxyacids that are easily ionized. During the thermal decomposition of $KMnO_4$, only a very small fraction of volatile oxyacids need to be present to be responsible for fog formation. For all these reasons, it seems that the main stabilizing component of the mists formed by the UV irradiation of moist air must have been nitric acid - just as Wilson had originally assumed.

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