

La química en la historia,
para la enseñanza.

The composition of air: Discovery of Argon

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Resumen

El desarrollo del conocimiento de la composición del aire pasó por cuatro etapas. En tiempos de los Griegos se le consideraba uno de los componentes fundamentales de la materia, junto con el agua, el fuego, y la tierra. Hacia fines del siglo dieciocho se pensaba que era uno de muchos principios primarios, porque no podía ser alterado o descompuesto por ningún método. Hacia fines del siglo XIX se suponía que el aire estaba compuesto de 21% en volumen de oxígeno y 79% en volumen de nitrógeno. En 1894 Rayleigh y Ramsay descubrieron la presencia de argón, un suceso que fue seguido casi inmediatamente por el descubrimiento del resto de los gases nobles.

Abstract

Development of the knowledge about the composition of air went through four stages. In time of the Greeks it was considered one of the fundamental constituents of matter, together with water, fire and earth. By the end of the eighteenth century it was thought to be one of many primary principles because it could not be altered or decomposed by any methods. By the end of the nineteenth century air was assumed to be composed of 21 percent volume oxygen and 79 per cent nitrogen. In 1894 Rayleigh and Ramsay discovered the presence of argon, an event which was almost immediately followed by the discovery of the other noble gases.

Empedocles of Acragas in Sicily (c.492-432 BCE) introduced the concept that there are four primordial elements of matter: earth, air, fire and water, which constitute the *rizomata* (roots) of all things, including all living creatures, by being mixed in different combinations and proportions. Each of the elements however, retained its own characteristics in the mixture, and each was eternal and unchanging. Although Empedocles did not base his hypothesis on any experimental evidence he showed

by trial that what we call atmospheric air was a body, was quite distinct from empty space on the one hand or from vapor or mist on the other. This he did by means of an experiment with the water clock (clepsydra) during which he showed that air could keep water out of a vessel, and that the water could only enter as the air escaped.

Empedocles ideas were taken to be definite by Plato and Aristotle and persisted throughout the middle Ages and into the Renaissance, profoundly affecting European thinking and culture until the beginning of modern science. At some times the number and nature of the primordial elements was reduced to three, the *tria prima*. Paracelsus (1493-1541), for example, thought that "it is well to have it thoroughly understood from the first that all things created by Nature consist of three principal elements, namely natural mercury, sulphur and salt in combination, so that in some substances they are volatile and in others fixed" (Paracelsus, 1894). As experimental evidence accumulated, chemists were slowly forced into accepting a much larger number of elements.

Robert Boyle (1627-1691) wrote (Boyle, 1692): "I conjecture that the atmospheric air consists of three different kinds of corpuscles; the first, those numberless particles which in the form of dry exhalations or vapours, ascend from the earth, water, minerals, animals, etc., in a word, whatever substances are elevated by the celestial or subterranean heat and thence diffused into the atmosphere. The second may be yet more subtle, and consists of those exceedingly minute atoms, the magnetic effluvia of the earth, with other innumerable particles sent out from the bodies of the celestial luminaries and causing, by their impulse, the idea of light on us. The third is its characteristic and essential property, I mean, permanently elastic parts."

John Mayow (1643-1679) showed that fire is supported not by air as a whole but by a more active and subtle part of it (Mayow, 1674). This part he called *spiritus igneo-aereus*, or sometimes *nitro-aereus*, for he identified it with one of the constituents of the acid portion of saltpeter (potassium nitrate), which he regarded as formed by the union of fixed alkali with a *spiritus acidus*. In combustion the particulae nitro-aereae, either pre-existent in the thing consumed or supplied by the air, combined with the

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material burnt, as he inferred from his observation that antimony, strongly heated with a burning glass, underwent an increase of weight, which could be attributed to nothing else, but these particles. He named the portion left behind after combustion *me-phitic air* (carbon dioxide) or air injurious to life and incapable of supporting combustion (Ramsay, 1896a).

Stephen Hales (1677-1761) noticed that vegetables and other materials (plums, cherries, peas, hog's blood, tallow, etc.) released air when placed under vacuum: "A good quantity of air was producible from vegetables... into exhausted and unexhausted receivers..." After much experimenting on the subject he wrote: "Whence it is reasonable to conclude that our atmosphere is a chaos, consisting not only of elastic, but also inelastic particles, which float in it, as well as sulphureous, saline, watery, and earthy particles" (Ramsay, 1896a).

According to Pierre-Jacques Macquer's (1718-1784) famous *Dictionnaire Chimique* (Macquer, 1766) air was a primary principle because it could not be altered or decomposed by any known methods. The primary integrant parts of air, although very small, were not as small as those of water or spirit of wine and oils, because the latter passed easily through the pores of substances such as paper and skin, through which air did not pass or passed with difficulty. According to Macquer, the experiments of Boyle and Hales proved that most vegetable and animal substances contained a prodigious quantity of air. Access to air was indispensable to maintain the combustion of bodies, but it was very difficult to find the true cause of this fact. The phenomenon of combustion seemed to prove that air materially coincided with the production of flame and was part of it. Macquer reasoned that a study of the phenomenon of combustion raised many interesting questions of difficult solution. Does the air which disappears during combustion form a new compound with the flammable principle of the new body; what is this compound and what becomes of it, or is the air only food of flame? If so, the air was not a simple body and what was then the nature of its principles and what became of them? A curious remark by Macquer was that some fixable air was inflammable and some was not.

Jean-Antoine Chaptal (1756-1832) in his chemistry book, *Éléments de Chimie* (Chaptal, 1790) wrote that air is a mixture of 72 parts of nitrogen and 28 of oxygen intimately mixed, which had not been found

separated or isolated. Each component was absolutely necessary for life. The composition of air varied according to the geographic location, although the one mentioned was the most common. The properties of vital air were modified by those of nitrogen; breathing pure vital air extinguished life and was as inappropriate as distilled water. Nature did not allow us to use these principles in their highest degree of perfection.

Another important step forward was taken by Joseph Black (1728-1799). He heated limestone (and magnesium carbonate) and found that it decomposed giving off a gas and leaving behind lime. The gas, which could be made to recombine with calcium oxide to form calcium carbonate again, was identical with Johannes Baptiste van Helmont's (1579-1644) *gas sylvestre*, but Black called it *fixed air* because it could be combined (fixed) in such a way as to form part of a solid substance. Black also showed that when calcium oxide was allowed to stand in air, it converted slowly to calcium carbonate, from where he deduced that there were small quantities of carbon dioxide in the atmosphere. Air was then a mixture of at least two distinct substances, ordinary air and carbon dioxide.

Black studied the properties of carbon dioxide and found that it would not support the burning of a candle. A candle lit in a closed container of ordinary air would burn but eventually would go out. Black asked one of his students, Daniel Rutherford (1749-1819), to study these phenomena in more detail. Rutherford kept a mouse in a confined quantity of air until it died, then he lit a candle in what was left until the flame extinguished. Phosphorus was now burned in the remaining gas until it would no longer burn. After the gas was passed through limewater or alkali to absorb the fixed air it was found that it did not support combustion, a mouse would not live in it and a candle would not burn. Rutherford and Black explained their findings in terms of the phlogiston theory. As mice breathed and as candles and phosphorus burned, phlogiston was given off and entered the air until the latter became saturated with it. That was why objects no longer burned in it. On this reasoning Rutherford called the gas he had isolated *phlogisticated air* (nitrogen) (Ramsay, 1896a).

Oxygen was discovered almost simultaneously by Carl Wilhelm Scheele (1742-1786) and Joseph Priestley (1733-1804); Priestley named it *dephlogisticated air* while Scheele called it *empyrean air*. Around

1771 Scheele discovered that manganese oxide, heated to incandescence, discharged a gas that he called *fire air*. He also obtained the gas by heating mercuric oxide, silver carbonate, magnesium nitrate, and potassium nitrate. He described the properties of oxygen and attributed them to phlogiston (Cassenbaum and Schuffle, 1975).

Priestley isolated oxygen by heating red oxide of mercury and also red lead. In his words: "There are, I believe, very few maxims in philosophy that have laid firmer hold upon the mind than that air, meaning atmospheric air, is a simple elementary substance, indestructible and unalterable, at least as much so as water is supposed to be... I was, however, soon satisfied that atmospheric air is not an unalterable thing; for that, according to my first hypothesis, the phlogiston with which it becomes loaded from bodies burning in it, and the animals breathing it, and various other chemical processes, so far alters and depraves it as to render it altogether unfit for inflammation, respiration, and other purposes to which it is subservient; and I had discovered that agitation in the water, the process of vegetation, and probably other natural processes, restore it to its original purity... a candle burned in this air with a remarkably vigorous flame, very much like that enlarged flame with which a candle burns in nitrous oxide, exposed to iron or liver of sulphur; ...I was utterly at a loss to account for it" (Priestley, 1790; 1794). Not only did flames burned strongly in this gas, but a mouse placed in a sealed container of this gas lived for a longer period of time than a mouse placed in a sealed container of ordinary air.

Priestley also used the phlogiston theory to explain his results. Since objects burned so easily in this gas, they must be capable of giving off phlogiston with unusual ease. Priestley therefore called his new gas *dephlogisticated air*.

In 1778 Antoine Lavoisier (1743-1794) conducted many experiments with dephlogisticated air and theorized that it made some substances acidic. He renamed the gas *oxygen* because one of the most general properties of this base was to form acids "...The union of this base with caloric we term oxygen gas, which is the same with what was formerly called pure or vital air" (Lavoisier, 1789). Lavoisier's respiration experiments invalidated the phlogiston theory despite the strong opposition from Priestley and Scheele.

In 1784 and 1785 Henry Cavendish (1731-1810) published two extensive memoirs reporting his ex-

periments on air (Cavendish, 1784; 1785), which may be considered the earliest clear evidence that air contains more gases than oxygen and nitrogen. The purpose of these memoirs was "to find out the cause of the diminution which common air is well known to suffer by all various ways in which it is phlogisticated and to discover what becomes of the air thus lost or condensed." According to Cavendish all animal and vegetable substances contained fixed air and released it by burning, distillation, or putrefaction. Common air did contain a little fixed air, which was not an essential part of it and could be easily separated by lime water. Fixed air was not produced by the explosion of the inflammable air obtained from metals, with either common or dephlogisticated air and it was not produced by the burning of sulphur or phosphorus.

Cavendish reached the important conclusion (Cavendish, 1784) that when a mixture of inflammable (hydrogen) and common air was sparked in the proper proportion, almost all the inflammable air and near one fifth of the common air lost their elasticity and were condensed into pure water. Hence dephlogisticated air was in reality nothing but dephlogisticated water, or water deprived of its phlogiston, or, in other words, water consisted of dephlogisticated air united to phlogiston, and inflammable air was either pure phlogiston, or water united to phlogiston. Cavendish closed the first paper with the comment that Lavoisier had read several papers to the Académie des Sciences in which he totally discarded the phlogiston theory and explained the phenomena previously attributed to this factor as actually taking place by the absorption or expulsion of dephlogisticated air, and that dephlogisticated air was the acidifying principle. Water would then consist of inflammable air united to dephlogisticated air.

Cavendish also made a series of experiments using limewater (Cavendish, 1784) by which demonstrated conclusively that carbon dioxide was not produced when air was sparked. He also showed that sparking either pure oxygen or pure nitrogen produced no diminution in volume, but a contraction always occurred when a mixture of the two gases was sparked. In the latter case his experiments yielded an unexpected result: "When the electric spark was made to pass through common air, included between short columns of a solution of litmus, the solution acquired a red color, and the air as diminished, conformably to what was observed by Dr Priestley. When lime water was used instead...we

can conclude that (it) was saturated by some acid formed during the operation...We may safely conclude, that in the present experiments the phlogisticated air was enabled...to unite to, or form a chemical composition with the dephlogisticated air, and was thus reduced to nitrous acid...".

According to Cavendish (1784) "when five parts of pure dephlogisticated air were mixed with three parts of common air almost the whole of the air was made to disappear" when sparked over sope-lees. This conclusion is of interest and significant because Cavendish was stating definitely that he regarded the atmosphere as consisting of a mixture of nitrogen and oxygen: "It must be considered that common air consists of one part of dephlogisticated air, mixed with four of phlogisticated, so that a mixture of five parts of pure dephlogisticated air, and three of common air, is the same thing as a mixture of seven parts of dephlogisticated air with three of phlogisticated".

In the second paper (Cavendish, 1785) Cavendish made another observation of great importance, which although he did not pursue it further is important to quote it in detail: "...we scarcely know more of the nature of the phlogisticated (nitrogen) part of our atmosphere, than that it is not diminished by lime water, caustic alkalis, or nitrous air, that it is unfit to support fire, or maintain life in animals, and that its specific gravity is not much less than that of common air...it is reasonable to suppose that part at least of the phlogisticated air of the atmosphere consists of this air united to phlogiston, yet it might fairly be doubted whether the whole is not of this kind or whether there are not in reality many different substances confounded together under the name of phlogisticated air (here Cavendish is guessing that the inert part of air is more than nitrogen alone). I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated atmosphere could be reduced to nitrous acid, or whether there was not a part of different nature from the rest, which would refuse to change...For this purpose I diminished a similar mixture of dephlogisticated and common air in the same manner as before...then in order to decompose as much as I could of the dephlogisticated air which remained in the tube, added some dephlogisticated air to it, and continued the spark until no further diminution took place...I let up some solution of liver of sulphur (formed by fusing sulphur with carbonates of the alkalis and consisting essentially of alkaline sulphides. Also called *hepar sulphuris*) to absorb the

dephlogisticated air, after which only a small bubble of air remained unabsorbed, which certainly was not more than 1/120 of the bulk of the phlogisticated air...so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude, that it is no more than 1/120 part of the whole."

The observant reader will note immediately that Cavendish's observations not only point out to the presence of the noble gases in air but also that their volumetric composition ($1/120 = 0.803\%$) is not very different from the one accepted today, 0.935 volume per cent.

As will be seen below, Cavendish's finding remained completely ignored for almost one century, until John William Strutt (Lord Rayleigh, 1842-1919) recognized its significance in connection with some puzzling results he had obtained when determining the density of nitrogen.

In 1804 Joseph-Louis Gay-Lussac (1778-1850) and Alexander von Humboldt (1769-1859) used Alessandro Volta's (1745-1827) eudiometric explosion procedure with measured volumes of hydrogen and obtained values for atmospheric oxygen and nitrogen more precise than those attainable by Cavendish's method (Gay-Lussac and Humboldt, 1805). Gay-Lussac and Humboldt argued that the relative volumes of hydrogen and oxygen, which combined to form water, were independent of the water vapor present. Greater precision was therefore possible if one dealt with volumes rather than weights. In 1846 Robert Wilhelm Bunsen (1811-1899) performed many experiments on the composition of air and other gas mixtures and concluded that atmospheric oxygen varied between 20.840 and 20.970 parts per hundred of air per volume (Bunsen, 1857).

By the 1890's it was generally accepted that the relative proportions of oxygen to nitrogen in air at sea level were almost constant, about 79 volumes of nitrogen to 21 volumes of oxygen, with small and variable amounts of carbon dioxide and water vapor, and trace amounts of substances like ammonia, hydrogen dioxide, and ozone (Hiebert, 1963). The best summary of the state of the art was given by Victor Regnault (1810-1878) in his book on chemistry (Regnault, 1850): "Air is essentially a mixture of oxygen and nitrogen in the same proportion in every point of the earth...It contains very small amounts of CO_2 , water vapor, and other gases or vapors released by the decomposition of organic matter." Regnault

gives a very detailed description of the analytical methods for sampling and analyzing air and makes the interesting comment that the invariability of the composition of air had led some chemists to believe that air was not a mixture of oxygen and nitrogen but a true combination of these gases. According to Regnault the easiest way to disprove this assumption was fact that the air dissolved in water had a different composition than atmospheric air.

In 1815-1816 William Prout (1785-1850) published two papers (Prout, 1815; 1816) in which he advanced the theory that the relative atomic weights of the elements are an exact and integral multiple of that of hydrogen and that elements are formed by a condensation or grouping of hydrogen atoms. Published anonymously at first, Prout quickly identified himself as the author when he found that his ideas had been accepted by Thomas Thomson (1773-1852), founder of the *Annals of Philosophy*. The papers dealt with the calculation of the specific gravities (relative densities) of the elements from the published data of other chemists. Prout derived an excellent value for hydrogen, which owing to its light weight had been very difficult to determine accurately by experiment. Prout's hypothesis, as it became known, stimulated discussion and improvement of analytical methods and forced interest in the determination of accurate atomic weights and, thereby, in the atomic theory and in the search for a system of classification of the elements.

In 1882, Rayleigh, in his presidential address (Rayleigh, 1882) to the Mathematical and Physical section of the British Association for the Advancement of Science discussed the two prevalent scientific approaches, one of experiments to resolve questions which appear still to be open, and the other to base decisions as far as possible upon deductions from experiments made by others. As an example he referred to Prout's law saying that some chemists disapproved strongly the importation of a priori views in to consideration of the question of atomic weights and maintained that the only numbers worthy of recognition were the immediate results of experiments. Others, on the contrary, believed that the close approximations to simple numbers could not be fortuitous and considered that the experimental evidence against the simple numbers more than outweighed the argument in favor of simplicity. Rayleigh believed that the time had come to re-determine the densities of the principal gases, "an undertaking for which he had made some preparations".

The appearance of a paper (Cooke and Richard, 1887) by Josiah Parsons Cooke (1827-1894) and Theodore William Richard (1868-1928; 1914 Nobel Prize in Chemistry) on the atomic weights of hydrogen and oxygen prompted Rayleigh to communicate the results he had obtained so far with respect to the relative densities of these gases (Rayleigh, 1888). Cooke and Richards's work was the first to bring direct evidence that the ratio between these atomic weights is less than 16 to 1. After two years of work with hydrogen of great purity prepared by several methods, they concluded that the atomic weight of hydrogen must be not far from 1.008 if oxygen is taken as 16.000. Rayleigh wrote: "The appearance of Professor's Cooke important memoir upon the atomic weights of hydrogen and oxygen induces me to communicate...the results that I have obtained with respect to the *relative* densities of these gases...to examine whether the relative atomic weights of the two bodies deviated from the simple ratio 16:1... "Rayleigh used Regnault's method for weighting gases because it made the results independent of atmospheric conditions and only small weights were required. The final result gave a ratio of 15.884 for the densities. Using the best available value of the ratio of atomic volumes, 1.9965, Rayleigh calculated that the ratio of the atomic weights is 15.912 (Rayleigh, 1888).

Rayleigh continued his work by modifying the preparation procedure of the gases. Hydrogen was now generated from potash in place of acid or liberated from aluminum. Purification of the gas by absorption in palladium did not improve the results; the density of the resulting gas did not change (Rayleigh, 1892a). Additional experiments were performed based on an independent determination of the relative weights by actual combustion of weighed quantities of the two gases. The final result was a ratio of the atomic weights of 15.926 (Rayleigh, 1889).

In 1892, after many experiments, Rayleigh achieved a result of 15.880, a value that he felt too low because of the presence of mercury vapor in his hydrogen (Rayleigh, 1892a). He believed that the only source of error that could bias the final result was impurity in the gases, especially in the hydrogen. He simplified the chemical procedures and used materials in such a form that the elimination of impurities went forward in the normal schedule of the process. The final results gave the ratio 15.88 for the atomic weights (Rayleigh, 1889; 1892a).

To shed a light upon this discrepancy, Rayleigh

published a letter in *Nature* (Rayleigh, 1892b) inviting criticism from “chemical readers” who might be interested in such questions. It is interesting to quote the main parts of this letter because it expresses an unusual frankness in a scientist unable to answer a question: “I am much puzzled by some recent results as to the density of nitrogen, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to two methods of preparation I obtain quite distinct values. The relative difference, amounting to about 1/1000 part, is small in itself, but it lies entirely outside the errors of experiment and can only be attributed to a variation in the character of the gas. In the first method the oxygen of atmospheric air is removed in the ordinary way by metallic copper...reduced by hydrogen from the oxide. The air, freed from CO₂ by potash, gives up its oxygen to copper heated in hard glass over a large Bunsen, and *then* passes over...red-hot copper in a furnace...The gas then passes through...sulphuric acid, then e again over...*copper oxide*, and finally over sulphuric acid, potash and phosphoric anhydride. In the second method of preparation, suggested to me by Prof. Ramsay, everything remained unchanged, except that the *first* tube of hot copper was replaced by a wash-bottle containing liquid ammonia, through which air was allowed to bubble. The ammonia method is very convenient, but the nitrogen obtained by means of it was 1/1000 part lighter than the nitrogen of the first method. The question is, to what is the discrepancy due?”

“The first nitrogen would be too heavy, if it contained residual oxygen. But on this hypothesis, something like 1 per cent would be required. I could detect none whatever by means of alkaline pyrogallate...On the other hand, can the ammonia-made nitrogen be too light from the presence of impurity? There are not many gases lighter than nitrogen, and the absence of hydrogen, ammonia, and water seems to be fully secured...it seemed the more probable supposition that the impurity was hydrogen, which in this degree of dilution escaped the action of the copper oxide. But a special experiment seems to preclude this explanation. Into nitrogen prepared by the first method, but before its passage into the furnace tubes, one or two thousandths by volumes of hydrogen were introduced...(by bubbling) the gas...through a small hydrogen generator...But the introduction of hydrogen had not the smallest effect upon the density, showing that the copper oxide was capable of performing the part desired of it.”

Rayleigh asked his fellow chemists: “Is it possible that the difference is independent of impurity, the nitrogen itself being to some extent in a different (dissociated) state?” Several readers wrote to Rayleigh privately and expressed their thoughts that they were inclined to think that the explanation was to be sought in a partial dissociation of nitrogen derived from ammonia.

Under the assumption that a similar gas should be obtained by physical and chemical methods, Rayleigh suggested four possible explanations: (a) atmospheric nitrogen was too heavy on account of imperfect removal of oxygen; (b) the ammonia nitrogen was too light because it was contaminated with gases lighter than pure nitrogen, for example, hydrogen; (c) part of the atmospheric nitrogen might have combined to form N₃ molecules analogous to ozone, and (d) some of the molecules in the nitrogen might have decomposed and thus decreased the density of the gas (Rayleigh, 1893; 1894; Weeks, 1956).

The first hypothesis was highly improbable for because of the very slight difference in the densities of oxygen and nitrogen, the contamination would have to be very large to account for the discrepancy of five parts in a thousand; as much as 1/30th part of oxygen would be necessary to raise the density by 1/200. Rayleigh showed experimentally that the nitrogen prepared from ammonia was entirely free from hydrogen (the experimental setup included passage through hot copper oxide). The third hypothesis was not encouraging for he was unable to increase the density of nitrogen by passing a silent discharge through it (Rayleigh, 1894; Weeks, 1956).

In order to exaggerate the discrepancy Rayleigh substituted pure oxygen for atmospheric air so that the whole, instead of only about one-seventh part of the nitrogen would come from the ammonia. The disagreement was at once magnified five times: The nitrogen obtained from ammonia proved to be about one-half per cent lighter than nitrogen obtained in the ordinary way from the atmosphere (Rayleigh, 1894; Hiebert, 1963). Rayleigh wrote: “Although the subject is not yet ripe for discussion...nitrogen prepared from ammonia, and expected to be pure, turned out decidedly lighter than the above. When the oxygen is burned by excess ammonia, the deficiency is about 1/1000th part. When oxygen is substituted for air so that all of the nitrogen is derived from ammonia, the deficiency of weight may amount to 0.5 percent. It seems certain

that the abnormal lightness cannot be explained by contamination with hydrogen, or with ammonia, or with water, and everything suggests that the explanation is to be sought in a dissociated state of nitrogen itself. Until the questions arising out of these observations are thoroughly cleared up, the above number for nitrogen must be received with a certain reserve” (Rayleigh, 1893).

In a paper published later (Rayleigh, 1895) Rayleigh summarized the results obtained by different means:

<i>1. Atmospheric nitrogen</i>	<i>Grams</i>
By hot copper (1892)	2.3103
By hot iron (1893)	2.3100
By ferrous hydrate (1894)	2.3102
<i>Mean</i>	2.3102
<i>2. Chemical nitrogen</i>	
From nitric oxide	2.3001
From nitrous oxide	2.2990
From ammonium nitrite purified at red heat	2.2987
From urea	2.2985
From ammonium nitrite purified in the cold	2.2987
<i>Mean</i>	2.2990

The column on the right gives the weights of gas in grams contained under standard conditions in the same globe employed for every experiment: “Examination of the table shows that the difference in weight between using atmospheric nitrogen and chemical nitrogen amounts to about 11 milligrams, or about one-half per cent; and proved conclusively that the nitrogen obtained from chemical sources was different from the nitrogen obtained from the air kinds of nitrogen in weight, and therefore, of course, in quality, for some reason up till now unknown” (Rayleigh, 1895). In addition, the results indicated that the weight per liter under standard conditions is 1.2511 for chemical nitrogen and 1.2572 for atmospheric nitrogen.

At the suggestion of Thomas Edward Thorpe (1845-1925), experiments were subsequently tried with nitrogen liberated from urea by the action of sodium hypobromite, together with CO₂ and H₂O. The additional component, carbon dioxide, was not

a problem because it would be absorbed by the large excess of alkali employed. Hence, the procedure suggested by Thorpe would have the advantage that the gas would require no further purification than drying. If it proved right, it would at any rate be free from suspicion of containing hydrogen. The results gave 2.2985 mg...” (Rayleigh, 1895).

According to Rayleigh, the experimental results definitely showed that nitrogen prepared from chemical means was lighter by about 1/1000 part than that derived from atmospheric air (Rayleigh, 1894).

The problems for accepting the presence of an unknown gas were also substantial. What is the nature of the lighter gas that contaminates nitrogen? “Of the possible impurities, lighter than nitrogen, those demanding consideration are hydrogen, ammonia, and water vapor. The last one may be dismissed at once and the absence of ammonia is almost equally certain. The question of hydrogen appears the most important. But this gas, and hydrocarbons such as CH₄, could they be present, should be burned by the copper oxide, and the experiments always referred to, in which hydrogen was purposely introduced into atmospheric nitrogen, prove conclusively that the burning would really take place” (Rayleigh, 1894).

The discovery of argon

William Ramsay (1852-1916; 1904 Nobel Prize in Chemistry), who had been closely following Rayleigh’s publications, asked from Rayleigh and received his permission, to undertake some experiments designed to explain the possible anomalous behavior of atmospheric nitrogen. Ramsay was interested in the subject because years before he had tried to combine hydrogen and nitrogen directly by passing them over heated metals. Elements such as boron, silicon, titanium, lithium, strontium and barium, magnesium, aluminium, manganese, and mercury, were known to combine directly with nitrogen. Hydrogen in the presence of acid and oxygen in the presence of alkali also reacted with nitrogen under the influence of electric discharge. In addition, a mixture of barium carbonate and carbon at high temperature was also known to be effective. The nitrides of boron, silicon, titanium, and aluminium had been prepared by heating the metal to whiteness; lithium nitride by heating the metal to dull red heat, and magnesium nitride by igniting the metal in a current of nitrogen. Nitrogen scarcely reacted with

mercury and the resulting compound was explosive. Ramsay's many experiments had shown that magnesium in the form of turnings was the best: when nitrogen was passed over magnesium heated in a tube of hard glass to bright redness combustion with incandescence began at the end of the tube and proceeded regularly until all the metal had been converted into nitride (Rayleigh and Ramsay, 1895a).

As a result, Ramsay thought that the way to solve the problem was to absorb carefully purified nitrogen in order to discover whether any portion of it was different from the rest (Tilden, 1918, Travers, 1956). After recycling the nitrogen several times and passing it over soda lime, phosphorus pentoxide, magnesium at red heat, copper oxide, and soda lime, he found that the residual gas was about 15/14 as heavy as the original nitrogen. Prolonged treatment left only 1/80 of the original volume, with a density of 19.086. The experimental evidence made it clear that the nitrogen thus treated increased progressively in density. Ramsay felt "that the result was encouraging and led to the probability of the nitrogen being altered in some way, or the presence of some new component in the atmosphere" (Tilden, 1918; Hiebert, 1963). Examination of the spectrum of the gas revealed "the bands of nitrogen... somewhat hazy bands, red, orange, yellow, and yellow green in color... and showed certain groups of red and green lines which did not appear to belong to the spectrum of any known gas" (Rayleigh and Ramsay, 1895a). William Crookes (1832-1919), a well-known spectroscopist, made a thorough study of the spectrum and observed nearly 200 lines (Crookes, 1895; Weeks, 1956).

A portion of the gas was then mixed with oxygen and submitted to a rapid discharge of sparks for four hours in the presence of caustic potash; the resulting contraction amounted to 15.4 per cent of the original volume. The question then aroused, if the gas contains 15.4 of nitrogen of density 14.014 and 84.6 per cent of other gas and if the density of the mixture were 19.086, what would be the density of the other gas? Calculation led to the number 20.0 (Rayleigh and Ramsay, 1895b).

Rayleigh consulted with James Dewar (1842-1923), who had done much work on the study of gases and their liquefaction, about what was known about atmospheric nitrogen being a pure gas. Dewar's answer was that to the best of his knowledge nothing had been done or found unusual, except for

Cavendish's findings. Rayleigh looked into Cavendish's original papers and was surprised to find that "Cavendish had himself put this question quite as sharply as he could put it" (Rayleigh, 1895).

The possibility of a new substance was a tantalizing question. Rayleigh thought that "regarding it as established that one of other of the gases must be a mixture, containing as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. It was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture and CO₂ had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, 0.5 per cent only by volume would be needed; or if the density were half as much again as that of nitrogen, then 1 per cent would suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected" (Rayleigh and Ramsay, 1895a).

On May 24, 1894, Ramsay wrote to Rayleigh (Travers, 1956): "Has it occurred to you that there is room for gaseous elements at the end of the first column of the periodic table? Thus: Li, Be, C, C, N, O, F, X, X, X ...etc. Such elements should have a density 20 or whereabouts, and 0.8 per cent (1/120th about) of the nitrogen of the air could raise so the density of nitrogen that it would stand to pure nitrogen in the ratio 230:231" (Tilden, 1918). In a following letter (August 4) Ramsay reported to Rayleigh that he had isolated the gas. Its density was 19.075 and it was not absorbed by magnesium.

In Rayleigh's reply he told Ramsay that he had concentrated X by diffusion. The air so prepared contained twice as much X as ordinary air. He suggested Ramsay to publish a joint paper (Hiebert, 1963).

On August 13, 1894, at the Oxford meeting of the British Association, Rayleigh made a brief announcement that he and Ramsay had found atmospheric nitrogen, carefully purified from every other known constituent of air, to be contaminated to the extent of 1 per cent with another gas even more inert

than nitrogen. The protocols of the meeting said succinctly “a joint meeting with Section A was held, in which Lord Rayleigh Sec. R.S. and Prof. W. Ramsay, F. R. S., gave a preliminary account of a New Gaseous Constituent of Air” (Rayleigh, 1882; Anonymous, 1894b). This discovery was also communicated to the French Académie des Sciences through Marcelin Berthelot (1827-1907) (Berthelot, 1895ab).

As reported in *Nature* (Anonymous, 1894a) “On Monday a large audience assembled to hear the announcement by Lord Rayleigh and Prof. Ramsay of the existence of a new gas in the atmosphere...Prof. Reynolds noted the place which the new substance, if proved to be an element, would occupy in Mendeléeffs table among the platinum metals. Prof. Roberts-Austen suggested that this gas might be the one which is frequently found as a residue among the gases extracted from steel...an observation (was) made by Prof. Dewar that while a mixture of pure liquefied oxygen and nitrogen forms a clear liquid, air in a similar state shows a turbidity (and that) the substance causing turbidity does not amount to one percent of the whole liquid” (Dewar, 1894). Dewar asked “can this substance be Rayleigh’s new nitrogen in the solid form? ...One is forced to the conclusion that the new nitrogen is a strange substance, being as volatile as nitrogen or oxygen...a small portion of the gas is condensed molecularly into an allotropic form, having 1.5 times its normal density...It is known that electrical stimulation of nitrogen produces two distinct spectra presumably due to different molecular conditions...the new substance is being manufactured by the respective experimenters and not separated, as they imagine, from ordinary air.” Dewar concluded: “It is not the first time that chemists and physicists have been tempted to believe in the production of an allotropic form of nitrogen, and to accept it as explaining certain curious phenomena, but hitherto the assumption has always broken down on more careful investigation. This time we may be permitted to hope that the elusive allotropic form has been fairly captured”.

The name argon and the symbol *A* was assigned provisionally to the new element, from $\alpha\rho\lambda\sigma\upsilon$ (work; plus α meaning not). Henry George Madan (1838-), the chairman of the meeting, proposed calling the new element *argon*, the lazy one.

Rayleigh and Ramsay published several extensive papers giving full details of their experiments and equipment and a lengthy discussion of the de-

vices used to separate argon on a large scale by means of magnesium (Ramsay, 1896a; Rayleigh and Ramsay, 1895ab; Ramsay, 1896b; Ramsay, 1898; Ramsay and Travers, 1898). In their attempts to isolate the gas by Cavendish’s method, Rayleigh and Ramsay utilized a Ruhmkorff coil of medium size actuated by a battery of five Grove cells, achieving a rate of absorption of 30 cm³ per hour, or 30 times as fast as Cavendish could work with the manual electrical of this time (Hierbert, 1963; Rayleigh and Ramsay, 1895b).

Additional proof of the presence of argon in air was done by diffusion. The resulting air was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen, and proved to be much denser than unprepared air (Rayleigh and Ramsay, 1895b).

Experiments done by Ramsay and Alexander Kellas (Kellas, 1895) showed that air contains about 0.923 per cent of argon or, 10,000 parts of air contain about 92 of argon (Ramsay, 1896ab)

Rayleigh and Ramsay used a very clever technique to demonstrate that argon is a monatomic substance. From the kinetic theory it is known that the internal energy of a compound is the resultant of the kinetic, rotational, vibrational, and electronic contributions. In the case of a monatomic substance, if the temperature is not very high (below that level at which electronic effects such as light will be induced) then the internal energy is due only to the translational movement of the molecules. For this situation it can be proven that, the ratio of the specific heats c_p/c_v , is equal to 5/3, that is, about 1.67. For polyatomic molecules, both specific heats increase with temperature, but their ratio decreases substantially, for example, for air it is about 1.40.

Rayleigh and Ramsay determined the value of for argon by measuring the velocity of sound in it and using the relation

$$n\lambda = \sqrt{\left[\frac{e}{d} (1 + \alpha t) \frac{C_p}{C_v} \right]}$$

where n is the frequency, λ the wave length of sound, v its velocity, e the isothermal elasticity, d the density, and $(1 + \alpha t)$ the temperature correction. Two sets of different observations made with entirely different samples of gas gave 1.65 and 1.61 respectively as the ratio of the specific heats, indicating that argon is a monatomic gas and that all its energy is translational (Rayleigh and Ramsay, 1895a).

An addendum by Ramsay reported that the value of the gas constant R for argon had been carefully determined between -87° and 248°C and found to remain essentially constant, indicating that argon behaves as a perfect gas and shows no sign of association on cooling, or of dissociation on heating. The molecular weight of argon was determined, therefore, to be 39.8 (Rayleigh and Ramsay, 1895a).

Soon after the discovery of argon Paul Émile Lecoq de Boisbaudran (1838-1925; discoverer of the elements gallium, samarium, and dysprosium) published a short note predicting that it might belong to a family of absolutely inert elements all of which were then unknown, and that their atomic weights would be 20.0945 , 36.40 ± 0.08 , 84.01 ± 0.20 , and 132.71 ± 0.015 . He also predicted that the first two of these elements would be more abundant than the others. De Boisbaudran gave no details of his calculations or the basis of his system of classification (De Boisbaudran, 1895). Shortly thereafter, C. J. Reed published a letter in *Chemical News* (Reed, 1895) claiming that ten years before he had published a classification of the elements based solely on the numerical relations between valence and atomic weight. His classification predicted (a) a group having a total of 15 possible undiscovered elements, characterized by valences zero or eight and having atomic weights of 4, 20, 36, 52, 68, 84, 100, 116, 132, 148, 164, 1809, 196, 212, and 228; (b) that the only elements of this group which were likely to be found in nature were 4, 20, 36, 84, 132, and 1196; (c) that these elements should be highly volatile and monatomic; and (d) that elements 4, 20, and 36 should be non-metallic and relatively abundant in nature.

Spectrum of argon

The spectrum of argon was determined by Crookes, using gas prepared by means of magnesium. According to Rayleigh and Ramsay (Rayleigh and Ramsay, 1895b) the spectrum, as seen in a vacuum tube at about 3 mmHg pressure, consisted of a great number of lines (119 in total), distributed over almost the whole visible field. Two lines, having wave lengths 696.56 and 705.6 nm, respectively, were especially characteristic; they were less refrangible than the red lines of hydrogen or lithium and served well to identify the gas when examined in this way. Other lines were located as follows: (a) a bright yellow line, more refrangible than the sodium one, at 603.84 nm; (b) a group of five bright green lines occurred next, besides a number of lines of less intensity. Of this

group of five, the second, which was perhaps the most brilliant, had a wave length of 561.00 nm; (c) next there was a blue, or blue violet line of wave length 470.2 nm and (d) last, in the less easily visible part of the spectrum, there were five strong violet lines, of which the fourth, which was the most brilliant, had the wave length 420.0 nm. The red lines, which were not to be mistaken for those of any other substances, were visible only at atmospheric pressure when a powerful jar discharge was passed through argon.

Crookes found that when the current was passed from the induction coil in one direction, the end of the capillary tube next to the positive pole had a redder hue while the end next to the negative pole had a bluer hue; in other words, "it is not improbable that...the gas argon is not a simple body, but is a mixture of at least two elements, one which glows red and the other blue, each having its distinctive spectrum" (Crookes, 1895). Edward Charles Cyril Baly (1871-1948), who had earlier noticed a similar phenomenon (Baly, 1893), attributed it to the presence of two gases. Baly wrote: "When an electric current is passed through a mixture of gases, one is separated from the other and appears in the negative glow." The conclusion was that what Rayleigh and Ramsay had assumed to be pure argon, was in reality a mixture of two gases, which had yet not been separated (Rayleigh and Ramsay, 1895a).

Properties

Rayleigh and Ramsay determined the solubility in water of argon at 12°C and 13.9°C as 3.94 and 4.05 volumes per 100 volumes of water, respectively. These results indicated that argon was about 2.5 times more soluble in water than nitrogen and as soluble as oxygen, and that the gases dissolved in rain water should be richer in argon. Experiments confirmed this prediction (Rayleigh and Ramsay, 1895a).

Ramsay provided Karol Olszewski (1846-1915) with a 300 cm^3 sample of argon to study its behaviour at low temperatures and high pressures. Four series of experiments were carried out, two with the object of determining the critical temperature and pressure and the vapour pressure of the gas at several other low temperatures, while the two other series served to determine its boiling and freezing points under atmospheric pressure, and the density at its boiling point. For the first two experiments Olszewski used a Cailletet apparatus with liquid ethyl-

ene under vacuum as the cooling fluid. The critical pressure was found to be 50.6 atm but the critical temperature showed slight variations around -121°C , which Olszewski attributed to the presence of nitrogen.

The vapour pressure was measured between -128.6°C (38 atm) and -139.1°C (23.7 atm). The boiling point at 740.5 mmHg was found to be -86.9°C and the density of the liquid at under the same conditions was approximately 1.5. The density of the vapour was found to be 19.9. These results proved that the density of liquid argon at its boiling point is much higher than that of oxygen. The melting point was found to be -189.6°C , solid argon freezing to a white solid resembling ice. Olszewski remarked that the unexpected low critical temperature and boiling point of argon seemed to be related to its simple molecular constitution (Olszewski, 1885).

Chemical reactions

Rayleigh and Ramsay tried unsuccessfully to react argon by means of a very large number of chemical reactions. It refused to combine under the circumstances in which nitrogen, a very inert gas, does combine. Several reactions were tried under the influence of an electric discharge: oxygen in the presence of alkali; hydrogen in the presence of acid or alkali; and chlorine, dry or moist. Many others were tested under extreme temperature conditions: phosphorus at red heat, and sulphur at bright redness; tellurium, sodium, and potassium could be distilled in a current of the gas. Argon did not react by passing it over fused red hot caustic soda, soda lime heated to bright redness; fused and bright red hot potassium nitrate; red hot sodium peroxide, and the persulfides of sodium and calcium. No reaction took place with wet oxidizing and chlorinating agents such as nitrohydrochloric acid, bromine water, bromine, and alkali, and hydrochloric acid and potassium permanganate, and with mixtures of sodium and silica and of sodium and boric anhydride. Argon was not adsorbed by platinum black and platinum sponge. A very detailed description of the procedures employed was given (Rayleigh and Ramsay, 1895a).

Rayleigh and Ramsay concluded: "We do not claim to have exhausted the possible reagents. But this much is certain, that the gas deserves the name argon for it is a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very opposite character... It will be interesting to see if fluorine also is without action, but for the present that experi-

ment must be postponed, on account of difficulties of manipulation" (Rayleigh and Ramsay, 1895a).

Ramsay provided Berthelot with samples of the gas for spectral analysis and for testing for possible chemical reaction. Berthelot tried reacting argon with several compounds with the help of electric discharges because he believed the method to be more efficient than using electrical sparks since it assured the survival of unstable compounds. When a mixture of argon with benzene vapors was subjected to the action of a variable silent discharge, a weak violet luminosity developed, visible in the dark. A fluorescent substance was formed that developed a beautiful green light and a special spectrum. The resulting product was a yellow smelly resinous substance, which condensed on the walls of the glass vessel and decomposed upon heating producing volatile products and leaving a very abundant carbonaceous residue (Berthelot, 1895c). Ramsay thought that Berthelot's resin was more of the nature of a solution of argon than a compound. Since argon is very soluble in water, it was probably carried down by sparks and entangled in some way in Berthelot's gum (Ramsay, 1896a).

In a following work Berthelot reported additional data on possible reactions of argon (Berthelot, 1895ef). It was known that carbon disulphide reacts with nitrogen under the action of a silent discharge. This suggested the possibility of a similar reaction with argon. The experience was positive; it gave place to a more rapid and complete reaction than with benzene. The absorption did not seem to be limited; it was accompanied by fluorescence visible at full daylight and yielding spectral lines. The appearance of these lines of fluorescence at atmospheric pressure suggested the existence of a hydrocarbonic combination of argon, of the type of acetylene or better HCN, in the state of electric dissociation.

Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry) tried to react argon with fluorine. First, titanium was heated to the melting temperature of glass in an atmosphere of argon; no reaction was observed and the titanium did not change its aspect. The same results were obtained with boron, although under the same condition the latter combines with nitrogen to form boron nitride. Similar results were attained with lithium, although under the same conditions lithium forms with nitrogen lithium nitride. Direct action of fluorine on argon produced no reaction; there was also no change in temperature,

and no reaction took place under electrical sparking (Moissan, 1895).

In following publications (Berthelot, 1895dg) Berthelot remarked that the yellow green fluorescence and spectrum, observed while subjecting a mixture of argon and benzene to the action of a silent discharge at atmospheric pressure, reminded him of that of the aurora borealis. He expressed the opinion that the characteristic lines of aurora borealis could be attributed to a special form or combination of argon and other unknown elements that accompany it. Berthelot found that the spectrum of the fluorescence contained, in addition to the hydrogen and the D lines, several others, green, yellow, blue, and violet, for which he was unable to determine their position because of the weak dispersion of the spectroscopy used and the difficulty in comparing fluorescence spectra. Particularly interesting was a brilliant line juxtaposed to the line D, from which it was separated by a fine black absorption ray, and two groups of bands, or large rays, one seen on the left of D, in the orange, and another to the right, in the yellow and green, grooved by fine absorption rays. The aspect of these bands was quite similar to the group of small rays reported by Georges Antoine Pons Rayet (1839-1906) in a memoir about the spectra of the aurora borealis (Pons Rayet, 1872). Berthelot believed that this observation might also help explaining the enigma of the aurora borealis by the generation of a fluorescent derivative of argon or relatives, produced in the atmosphere under electrical discharges, that is, under conditions similar to those of his experiments.

In the search for argon compounds Ramsay also looked on the possibility of their existence in natural form. Henry Alexander Miers (1858-1942), a famous mineralogist, trustee of the British Museum, told Ramsay of some curious results published by William Francis Hillebrand (1853-1925) (Hillebrand, 1892). Hillebrand analyzed different minerals containing uranium and discovered "a hitherto unsuspected element in uraninite, existing in a form of combination not before observed in the mineral world...nitrogen, which is given off in a gaseous form on heating the mineral with a non-oxidizing acid, or...by fusing it with an alkaline carbonate...The gas was colorless, odorless, a nonsupporter of combustion, unchanged by mixture with air...not absorbed by alkalis...the gas afforded the fluted spectrum of pure nitrogen." Ramsay believed that it was unlikely that the mineral treated with sulphuric

acid would release nitrogen. Since uraninite, the principal mineral treated by Hillebrand, was hard to obtain, he repeated Hillebrand's experiments using clévite, a similar uranium mineral, "in the hope that if this substance turned out to contain argon, it would give a clue to a method of forming other compounds, and that it would be worthwhile trying other minerals as well as those containing uranium. On investigation, the gas turned out not to be argon at all, giving a spectrum which was different from that of nitrogen." It showed a brilliant yellow line, which originally Ramsay took to be the line of sodium. He sent a sample to Crookes who reported that the new line was coincident in length with the line of helium, which had been previously discovered by Joseph Norman Lockyer (1836-1920) and Edward Frankland (1825-1899) in 1869 (Ramsay, 1896a): "The search then, for compounds of argon led to the discovery of helium. Many minerals were investigated in order to see if they contained helium, and it turned out that a great many contained it." In particular, it was found in monazite, which is mined in large quantities in the U.S. and used for making mantles for incandescent gas burners (Ramsay, 1896; 1869).

Helium and argon were found to be very good conductors of electricity. Ramsay was convinced that valuable results would be obtained from this discovery (Ramsay, 1896a; Frankland and Lockyer, 1869).

The high inertness of argon explains its many uses today for purging instruments, blanketing products, carrier gas for analytical instruments; protection of welds against oxidation, reduction of welding emission; stainless steel production at AOD process (to avoid the formation of nitrides); and used ultra-pure to protect against impurities in the production of semiconductors (as a protective atmosphere for growing silicon and germanium crystals). Argon is used in aluminum manufacture to aid degasification and to remove dissolved hydrogen and particulates from molten aluminum. It is also used as an inert gas in the manufacture of titanium to avoid oxidation and reaction with nitrogen (titanium is the only metal that will burn in a 100% nitrogen atmosphere).

Argon is used extensively in the incandescent lamp industry for the filling of light bulbs, in fluorescent tubes at a pressure of about 3 mm; in phototubes, glow tubes, lasers, etc.

Reactivity of the inert gases

The inertness of argon and the other noble gases has

played a central role in the developing of electronic theories of chemical bonding. For this reason it is appropriate to discuss the subject in general.

In their groundbreaking papers of 1916 papers (Kossel, 1916; Lewis, 1916), both Gilbert Newton Lewis (1875-1946) and Walther Kossel (1888-1956) pointed out that the electron configurations of these elements was especially stable, a fact supported by the many early failures to make compounds of the gases. In 1916 Kossel made the clever observation that the elements having one electron less (Group 7) that a member of the family of noble gases (group 0) tends to have a valence of 1. Similarly, elements following the group of noble gases (Group 1) are also univalent. Kossel hypothesized that atoms gain or loss electrons so as to attain the electronic configuration of the noble gases, that is, an external shell with eight electrons.

In the same year, Lewis pushed this idea farther to include a much larger class of compounds, which today we call covalent. Lewis introduced the concept that electrons can be shared between two atoms and thus they assist each atom in attaining a more stable configuration. The central thesis is that the atom tends to adopt for its most external shell an electronic configuration identical to the closest noble gas; that is, they hold an even number of electrons in the shell, mostly eight, which are normally arranged symmetrically at the eight corners of a cube. The latter idea was advanced by A. L. Parson, who assumed that the electron is not merely an electric charge but also a small magnet, a magneton. According to Parson, argon was a system of concentric cubes, neon was a similar system with one less cube, and helium was similarly constituted. Lewis disregarded the latter conclusion on the basis of evidence from radioactive phenomena and from Moseley's study of the X-ray spectrum, and concluded that helium had a total not of eight but of either two or four electrons.

On the basis of the first ionization potentials of the gases, Kossel noted that xenon was most likely to have the capability of forming fluorides and oxides. He also speculated that a krypton fluoride might be made. Similar predictions were made later, by Andreas von Antropoff (1878-1956) and by Linus Carl Pauling (1901-1994; 1952 Nobel Prize in Chemistry; 1962 Nobel Peace Prize), based on chemical trends in the periodic table. In 1933 these predictions led Don M. Yost (1893-1977) and Albert L. Kaye to attempt (and fail) synthesizing a xenon chloride or

fluoride by irradiating mixtures of xenon with the halogen with the light of a mercury lamp, a carbon arc, or by high voltage bursts (Yost and Kaye, 1933; Bartlett, 2003).

In 1962 Neil Bartlett (1932-) (Bartlett, 1862) took advantage of the oxidizing properties of hexafluoroplatinate in generating the salt $O_2^+[PtF_6]^-$ to prepare the first true compound of xenon, $Xe^+[PtF_6]^-$. Later in the same year, Claassen *et al.* found that xenon and fluorine react readily to form a solid compound XeF_4 that is stable at room temperature and can be sublimed easily (Claassen *et al.*, 1962). This tetrafluoride is a colorless solid having a negligible vapor pressure at $-78^\circ C$ and roughly 3 mmHg at room temperature. Syntheses of other fluorides and oxyfluorides followed quickly.

Many recent findings, including the first evidence for an argon compound, have come from matrix-isolation studies done by Markku Räsänen and coworkers in Finland. For example, in a paper published in 2000 (Kriachtchev *et al.*, 2000) they reported that the photolysis of hydrogen fluoride in a solid argon matrix leads to the formation of argon fluorohydride (HArF), which was identified by probing the shift in the position of vibrational bands on isotopic substitution using infrared spectroscopy. *Ab initio* calculations indicated that HArF is intrinsically stable, owing to significant ionic and covalent contributions to its bonding, thus confirming computational predictions that argon should form a stable hydride species with properties similar to those of the analogous xenon and krypton compounds reported before.

Geochemistry (Goldschmidt, 1958; Fairbridge, 1972)

According to Goldschmidt (Goldschmidt, 1958) the geochemistry of the inert gases presents a number of very interesting problems many of which are still unsolved. One general problem is their scarcity in terrestrial materials as compared with their abundance in the solar and stellar atmospheres and nebulae. Spectroscopic evidence proves that the inert gases are quite abundant in the sun, stars and nebulae, and that their abundance seems to conform to their even atomic weights, that its nuclear charges, making their nuclei more frequent than those of neighboring odd-numbered elements. The spectrum of argon has never been observed in the fixed stars or in the sun, while that of helium is common in the light from many of the fixed stars. Argon-36 is believed to be the most abundant argon isotope cosmi-

cally; and virtually all the argon in the atmosphere is argon-40.

Ramsay analyzed meteoric iron and found the presence of large amounts of hydrogen accompanied by small amounts of helium and argon (Ramsay, 1896a). Although most argon in meteorites has been produced by radioactive decay of potassium, considerable amounts of cosmogenic argon haven been produced in meteorites by interactions between cosmic rays and calcium nuclei.

According to Goldschmidt (Goldschmidt, 1958): "in terrestrial materials the inert gases occur mainly in the atmosphere; only small amounts are known to occur in rocks and minerals, e.g. the helium of radioactive origin. Very small amounts are dissolved in seawater. The relative amounts in volume percent in the atmosphere are helium 0.0005; neon 0.0018; argon 0.93, krypton 0.0001, and xenon 0.00001... The general scarcity of the inert gases in the atmosphere of the earth must be due to a common cause." Although helium and neon are too light to be retained in the atmosphere at the primordial high temperatures, this cause does not seem apply for the heavy atoms of argon, krypton, and xenon.

The geochemistry of argon presents some puzzling problems of its own. The isotopic constitution of argon seems to explain is high increase in proportion to other inert gases. 99.63 per cent of atmospheric argon consists of the isotope of mass number 40 and only 0.31 per cent of the isotope 38 (Goldschmidt, 1958).

A major portion of terrestrial argon has been produced, since the Earth's formation, in potassium-containing minerals by decay of the rare, naturally radioactive isotope potassium-40. The gas slowly leaks into the atmosphere from the rocks in which it is still being formed. Since argon is chemically inert, it remains in the atmosphere and is not reincorporated into sediments. The production of argon-40 from potassium-40 decay is utilized as a means of determining the Earth's age (potassium-argon dating) since its total half-life is approximately 1.3 billion years. On Earth, naturally occurring argon is a mixture of three stable isotopes: argon-36 (0.34 percent), argon-38 (0.06 percent), and argon-40 (99.60 percent). The main isotopes of argon found on Earth are Ar-40, Ar-36, and Ar-38. Naturally occurring K-40 with a half-life of 1.250×10^9 years, decays to stable Ar-40 (11.2%) by electron capture and by positron emission, and also transforms to stable Ca-40 (88.8%)

via beta decay. These properties and ratios are used to determine the age of rocks. In the Earth's atmosphere, Ar-39 is made by cosmic ray activity, primarily with Ar-40. In the subsurface environment, it is also produced through neutron capture by K-39 or alpha emission by calcium. Argon-37 is created from the decay of calcium-40 as a result of subsurface nuclear explosions. It has a half-life of 35 days.

Armand Gautier (1837-1920) analysed the volatile emissions which were being released 3 and 18 months after the 1906 eruption of the Vesuvius and concluded that the composition of the gases that accompany the fumaroles is in general similar to the one released when primitive rocks (such as granites, porphyrites, ophites, basalts, andesites, etc.) are subject to a red-hot distillation. In these rocks, as well as in the fumaroles, water vapour, hydrogen, CO₂, nitrogen, argon, and traces of methane, CO, H₂S, etc., are found. According to Gautier, the spectrum of the fumaroles indicates clearly the presence of argon and neon. An additional finding is the presence of about 0.012 per cent of argon and inert gases in the emissions of the ancient crater at Agnano, near Naples (Gautier, 1909).

The fumaroles of Mont Pelee in Martinique during the eruption of 1902 were examined by Alfred Lacroix (1863-1948), and the vapors analyzed by Moissan, who found that they consisted chiefly of water vapor, with hydrogen chloride, sulphur, carbon dioxide, carbon monoxide, methane, hydrogen, nitrogen, oxygen and argon, the latter to the extent of 0.71%. These vapors issued at a temperature of about 400°C.

Epilogue

In the last chapter (The Epilogue) of his book *The World of the Wars* (Wells, 1946) Herbert George Wells (1866-1946) writes "At any rate, all the bodies of the Martians that were examined after the war, no bacteria except those already known as terrestrial species were found...Neither is the composition of the Black Smoke known, which the Martians used with such deadly effect...Spectrum analysis of the black powder points unmistakably to the presence of an unknown element with a brilliant group of three lines in the green and it is possible that it combined with argon to form a compounds which acts at once with deadly effect upon some constituent in the blood." ■

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(Rayleigh appears under as Lord Rayleigh)

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