THE INERT GASES OF THE ATMOSPHERE.*

BY WYATT W. RANDALL.[1]

I.

In the case of any classical research, interest in the mental processes of the investigators as they worked upon the material which was available, may long outlast that in the actual facts brought to light. These last are soon absorbed into the great mass of scientific data stored in works of reference and the romance of their discovery is in large measure lost to the average student. Hence it is most desirable that what may be called their anecdotal history should be preserved and should be available to inspire those who are seeking to enlarge the domain over which exact science maintains its sway. The average school boy of to-day can tell you facts concerning the atmosphere which were not even suspected by the most profound student of chemistry thirty-five years ago, yet it may safely be predicted that, two hundred years from now, the investigations conducted by Lord Rayleigh and Professor Ramsay will continue to stimulate, and to awaken admiration in, the chemist of that time.

In his efforts to secure the greatest attainable accuracy in the determination of the weight (under standard conditions of temperature and pressure) of a liter of each of the lighter elementary gases, Lord Rayleigh strove to avoid any possible source of error: (*a*) in the production of pure samples; (*b*) in the determination of the temperature and pressure at the time of filling his glass container; (*c*) in the weighings; (*d*) in determining the volume of the container. The ingenious devices employed to secure one or other of these ends cannot be discussed at length here. Most important of all was the decision to prepare samples of each gas by at least two different methods, in order to avoid the introduction of a constant source of error. This decision led to the discovery of the inert gases of the atmosphere: for, after a satisfactory series of weighings had been made with "nitrogen" secured by the removal of all other known constituents from air, he followed this up with another series in which the gas had been produced by passing a mixture of air and ammonia through a hot tube. The density of the latter gas was about 1/1000th lighter than atmospheric "nitrogen." Experiments of various kinds failed to show the presence of any impurity in this "chemical nitrogen." Instead of assuming that some annoying and probably undiscoverable source of error vitiated his later results, and letting it go at that, Lord Rayleigh doggedly set to work to *increase,* if possible, the discrepancy observed. He prepared nitrogen from pure oxygen and ammonia: this would contain no atmospheric nitrogen. The discrepancy between the density figures of atmospheric "nitrogen" and "chemical" nitrogen was found to be now 6–7 times as great as before. Suspicion, therefore, began to involve the atmospheric "nitrogen," in spite of the fact that all previous researches, as well as that now in hand, had been based upon the (apparently safe) assumption that pure nitrogen was obtained when dry air, free from carbon dioxide, had been

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caused to pass repeatedly through a tube filled with red-hot copper filings. Lord Rayleigh now prepared atmospheric "nitrogen" by the use (*a*) of iron filings and (*b*) of ferrous hydroxide, in the place of copper. The gas obtained in each case exhibited the same density as did that obtained from the air with the aid of copper.

Was the trouble after all with the "ammonia nitrogen?" He prepared "chemical nitrogen:" (*a*) from nitric oxide, (*b*) from nitrous oxide, (*c*) from urea, (*d*) from ammonium nitrite purified by two different methods: in each case practically the same results were obtained as with "ammonia nitrogen:" not only did the discrepancy remain, but it was constant in amount.

Lord Rayleigh's attention was now called to an experiment performed by Cavendish about 115 years before, in which a stream of sparks from a frictional electric machine had been sent through a quantity of air mixed with pure oxygen and contained in a glass tube over mercury. After removal of excess oxygen and of gases soluble in alkali solution, Cavendish had found there was a small bubble of gas remaining which refused to yield to the action of his agents. Lord Rayleigh, therefore, set to work to repeat Cavendish's experiment on a large scale and, at the same time, suggested to Professor Ramsay that he, too, endeavor to solve the problem which the nitrogen results had shown to exist.

The outcome is well known. Lord Rayleigh, by the prolonged action of an electric arc upon a mixture of air and oxygen contained in a large vessel over strong soda solution; and Ramsay, by passing purified air repeatedly over hot magnesium contained in a glass tube; succeeded (1894) in removing from air all its constituents known up to that time: about 1% of the original volume of the air remained, and to this residue they gave the name of "argon," the inert one.

From this point on, the interest centers chiefly about the work of Ramsay. The density of the new gas was determined with great care and its spectrum was mapped. The ratio of its specific heats, its behavior towards reagents, its coefficient of expansion with heat, etc., showed that it was monatomic, with no capacity to form compounds. Search for possible compounds led Ramsay (1895) to examine a gas—supposedly nitrogen—given off from certain rare minerals under the influence of high temperature. After purification from known constituents, spectrum examination showed that this gas was not argon, but a new inert element whose presence in the sun's higher atmosphere had been detected 25 years before and which now was shown to be present in minute quantity on the earth—helium.

Prolonged study of the behavior of helium and argon led to the conclusion that the former has an atomic weight of nearly 4—following hydrogen and preceding lithium in the Periodic System—and that the latter has an atomic weight of nearly 40, thus following chlorine and preceding potassium in the Table. Ramsay argued that if an inert gas comes just after chlorine, there ought to be one just after fluorine, another just after bromine, another just after iodine. Similarly, if one is known which precedes lithium and another which apparently precedes potassium, there ought to be one to precede sodium, one to precede rubidium and one to precede caesium. In other words, are there inert, monatomic gases whose atomic weights are approximately 20, 82 and 128, respectively? And where should one expect to find them? Might not argon, after all, turn out to be a mixture?

This last question had frequently been asked, for the density of argon pointed to an atomic weight (39.92) higher than that of potassium, whereas its properties showed that its place in the Periodic System is evidently before potassium. If argon is a mixture, it might consist of a chief constituent, say, of atomic weight 38 and of one or more heavier gases (in small quantity) which would raise the average density to 20, as compared with that of hydrogen taken as unity. Moreover, certain lines in the helium spectrum coincided with lines in the argon spectrum: this suggested the presence of a common constituent. But if argon is a mixture of *inert* gases, how can they be separated from one another? Chemical methods would obviously be of no avail. Ramsay attacked the problem from two directions: making use of (1) assumed differences in density, and (2) assumed differences in volatility.

The details of this experimental work cannot be gone into here. Suffice it to say that, by the use of boiling liquid air as a cooling agent, a lighter fraction was separated from argon, and this in turn, by the use of *boiling liquid hydrogen*, was separated into helium (which was under these conditions still a gas) and a (liquefied) new gas, neon, whose density was half that of argon and its atomic weight therefore 20. The first of the gases looked for had been found!

Various facts led to the conclusion that if heavier constituents exist in what had been called argon, they must be present in very small quantity. Obviously their separation in a reasonably pure form would thus be a matter of extreme difficulty; nevertheless it was done. By *fractional distillation* of liquefied argon, and separation and redistillation of the several fractions obtained—the process being repeated again and again—it was ultimately possible to separate and purify two heavier gases; krypton, with an atomic weight of 81.56, and xenon, with an atomic weight of 128.0. All the gases sought had been isolated, and each fitted perfectly into its place in the Table!

Some idea of the difficulties involved in this work can be gained if one bear in mind the relative amount of each of these gases in the atmosphere. In twenty million volumes of air there are contained about:

187,400 volumes of argon
300 volumes of neon
30 volumes of helium
20 volumes of krypton
1 volume of xenon

Various physical constants were determined for each of these gases in turn. And yet Ramsay had only a little over 2 cc. of gaseous xenon to work with!

The discovery of krypton and xenon has not solved the problem of the atomic weight of argon; this seems to be approximately 39.96 and therefore distinctly greater than that of potassium.

II.

Let me now turn to an informal discussion of some of the details of technique which, to me at least, were a source of intense interest. And let me begin by saying that I am relying in large measure upon my memory, for by no means were all these devices, so far as I can recall, described in print.

(1) The method employed by Lord Rayleigh in determining the relative densities of the several elementary gases and their several weights per liter under standard conditions, was only a modification of that which had been used by

Regnault, von Jolly, Leduc, Cooke, and others. It consisted essentially in weighing a glass balloon provided with a tap, (*a*) when vacuous and (*b*) when filled at a known temperature and pressure with each of the gases in turn. The capacity of the balloon up to and including the bore of the tap, was approximately 1836 cc.; this was determined by filling it with water at 0° C. and weighing it in a room whose temperature was close to 6° C.; under these conditions there was no overflow from the tap.

(2) The buoyant effect of the air upon the globe at the time of a weighing had to be determined with great care. It was found that the globe when vacuous was smaller by an appreciable amount than when filled with gas at approximately atmospheric pressure; this was allowed for in the calculations.

(3) One of the most formidable difficulties connected with work of this kind is that due to atmospheric moisture deposited upon the glass balloon and so adding an indeterminate amount to its weight. Many investigators have attempted to overcome this difficulty by drying as completely as possible the air in which the balloon was hung while the weighing was in progress—in other words, the balloon was suspended in a desiccator prior to and during the weighing. Lord Rayleigh saw that if a *constant* hygroscopic condition could be maintained in the balance room, it made no difference how much moisture was deposited on the balloon: if it were a constant amount, it would be weighed each time as was the glass of the balloon itself. Accordingly, prior to each series of weighings, he hung around the balance room a row of blankets which had been baked in an oven; in a comparatively short time equilibrium was established between the atmosphere and the blankets and—which is the important thing—the hygroscopic state of the air in the room was the same, day after day, whatever it might be in the open.

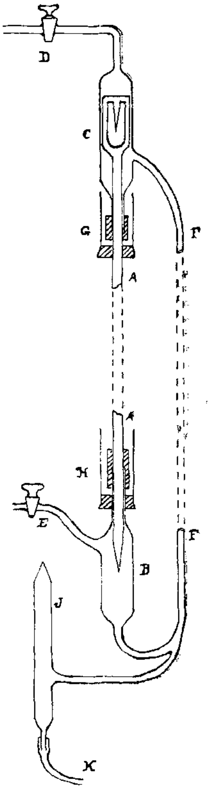
(4) It goes without saying that, in weighings where a hundredth of a milligram plays a part of some importance, the presence of a person close to the balance may cause an appreciable error. To avoid an error of this sort, Lord Rayleigh made it a practice to suspend the balloon from the balance, to adjust the weights, to arrange the blankets in position, to start the balance swinging, to close the room and—as this was done in the evening—then to go to bed. In the morning, from another room a beam of light was thrown on the balance-scale and, by means of a telescope set in the wall, the swings of the pointer were noted.

(5) The balloon was always surrounded by melting ice at the time of filling; temperature control was therefore easily secured. The exact determination of the pressure exerted upon the gas inside the balloon was, however, a difficult matter. Lord Rayleigh solved this difficulty in characteristic fashion: instead of referring the filling pressure to the barometric height at the time, he made use of a manometer and always filled the balloon at the same pressure; this called for but one pressure adjustment and removed all fear of inaccurate barometric readings due to varying meniscus form. A stout iron rod, provided at each end with a sharp point turned down, was enclosed in the manometer in such a way that the upper point was close to the mercury surface in a chamber connected with the air-pump, while the lower point was close to the mercury surface in a chamber connected with the glass balloon; the glass tube through which connection was established between the mercury in the upper chamber and that in the lower, was, like the chambers themselves, protected by insulating material. The temperature of the mercury

was noted. When each point was brought, by adjusting the mercury reservoir, to coincide with its reflection in the mercury surface, the gas in the balloon was under a pressure corresponding to that of a mercury column equal in vertical height to the distance between the two points on the iron rod. The vacuum in the upper chamber could be tested at any time by means of the pump; proper precautions eliminated any possibility of an error due to changing length in the iron rod. The exact length of the latter, between the two points, having been determined once for all—it was a little over 762 mm.—all pressure measurements could be reduced to terms of standard pressure at 45° latitude.

(6) I cannot forbear introducing a reference to Lord Rayleigh's Töppler pump. When I first went to work in his laboratory, it fell to me to transfer a quantity of (at that time) most precious helium which I had brought from London, from a sealed glass container to his interferometer. One look at the pump appalled me, and my concern filled him with amusement. It turned out that, two years before, someone, in handling the pump carelessly, had allowed mercury (with atmospheric pressure behind it) suddenly to enter the vacuous bulb—with the result that a hole the size of a half-dollar had been knocked in the side. On examination, however, he had found that a single piece of glass had been broken out, that this had not been chipped, that there were no cracks in the bulb and that the piece would stay in its place if put back and held by pressure from outside! The pump was needed at once; to secure a new bulb and install it would have caused several days' delay; so Lord Rayleigh had caught up a lot of old examination papers, had tied them like a cornucopia around the bulb of the pump and, after restoring the piece of glass exactly to its place, had filled the cornucopia with mercury until the damaged part of the bulb had been drowned in a mercury seal. The paper cornucopia was begrimed with dust and the mercury it contained was hardly recognizable. Truth compels me to say that appearances were distinctly against that pump—but it worked perfectly!

(7) And now a few words about Lord Rayleigh's results. Before the work upon nitrogen was begun, he had determined the ratio between the densities of hydrogen and oxygen. Three different methods were used for the preparation of oxygen: (*a*) by heating a mixture of potassium and sodium chlorates, (*b*) by heating potassium permanganate, (*c*) by electrolysis. Five weighings of chlorate oxygen yielded figures ranging from 2.6273 to 2.6266 grams; three of permanganate oxygen, figures ranging from 2.6273 to 2.6270; electrolytic oxygen gave the figures 2.6271 and 2.6272. Reduced to standard conditions, these



In the sketch, the iron rod, with its points at C and B, passes through a contracted portion (G) of the upper glass chamber, where a tight joint is made with stout rubber tubing, wired down and covered with a mercury seal. A similar connection is made with the lower chamber at H. The lower portion of each chamber is filled with pure mercury, as is the connecting tube FF. At D is a connection with the Töpler pump; at E the connection with the balloon and the gas reservoir. J is a trap where can be collected any mercury whose surface may have become fouled. K is connected with the adjustable mercury reservoir.

yield as a mean for the weight of a liter of oxygen: 1.42952 grams.

In the case of nitrogen, samples were prepared from air by three different methods: according to the method employed, average weighings of 2.3103, 2.3100 and 2.3102 grams, respectively, were obtained. "Chemical" nitrogen, prepared by five different methods, yielded average weighings of 2.3001, 2.2990, 2.2987, 2.2985, 2.2987 grams, respectively. The mean of the former is 2.3102 grams, of the latter 2.2990 grams—differing therefore by about 1 part in 205. Assuming the density 20 for argon (as compared with nitrogen = 14), this indicates the presence of about 6.91 cc. of the heavier gas in one liter of atmospheric "nitrogen," or of about 8.74 cc. of argon in each liter of air. Later results showed that the percentage by volume is a little greater: 0.937.

To give some idea of the remarkable accuracy of these results when the difficulties surrounding their attainment are taken into account, I would suggest that you be called upon to determine the *exact* percentage content of a solution of common salt by means of a huge pycnometer which weighed, say, 500 grams, yet had a capacity of only 2 cc. Bear in mind that such a determination would involve almost none of the difficulties connected with temperature- and pressure-measurements which are a necessary concomitant of work with gases—and then note, nevertheless, how your courage would ooze away!

(8) The removal of nitrogen from a mixture of that gas with argon, whether by Lord Rayleigh's method or by Ramsay's, was comparatively easy and rapid until the volume had been reduced to but a few per cent. of that at the beginning; then progress became slower and slower. In addition, the likelihood of the glass apparatus giving way, with all that *that* involved, was nerve-racking. Lord Rayleigh's electric arc and Ramsay's furnaces subjected bulbs and tubes to a severe stress. The latter devised an ingenious apparatus by means of which impure argon was drawn from a reservoir, passed over red-hot magnesium, red-hot copper, red-hot copper oxide, caustic potash and phosphoric anhydride, in turn, and then restored to the reservoir—all without coming in contact with anything except these reagents, glass, rubber and mercury! (Rubber connections had to be used where hard-glass tubes were joined to those of soft glass.) No air was allowed to enter the apparatus and no argon to escape, and yet the enclosed gas was kept continuously moving through the system of purifying tubes. This circulating apparatus was often kept going for two days or more on a stretch, while samples drawn off from time to time and weighed, showed that the density of the residual gas was slowly rising—or, if helium was being purified, slowly falling. Sparking-tubes were also constantly brought into use to note the fading of the nitrogen spectrum.

(9) The methods developed for the isolation and purification of argon stood Ramsay in good stead when "cleveite gas" came to be studied. To secure a large volume of argon in pure condition had become merely a question of time: there was plenty in the atmosphere; but from whence was any considerable volume of helium to come? Laboratory technique had to be yet further refined and, at last, when there were separated from argon—*and from each other*—four gases whose volume combined was not as much as 1 part in 500 of argon, it is no wonder that a chorus of praise arose from Ramsay's contemporaries. To use liquid air as a cooling agent was, at that time, not uncommon; to produce liquid *hydrogen* in quantity and to

employ it to render neon non-volatile while the helium with which it was mixed was being completely removed, was certainly something new in laboratory technique. The separation of minute quantities of krypton and xenon from argon was another triumph of patience and manipulative skill.

(10) It is hazardous always to indulge in comparisons. Lord Rayleigh possessed to an extraordinary degree the power of devising simple means to produce desired results. Whether he possessed anything comparable with Ramsay's skill in constructing before the blowpipe, and later, manipulating delicate pieces of glass apparatus, I am in doubt. Both men were doubtless highly ingenious: Lord Rayleigh in avoiding difficulties, Ramsay in overcoming them. Each possessed a charming personality—was blessed with a fund of humor and a delightful courtesy. To offer genuine hospitality to the stranger, to show generous appreciation of his efforts, however modest, seemed to be instinctive with each of them. To have enjoyed a friendship such as they bestowed is, to this writer, a source of pride and will always keep alive towards them a profound sense of gratitude.

BELLADONNA PLASTER.

STANDARDS AND TESTS.

BY FRED B. KILMER AND F. L. HUNT.

There is a long, long trail of history behind such a commonplace thing as a Belladonna Plaster.

Through the maze of legend and written history, we find that the cave man and the nomad had, in some way, gathered a knowledge of the Narcotic Solanums, and applied them for their pain-relieving power.

Hyoscyamus and the Daturas, the famous Mandragora and the Belladonna, have been the pain-relieving Nightshades of widely separated primitive races. The leaves of these plants were applied as poultices, their juice was spread on skins, or made into salves and then spread as a plaster.

Somewhat interesting is the fact that when the Spanish invaded South America, they found the Indians applied a compound of stramonium and pepper as a pain-dispelling poultice or plaster. Here perhaps is the primitive origin of the now popular Belladonna and Capsicum Plaster.

In running through the ages it is of further interest to note that men have, from the beginning, gathered the Narcotic Solanums into a group, owing to their peculiar pain-relieving power, and to them they applied a group name that in widely separate tongues works out into "Nightshade." Further, we find that whatever species of Nightshade may have been peculiar to a country, it was the equivalent of the Narcotic Nightshades of other lands.

Thus, the Datura of India, the Mandragora of Syria, the Hyoscyamus of Egypt, and the Belladonna of Europe, appear confusedly in literature and lore as equivalents in properties and in name. In our own land, the *Solanum nigrum* is quite commonly called Belladonna, and with the Zuni Indians, the *Datura meteloides* is "Indian Belladonna."