FROM THE HISTORY OF PHYSICS

'Prout's law' and the discovery of argon *

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<u>Abstract.</u> The discovery of the first noble gas, argon, is described — an achievement which was awarded with a double Nobel Prize in 1904.

1. Introduction

The discovery of noble gases has received little attention in the physical literature; but the history of this discovery at the borderline of chemistry and physics is instructive and very interesting.

It seems appropriate to begin the story of this discovery with a note that natural history offers no clear definition of 'the discovery of an element.' Certain elements are considered to have been discovered from the time they were purified from substances that contained them. A typical example is fluorine. A fluorine-containing mineral, fluorspar (CaF₂), had been known since the Middle Ages, and hydrofluoric acid, HF, was synthesized as early as 1670. In 1780, the Swedish chemist K Sheele suggested that hydrofluoric acid should contain an unknown element. In 1793, A-L Lavoisier placed the radical of hydrofluoric acid (i.e., fluorine) in a table of simple bodies. However, it is generally accepted that fluorine was actually discovered in 1866 by the French chemist H Moissan, who obtained it as a pure gas [1, book 2, p. 3].

An alternative criterion for 'the discovery of an element' is isolation of a specific compound containing this element. By way of example, the German chemist M H Klaproth used (in 1789) pitchblende excavated in Saxony to isolate uranium dioxide, UO_2 , which he thought to be a new metal and designated it as uranium. Since then, uranium is regarded to

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Received 28 February 2005, revised 4 April 2005 Uspekhi Fizicheskikh Nauk **175** (12) 1357–1381 (2005) Translated by Yu V Morozov; edited by A M Semikhatov have been discovered in the year of 1789, even though it was only in 1841 that the French chemist E-M Peligot obtained pure uranium and showed that Klaproth's 'uranium' was a dioxide rather than an element [2, p. 203].

Finally, some elements are considered to have been discovered from the time of their identification in nature by physical and chemical methods. For example, thallium is believed to have been discovered in 1861 by the English scientist W Crookes by observing a new light-green spectral line generated in the flue dust from the manufacture of sulfuric acid. However, pure thallium was isolated in the same year by the French chemist C-A Lamy. On the other hand, P Janssen of France and J Lockyer of Britain, who were the first to observe (in 1868) a prominent yellow line in the solar spectrum corresponding to the D3 line of the helium triplet state, are not universally credited with the discovery of this element. It is usually attributed to the English chemical physicist W Ramsay and also to P T Cleve and N A Langle of Sweden, who discovered helium independently in 1895 [1, p. 55]. Interestingly, the helium line in the volcanic gases of Vesuvius was first observed by the Italian scientist Palmieri as early as 1881 [1, book 1, p. 28]. The case of helium may be interpreted as follows: this new element was first reported to exist in 1868, but the discovery of helium as a noble gas dates to 1895.¹

It follows from the aforesaid that the first noble gas, i.e., a new chemical element, was discovered in 1894, even if pure argon had been isolated by the eminent British chemical physicist H Cavendish in 1785.

It needs to be mentioned in connection with the history of argon that the principal gases contained in the dry atmospheric air were known to chemists as early as the 18th century. Nitrogen was discovered by D Rutherford of Scotland in 1772, oxygen by the English chemist J Priestley and in Sweden by the chemist C Sheele (independently) in 1774, carbon dioxide by the British chemist J Black in 1756, and hydrogen (as a constituent of water) by Cavendish in Britain in 1766. It is known at present that argon is the third major component of the earth's atmosphere after nitrogen (78.09%) and oxygen (20.95%); it constitutes 0.93% of the

¹ These examples indicate that the history of science, unlike science itself (understood here as natural science), is a matter of subjective opinion that emerges even in such seemingly objective thing as dating a scientific discovery.

atmosphere by weight. In other words, roughly each 107th molecule of air is argon. The argon content of the atmosphere is approximately 30 times that of carbon dioxide and 17,500 times the hydrogen content. Throughout most of the 19th century, chemists and physicists believed that there was no gas in the atmosphere left unknown to them, although physically pure argon had actually been isolated from the air by Cavendish as early as 1785! It seems strange now that neither Cavendish himself nor anyone else attached much importance to this discovery.² Moreover, nobody tried to purposefully seek an inert constituent of the atmosphere during the next 100 years.

Paradoxically, Mendeleyev's 'periodic law' did not contribute in any way to the discovery of the first noble gas, even though it was first formulated in 1869 in a publication entitled "Relationship Between Properties and Atomic Weights of Elements" as follows: "Elements arranged in order of increasing atomic weight show a periodicity of properties" [3, p. 76]. Moreover, the incorrectly worded theoretical 'makeweight' (in the form of the above 'periodic law') to the empirically developed periodic table made Mendeleyev dispute the discovery of argon (from August 1894 until March 1900) because the existence of this element was evidently in conflict ³ with his 'periodic law.'

In a word, although the discovery of argon may be regarded as accidental (in the sense that nobody suspected its existence), it nevertheless resulted from a well-targeted physical study undertaken by the British physicist J W Rayleigh to verify the hypothesis of his compatriot physician and amateur chemist W Prout.

2. Background

It is universally known that the atomistic concept first emerged in ancient Greece, even though people of those times had no idea of natural history as it is understood in our time. They satisfied themselves with philosophy. Ancient philosophers explained all phenomena known to them metaphysically, introducing numerous arbitrary ideas in their interpretations.

An immediate source of the atomistic concept was one of the achievements of ancient geometry, that is, the proof of incommensurability of the diagonal and the side of a square, which gave rise to the notion of infinite divisibility of space; the atomistic concept was a by-product of the emptiness problem reduced to the question of whether emptiness is real. As usual, opinions differed. Here is a characteristic example of arguments provided by Melissus of Samos [4]: "There is no emptiness because emptiness is nothing. Nothing is non-existent. Likewise, there is no movement."

If there is no movement, neither matter nor space is infinitely divisible. Such was the view of Anaxagoras (the teacher of Socrates), Plato, and Aristotle; Kant shared this opinion in the 18th century.

It is almost a rule in philosophy that as soon as one says 'no' there is always someone who says 'yes' to the same question. It was exactly the case with Leucippus and Democritus, his disciple (5th century BC), who saw the problem of emptiness in a different light. They believed in the existence of emptiness and that matter cannot be infinitely divided. For example, a drop of water cannot be divided infinitely. Sooner or later, the division stops, and the final smallest particle cannot be divided further. Hence, the term an 'indivisible' atom (from the Greek $\alpha\tau\rho\mu\sigma\varsigma$).

Giving rein to his imagination, Democritus maintained that there is an infinite number of different atoms differing in terms of shape and other properties. He attributed a variety of things to the difference in the number of atoms and their distribution patterns. Democritus stated that the human soul consists of thin, smooth, and round atoms reminiscent of the atoms of fire. It appears that Democritus fantasized a great deal, his atomistic concept being a personal conjecture having nothing in common with the modern theory except the term 'atom.' However, none of the participants in vain philosophical disputes managed to prove his view.⁴ After Greek civilization collapsed, the Christian Church oppressed the secular society of Europe and slowed down the progress of natural science by rejecting the concept of atomism and accepting the doctrine of Aristotle, who had considered matter to be an eternal continuous entity composed of four elements: heat, cold, dryness, and moisture. Aristotle attributed variations in the properties of substances to different content of these four elements. It was prohibited in Europe to profess other views, for fear of best torturers and agonizing death, for almost one thousand years (throughout the Middle Ages).

New attempts to revive atomism were made only when the era of religious obscurantism was coming to an end in the XVII-XVIIIth centuries. Many physicists and chemists are credited with the development of a hypothesis that matter is made up of indestructible particles. However, it was John Dalton (1766–1844), a self-educated teacher of mathematics, physics, and chemistry of Manchester, who is considered to have made the greatest contribution to the revival of the scientifically grounded atomic theory. Dalton made his first fairly uncertain statement about the discreteness of matter in a work "On the Absorption of Gases by Water and Other Liquids" that he presented to the Manchester Literary and Philosophical Society on October 21, 1803. In the concluding section of his publication entitled "The Theory of Absorption of Gases by Water" (paragraph 8), Dalton offered the following answer to the question why various gases are differently absorbed by water: "This question I have duly considered, and though I am not yet able to satisfy myself completely, I am nearly persuaded that the circumstance depends upon the weight and number of the ultimate particles of the several gases: those whose particles are lightest and single being least absorbable...." [5, p. 25]. In the same work, Dalton ascertained the relative weights of atoms (the smallest particles of matter) and arranged them into a table, even if a very primitive one.

Thus, purely physical considerations (even if indirect and therefore wavering) brought Dalton to the idea of 'ultimate particles' of matter, while differences of atomic weights prompted the possibility of formation of 'compound particles' from 'simple elementary particles.' This logically led him to the law of multiple proportions, and Dalton proposed a method for its experimental verification, which is considered to be his most powerful argument in support of the atomic theory.⁵

² The Cavendish experiment is described in Section 3.

³ Because of the potassium – argon anomaly.

⁴ It is high time to stop making natural history students study philosophy and those seeking a scientific degree pass a candidate exam on philosophy. Philosophy must be studied in higher-education institutions as an elective discipline.

⁵ It is often argued that Dalton had first discovered the law of multiple proportions and only later came to the idea of atomism.

Table 1.

Dalton deduced the law of multiple proportions ⁶ as early as 1804 when he studied the composition of nitrogen oxides and compounds such as methane CH_4 , ethylene C_2H_2 , carbon monoxide CO, and carbon dioxide CO₂.

When compound B combines chemically with compound D in two or more ways to form compounds E and F, then (at a constant mass of compound B) the ratio of masses of compound D in the reaction products E and F is a ratio of small integer numbers.

For example, nitrogen combines with oxygen giving rise to a variety of compounds. At a constant mass of nitrogen, e.g., 100 g, this amount may combine with 57.1, 114.2, 171.3, 228.4, and 285.5 g of oxygen, the masses of oxygen involved in the respective reactions being in the ratio 1:2:3:4:5. It is well known at present that these reactions yield N₂O, NO, N₂O₃, NO₂, and N₂O₅.

The law of multiple proportions provided one of the earliest experimental bases (along with the law of constant proportions formulated by the French chemist J L Proust ⁷ in 1799) on which Dalton developed his atomic theory.

Indeed, the sole verisimilar interpretation of such a law could be the assumption that the combining chemical compounds behave as discrete entities (atoms) having a definite mass. Later, Dalton wrote to the famous Swedish chemist J Berzelius in a letter dated September 20, 1812: "The concept of definite proportions seems to me a mystical one unless we accept the atomic hypothesis. Kepler's propositions looked equally mystical until they were so successfully explained by Newton" [6, p. 46].

Dalton was doubtlessly influenced by the Greek philosophical tradition and erroneously believed, following Democritus, that the atoms of a certain element are perfectly alike.

Interestingly, the law of multiple proportions was first published by the Scottish chemist professor T Thomson of Edinburgh, "who had come to know about the discovery from a talk with Dalton and, understanding its importance, published it" (with reference to Dalton and with his permission) [7, pp. 40, 41] in the 3rd edition of his book *A System of Chemistry* that appeared in Edinburgh in 1807. Dalton himself expounded the law of multiple proportions and the atomic hypothesis in the first part of his own book *A New System of Chemical Philosophy* published in Manchester in 1808. In the supplement to the first part of this book, Dalton presented a table of atomic masses. Table 1 quotes the atomic weights assigned by Dalton to 'elementary particles' of twenty elements.

It can be seen that Dalton included in the table, probably out of sheer inertia, some oxides that the advocates of the phlogiston theory regarded as elementary constituents of matter and the respective metals as compounds of an oxide and phlogiston.⁸

Elementary particle	Relative weight	Elementary particle	Relative weight
Hydrogen	1	Strontites	46
Azote	5	Barytes	68
Carbone	5	Iron	38
Oxygen	7	Zinc	56
Phosphorus	9	Copper	56
Sulphur	13	Lead	95
Magnesia	20	Silver	100
Lime	23	Platina	100
Soda	28	Gold	140
Potash	42	Mercury	167

However, it is not only ranking oxides as elementary compounds that is unacceptable for a modern physicist or chemist. The most striking thing is the difference between numerical and real values of atomic masses despite the considerable progress in quantitative chemical analysis achieved by the beginning of the XIXth century due to the pioneering works of the eminent French chemist A Lavoisier and his successors. By way of example, Lavoisier found that carbon dioxide contains 28% carbon and 72% oxygen by weight [7, p. 33] (current values are 27.292 and 72.708%, respectively).

Dalton incorrectly obtained many atomic masses not only because he had imperfect purification and weighing techniques at his disposal at the break of the XVIIIth century but also because he believed in the wrong concept of 'greatest simplicity' and applied it to determine the number of simple atoms contained in a particle. Dalton a priori assumed that compound atoms are largely produced through a paired combination of simple ones. In other words, he thought water was HO, ammonia NH, etc. Knowing experimental values (as noted above, they differed from present ones at least by several percent), Dalton affirmed that the atomic weight of oxygen was 8 based on hydrogen as one (the ratio in which the two elements combined in the formation of water). By the same reasoning, the atomic weight of nitrogen was found to be $14/3 \approx 4.7$. Hence, the mass ratio of these two atoms was $4.7/8 \approx 0.59$, i.e., significantly smaller than the real value $14/16 \approx 0.88$, which Dalton could easily deduce from the composition of nitrogen oxide, NO, perfectly known to him. Dalton chose not the best way out by arbitrarily lowering the atomic weight of oxygen and overstating that of nitrogen. Moreover, he approximated the values to integers, evidently attaching no additional importance to this operation.

In other words, the perfectly correct atomic theory that received the most powerful support from the law of multiple proportions was supplemented by a table of atomic masses⁹ underlain with the rule of 'greatest simplicity' that obviously

9 Dalton continuously modified his table.

⁶ Amazingly, Dalton was slow on publishing his discovery, although he was doubtless fully aware of its importance. However, he developed an absolutely fantastic idea of atoms. A detailed history of the revival of the atomistic concept is far beyond the scope of the present paper. For this reason, modern scientific terminology is applied in what follows, which is certainly at variance with that used by Dalton.

⁷ It is worth noting that another French chemist, C L Berthollet, contested Proust's findings till 1808.

⁸ This observation applies to magnesia (magnesium oxide), lime (calcium oxide), soda (sodium oxide), potash (potassium oxide), strontites (strontium oxide), and barytes (barium oxide). By that time, however, Dalton no longer insisted that all the twenty elements listed in the table were 'elementary particles' because he knew about the studies of the English chemist and physicist H Davy, who had shown that soda and potash were compounds of metals with oxygen.

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came into conflict with the results of quantitative chemical analysis of that time. $^{10}\,$

Therefore, it was difficult to share Dalton's atomistic views, but the idea was very attractive and the law of multiple proportions provided a powerful argument in its support. Thomson was among the first advocates of Dalton's atomic theory able not only to understand it but also to undertake his own experiments to verify the new concept. In 1808, Thomson and another British chemist and physicist, W Wollaston, independently obtained experimental data that confirmed the validity of the law of multiple proportions for more complex compounds, such as potassium salts of oxalic acid.¹¹

A path to the rapid determination of molecular composition and atomic masses was found very soon. In 1808, the French physicist and chemist J L Gay-Lussac discovered the law of combining volumes (if gas A combines with gas B to form gas C and all gases are at identical temperature and pressure, then the ratio of the volumes of A, B, and C is a ratio of small integer numbers). Dalton questioned the validity of this law, but T Thomson took the right stand again and supported Gay-Lussac.

The Swedish chemist J J Berzelius used Gay-Lussac's discovery to accurately determine the relative 12 number of atoms in various compounds. Specifically, he determined the composition of water as H₂O but failed to solve all problems pertaining to molecular composition in general.

In 1811, the Italian physicist and chemist A Avogadro brought the laws of multiple proportions and combining volumes into agreement by distinguishing between the notions of an atom and a molecule and suggested a rule currently known as Avogadro's law: equal volumes of gases at the same pressure and temperature contain equal quantities of molecules.¹³

The discovery of the volumetric law by Guy-Lussac and its interpretation by Avogadro could have given a clue to the correct deciphering of the molecular composition of various substances had the ideas of Avogadro been accepted by his contemporaries. But this was not the case. The disputes over Avogardo's concept continued for almost half a century. Suffice it to say that a central problem at the conference held in Karlsruhe in 1860 (the first international scientific meeting in history) was "whether the words molecule and atom need to be distinguished."

In 1815, the *Annals of Philosophy*¹⁴ published an anonymous article "On the Relation between the Specific Gravities of Bodies in Their Gaseous State and the Weights of

¹⁰ The author of the present review believes that the main attention in the history of science should be paid to the origin and development of newly emerging concepts, i.e., ongoing views of the organization of nature. All faulty theories taken together make up a story of errors and false beliefs of the human mind rather than the history of natural sciences, even though such a history also has the right to exist. Dalton had by necessity many fantastic ideas about atoms that are not touched upon in this publication. They are described at greater length in Refs [6, 8].

¹¹ Oxalic acid HOOC–COOH has acid salts of the general formula HOOC–COOK and normal salts KOOC–COOK. Thomson noted [9] that the amount of oxalic acid needed to produce a normal salt is practically twice as low as that necessary to obtain an acid salt (given the amount of potassium is constant).

¹² Clearly, the absolute number of atoms in a molecule was impossible to determine at that time.

¹³ The French chemist A M Amper came to the same conclusion independently in 1814.

¹⁴ The full title of the Journal issued in London by professor T Thomson of Edinburgh was *Annals of philosophy, or, Magazine of chemistry, mineralogy, mechanics, natural history, agriculture and the arts.*

Their Atoms" [10]. The anonymous author purposely chose this journal because Thomson, its publisher, had greatly contributed to the support of the atomistic theory then recently revived on scientific grounds. The author did not yet use Avogadro's law in full measure and only referred to the 'doctrine of volumes' as first generalized by Guy-Lussac¹⁵ in his search for a path free from the controversies of Dalton's approach to the determination of atomic masses based on the results of quantitative chemical analysis and measurements of gas densities.

The paper started from the calculation of specific gravities of 'elementary gases,' i.e., constituent components of the air, on the assumption that the air consisted of four volumes of nitrogen and one volume of oxygen.¹⁶ The anonymous author suggested that if the ratio of the atomic masses of oxygen and nitrogen were 10:17.5, ¹⁷ then the ratio of their weights in the formation of air would be of the order of one oxygen atom to two nitrogens.¹⁸ Hence, the percent content of oxygen and nitrogen in the air (by weight) was calculated to be 22.22 and 77.77, respectively.

Based on the volume and weight content of oxygen and nitrogen in the air, the anonymous author made a simple calculation and obtained specific gravities of the pure gases (1.1111 and 0.9722 respectively) expressed in units of the specific weight of air that are very close to the presently adopted ones. The author compared his estimates with the corresponding experimental data and found fairly good agreement between them. For example, the relative specific gravity of nitrogen (0.9722) compared with that found by the French physicists J B Biot and D F J Arago (0.969) and the specific gravity of oxygen (1.1111) with that reported by Thomson (1.104) [10, p. 326].

Thereafter, the author moved to hydrogen and emphasized the difficulty of experimental measurement of its specific gravity. He proposed instead to calculate this parameter using the correct formula for ammonia, NH₃, and its specific gravity (relative to air) found by H Davy, J Biot, and D Arago to be 0.5902. Bearing in mind the volume composition of ammonia (with three volumes of hydrogen and one volume of nitrogen making two volumes of ammonia, in excellent agreement with the volumetric concept of Guy-Lussac rejected by Dalton!), the author derived the following equation for the calculation of hydrogen's gravity¹⁹: (3x + 0.9722)/2 = 0.5902;specific hence, x = 0.0694 (relative to air).

It follows from these calculations that the ratios of oxygen's to nitrogen's specific gravities expressed through

¹⁶ By that time, the most accurate data were obtained by Guy-Lussac and A Humboldt, who showed in 1804 that air is a mixture of 79 nitrogen and 21 oxygen volumes [11]. These values were generally accepted until the discovery of argon. For comparison, the current definition of the standard atmosphere is a mixture (by volume) of 20.9476% oxygen, 78.084% nitrogen, 0.934% argon, and a small amount of other gases [12, p. 1193]. ¹⁷This ratio corresponds to the atomic mass ratio 8 : 14 rather than 16 : 14. Here, the anonymous author puts the atomic weight of oxygen twice lower than its actual value (following Berzelius).

¹⁸ It is a 'compensation error' of the author resulting from the fact that he took oxygen concentration to be twice that of nitrogen. Naturally, in such a case, the number of oxygen atoms in one volume should be only two times smaller than the number of nitrogen atoms in four volumes.

¹⁹ This equation follows from the mass conservation law.

¹⁵ Practically speaking, this meant a digression from Avogadro's concept in that, as we would put it today, the concentration of an ideal gas composed of molecules of several gases was twice overestimated, whereas the atomic weights were underestimated by the same factor.

hydrogen specific gravity are almost integers. Indeed, 1.111/0.0694 = 16.01 and 0.9722/0.0694 = 14.01 (for comparison, the current values are 15.90 and 13.91, respectively [12]). In other words, the error of calculations made in 1815 was 0.7%. Similar calculations were performed by the same author for a number of other simple and compound substances.²⁰ In all the cases, specific gravities of gases expressed in terms of hydrogen's specific weight were found to be close to integers.

The results were summarized in four large tables. It turned out that the relative weights of all atoms (expressed in terms of hydrogen's atomic weight) used in the calculations were integers, with good agreement between the computed densities of gases and experimental values thoroughly collected by the author from numerous sources (the difference within 10%). Table 2 shows atomic weights of certain elements illustrating the results in Ref. [10]. For comparison, the corresponding currently accepted values are included borrowed from [2] and also expressed in terms of hydrogen's atomic mass.

Table 2.

Element	Relative weight [10]	Current value	Element	Relative weight [10]	Current value
Hydrogen	1	1	Iron	28	55.41
Carbon	6	11.92	Zinc	32	64.87
Azote	14	13.90	Chlorine	36	35.18
Phosphorus	14	30.73	Potassium	40	39.63
Oxygen	8	15.87	Barytium	70	136.3
Sulphur	32	31.81	Iodine	124	125.9

It can be seen that the atomic weights of certain elements (carbon, phosphorus, oxygen, iron, zinc, and barium) were underestimated by one half. However, this did not influence the results of calculations of the parameters of interest in the beginning of the XIXth century (e.g., specific gravities, as exemplified above by the calculations of nitrogen and oxygen densities) because the anonymous author automatically overstated the concentration of the respective elements by the same factor.

Leaving aside the two-fold underestimation of the atomic weights of certain elements (that need to be mentally multiplied by 2), the accuracy of estimations achieved in the work under consideration is amazingly high (in most cases, the error did not exceed 1%).²¹

Commenting on the results obtained, the anonymous author drew the attention of the 'chemical community' to the integer values of relative atomic masses (expressed in terms of hydrogen's atomic mass) that did not contradict a large set of experimental data. After a conclusion of small import that even the most thorough drying of a gas left some water in the volume, the author suddenly asked: "And are all substances compounded of these two elements?"

The line of his reasoning that provoked this question is difficult to understand.²² In a year, the anonymous author rejected his own arbitrary hypothesis and proposed a new and more attractive one. In 1816, he published a short note in the same journal issued by Thomson, in which the integer values of atomic weights were explained as follows: "If the views we have ventured to advance be correct, we may almost consider the $\pi\rho\dot{\alpha}\tau\eta$ $\dot{\alpha}\lambda\eta$ of the ancients to be realized in hydrogen; an opinion, by the by, not altogether new."

In other words, the anonymous author proposed regarding all atoms as certain entities constituted by hydrogen atoms and the matter of the hydrogen atom as primary matter ($\pi\rho\omega\tau\eta \ \delta\lambda\eta$), the idea of which originated in the mind of ancient Greek philosophers.

To wind up the story, Thomson further developed the simple idea of the anonymous author by publishing a paper in the *Annals of Philosophy* under the title "Some Observations on the Relations between the Specific Gravity of Gaseous Bodies and the Weights of their Atoms" [14] in which he disclosed the authorship of the two 'valuable' anonymous publications [10, 13]. The author was William Prout (1785–1850), a previously unknown physician who had been given the degree of doctor of medicine by the University of Edinburgh in 1811 [15], that is, only four years before his 'discovery' of the integer values of atomic weights.

Naturally, Prout's idea attracted much attention and eventually became known as 'Prout's hypothesis' and even 'Prout's law.' Most British chemists, including Thomson, regarded the Prout hypothesis as an absolute truth [16]. Only Dalton rejected it, alluding to the ancient Greek dogma of indestructible atoms²³ on the assumption that various atoms correspond to a large number of "elementary principles that can in no way be converted one into another" [17].

In 1822, 'the king of chemists,' J Berzelius (1779–1848), undertook to verify Prout's hypothesis [7, p. 71]. His studies were focused on quantitative proportions in which substances combine with one another and on the development of the atomistic theory. By 1818, Berzelius determined the atomic masses of 45 chemical elements and published them in the form of a table. By continuously improving his measuring techniques, Berzelius arrived at another table known in the history of chemistry as the table of the year of 1826. Apart from a few cases, the atomic weights included in this table are in excellent agreement with the currently accepted ones. For example, the atomic mass of chlorine in the 1826 table of Berzelius was 35.47, to be compared with the real one of 35.45 (in oxygen units, assuming the oxygen mass to be equal to 16). Without going into details of Berzelius's works, it should be noted that the author obtained the atomic weights of chlorine, lead, and some other elements that were inconsistent with the Prout hypothesis; therefore, Berzelius rejected it.

The majority of the continental chemists shared the opinion of the 'king.' In Britain, however, Thomson was

²⁰ These included carbon, nitrogen, phosphorus, oxygen, sulfur, calcium, sodium, iron, zinc, chlorine, potassium, barium, and iodine.

²¹ At the dawn of the atomic theory, chemists and physicists all of a sudden had to deal with divisible molecules composed of atoms instead of an infinite number of Democritus' atoms. It was necessary to learn how to distinguish between simple and complex substances, to understand that the former also consist of molecules, each containing several atoms, and to find the way to determine the number of atoms in simple and complex substances to be able to consistently calculate atomic masses. Of course, it was impossible to resolve the entire set of problems during the seven years between Thomson's publication concerning the atomic theory of Dalton and the anonymous paper that appeared in 1815.

²² Why was oxygen chosen in addition to hydrogen?

²³ Although the successors of Prout never insisted on the division of heavy atoms, an idea to which they might be brought by Prout's hypothesis.

ranked higher than Berzelius, and Prout's hypothesis was considered valid. The British Association of the Advancement of Sciences applied to the country's best analyst, Professor Turner, with a request to reproduce Berzelius's experiments. Turner reported the results of his experiments in 1833 [7, p. 72]. He had repeated measurements of atomic weights of lead, silver, barium, and chlorine and obtained values identical to those of Berzelius. This seemed to be an argument to give up the Prout hypothesis as a bad job despite the interest of the greatest chemists of the century and its contribution to the development of analytical techniques.

However, the eminent French chemist J B Dumas poured oil on the flames by reporting in 1840 that the atomic weight of carbon ²⁴ was 6 and that of oxygen 8, in agreement with the Prout hypothesis. Berzelius disagreed, stating (in 1842) that "Dumas wants, with the stroke of the pen, to cast a shadow of suspicion on the correctness of measurements of all atomic weights."

This review is not intended to discuss numerous attempts at the verification of Prout's hypothesis. It is worthwhile mentioning only the measurements made in the 1860s by the Belgian chemist J Stas, who determined atomic weights with a higher degree of accuracy than Berzelius. The works of Stas once again compromised Prout's hypothesis. Nevertheless, increasingly more scientists adhered to this hypothesis in continental Europe, to say nothing of Britain! Greek philosophy was still influential; hence, the belief in a priori statements indiscriminately prevailed over experimental evidence. By way of example, professor Maryniak of Geneva supported the Prout hypothesis on the grounds that because the majority of the atomic weights were being expressed as values close to integers, the theory of probability argued in favor of rather than against it [7, p. 334].

3. The discovery of argon

It follows from the above that belief in the 'Prout law' persisted as long as 1880 despite its having been disproved by the highly precise measurements of Berzelius, Stas, and many other chemists. It is only in 1882 that the English physicist Lord Rayleigh, also known as J W Strutt (1842-1919),²⁵ summoned the world's scientific community to undertake extensive verification of 'Prout's law.' The scientific interests of Lord Rayleigh embraced the whole range of classical physics, to which this 'last individualist scientist' [18] made such a great contribution. Besides 446 papers, he wrote the famous 'Theory of Sound,' translated into many languages and published twice in Russia. However, he was internationally most renowned during his lifetime for the experiments in which he measured densities of gases, which eventually led him to the discovery of argon, of which "the majority of modern non-British physicists have not the slightest idea" [18].

Rayleigh believed in Prout's hypothesis and did not regard it as disproved. In his capacity as a professor of experimental physics at Cambridge University and the head of the Cavendish Laboratory, Rayleigh encouraged work in its support. He exposed his line of reasoning in his presidential speech at a meeting of the British Association of the Advancement of Sciences ²⁶ [26]:

"Some chemists have reprobated strongly the importation of à priori views into the consideration of the question, and maintain that the only numbers worthy of recognition are the immediate results of experiment. Others, more impressed by the argument that the close approximations to simple numbers cannot be merely fortuitous, and more alive to the inevitable imperfections of our measurements, consider that the experimental evidence against the simple numbers is of a very slender character, balanced, if not outweighed, by the a priori argument in favour of simplicity. The subject is eminently one for further experiment; and as it is now engaging the attention of chemists, we may look forward to the settlement of the question by the present generation. The time has perhaps come when a re-determination of the densities of the principal gases may be desirable -an undertaking for which I have made some preparations."

As the first step towards the verification of 'Prout's law,' Rayleigh decided to measure the atomic mass of oxygen in hydrogen units, which had to be equal to 16 if Prout were right. Rayleigh appears to have had a well-considered plan when he chose oxygen. We try to conceive his line of reasoning.

In order to derive the oxygen-to-hydrogen atomic mass ratio $m_{\rm O}/m_{\rm H}$ in the XIXth century, one had to determine the density ratio of these gases $\rho_{\rm O}/\rho_{\rm H}$ (at a known temperature and pressure) and thereafter measure their volumes that completely reacted with each other (yielding water), i.e., such volumes of hydrogen $V_{\rm H}$ and oxygen $V_{\rm O}$ in which the numbers of molecules were related as $N_{\rm H} = 2N_{\rm O}$.

Because $\rho_{\rm O} = m_{\rm O}N_{\rm O}/V_{\rm O}$ and $\rho_{\rm H} = m_{\rm H}N_{\rm H}/V_{\rm H} = m_{\rm H}2N_{\rm O}/V_{\rm H}$, the measurement of densities and completely reacted volumes yielded the following relation for the atomic masses of the two gases:

$$\frac{m_{\rm O}}{m_{\rm H}} = \frac{\rho_{\rm O}}{\rho_{\rm H}} \frac{2V_{\rm O}}{V_{\rm H}} \,. \tag{1}$$

Had oxygen and hydrogen behaved as ideal gases, the completely reacted volumes of hydrogen $V_{\rm H}$ and oxygen $V_{\rm O}$ would have been related as $V_{\rm H} = 2V_{\rm O}$ and the ratio of their atomic masses reduced [as follows from (1)] to a simple density ratio. However, both hydrogen and oxygen are real gases (even if very close to ideal ones under normal conditions); therefore, measuring their completely reacted volumes is an indispensable prerequisite for the determination of atomic weights.

Rayleigh thought it easier to measure the completely reacted volumes of oxygen and hydrogen by the so-called eudometric technique,²⁷ which provided a high degree of precision.

This method, developed by A Volta, consists of an explosion of the given volumes of oxygen V'_{O} and hydrogen V'_{H} that produces water. The removal of water is followed by the measurement of an excess volume, e.g., of oxygen V'_{O} , corrected for the initial pressure and temperature. Then, obviously, $V_{O}/V_{H} = (V'_{O} - V''_{O})/V'_{H}$.

We omit a detailed description of the measurement of the ratio of completely reacted hydrogen and oxygen volumes as

²⁴ The atomic weights were put twice lower than they should be, probably because Dumas based his calculations on the Berzelius concept.

 $^{^{25}}$ J W Strutt succeeded to the title of the 3rd Baron Rayleigh in 1873, on the death of his father. See [18, 19] for a detailed biography of Lord Rayleigh.

²⁶ Rayleigh was President of the mathematical and physical sections of the Association in 1882.

 $^{^{\}rm 27}$ The eudometer is a small graduated glass tube for the measurement of a gas mixture volume.

having little to do with our story. It should be only noted that both hydrogen and oxygen show a deviation of several tenths of a percent from ideal gas behavior under normal conditions. In 1887, the English experimenter A Scott reported the value $V_{\rm H}/V_{\rm O} = 1.994$ as the most likely estimate [21]. However, in less than one year, he informed Rayleigh by way of personal communication that more thorough measurements [28] gave $V_{\rm H}/V_{\rm O} = 1.9965$.²⁸ It followed from Scott's findings that the atomic mass ratio was 2/1.9965 = 1.0018 times higher than the density ratio of the gases. Today, we know that the situation is quite the opposite of the description given by A Scott.

Rayleigh is sure to have been aware of the oxygen and hydrogen densities measured by the French physico-chemist Henri Victor Regnault in 1845, according to whom $\rho_O/\rho_H = 15.963$. Multiplication of this ratio by 1.0018 yielded the oxygen-to-hydrogen atomic mass ratio 15.992; this value was close to the integer 16.

In the hope of improving the method for measuring gas densities first developed by Regnault, Rayleigh decided to check the values of oxygen and hydrogen densities reported by the French researcher in 1845.

Unfortunately, there are practically no publications in the Russian language about the works of the outstanding French physico-chemist Regnault (1810-1878), a member of the Paris and St. Petersburg Academies of Sciences [22].²⁹ The majority of modern physicists do not know much about experimental problems that their predecessors had to face in the XIXth century. Suffice it to say that university students of our time are not told about methods for the measurement of gas densities. Such methods were for the last time described in a textbook of general physics in 1923 [23]. It is therefore worthwhile reminding ourselves here one of such method proposed by Regnault in his paper "On the Determination of Gas Densities" first published in the proceedings of the French Academy and thereafter in the German language [24]. First, knowledge of the Regnault method is necessary to understand the works of Rayleigh (Rayleigh himself simply referred to Regnault, without dwelling at any length upon his method). Second, the poorly known approach employed by Regnault is aesthetically appealing as an example of a witty solution to a nontrivial experimental task, taking into account that 1 liter of pure hydrogen has the mass 89.9 mg, i.e., much smaller than the variable Archimedes' buoyant force of the air that depends on its pressure, temperature, and humidity.

Regnault resolved the problem of gas density measurement by making two thin-walled glass vessels, each having a volume of about 10 l, with identical external capacities and weights (after the removal of the air). ³⁰

³⁰ The reader is invited to appreciate Regnault's ingenuity by trying to think up a way of making such vessels. Regnault's approach is expounded below.



Figure 1. Experimental setup for the measurement of gas densities (Regnault, 1845).

Two hollow glass spheres A and B were suspended from the pans of a beam balance and placed in wooden boxes to avoid the effects of air flows on them, as shown in Fig. 1. Evidently, the condition of identical external volumes and weights of the sealed spheres guaranteed equilibrium of the beam regardless of ambient air changes (pressure, temperature, water content, concentration of carbon dioxide and other gases). Regnault noted in connection with this: "There is no longer need to continuously follow the readings of a thermometer, barometer or hygrometer; suffice it to wait till the two spheres are in temperature equilibrium; as soon as they reach an equilibrium state, it can last infinitely long" [24]. One glass sphere was then filled with the gas of interest to a predetermined pressure, at a given temperature. While filling up the sphere, Regnault connected it with a manometer and put in melting ice, thereby automatically keeping its temperature at 0 °C.

Thus, there was a glass sphere of a volume V filled with the gas being studied at the temperature 0 °C and pressure P. The mass of the sphere measured by weighing was $M_{\rm sph} = M_{\rm gas} + M_{\rm glass}$, where $M_{\rm sph}$ is the total mass and $M_{\rm gas}$ and $M_{\rm glass}$ are the masses of the gas and the glass.

The pressure was then reduced by p and the weighing was repeated to determine $m_{\rm sph} = m_{\rm gas} + M_{\rm glass}$. Neglecting the nonideal behavior of the gas, $P/p = M_{\rm gas}/m_{\rm gas}$. Then, the obvious chain of equalities $M_{\rm sph} - m_{\rm sph} = M_{\rm gas} - m_{\rm gas} = M_{\rm gas}(1 - p/P)$ was used to calculate the mass of the gas in the sphere at the pressure P:

$$M_{\rm gas} = rac{P(M_{\rm sph} - m_{\rm sph})}{P - p}$$

The density of the gas was calculated by dividing its mass by the volume. Evidently, the density ratio of two gases depended neither on the sphere volume nor on the characteristics of the ambient air.

The higher gas pressure (P) was chosen by Regnault to be of the order of atmospheric pressure and the lower pressure papproximately 10 Torr by measuring the densities of the air, oxygen, hydrogen, and carbon dioxide. The experimental

²⁸ The currently accepted ratio is $V_{\rm H}/V_{\rm O} = 2.004$. In other words, the concentration of hydrogen under normal conditions is slightly lower than that of oxygen, whereas Scott's data led to the opposite conclusion.

²⁹ Regnault greatly contributed to the development of experimental physics in the XIXth century by his practically important and highly precise measurements of many characteristics of gases, liquids, and solids: he "specifically performed measurements of thermal expansion of solids, liquids, and gases, gas densities, the speed of sound in gases, evaporation heat, specific heats, etc. Also, he devised an air thermometer, hygrometer, and pyrometer, proposed tables of gas and mercury expansion and gas elasticity. He most accurately evaluated the mechanical equivalent of heat." [22].

data obtained by Regnault [24] indicated that the oxygen-tohydrogen density ratio under normal conditions was 15.963.

Rayleigh decided to verify 'Praut's law' using oxygen in the hope of obtaining the mass ratio equal to the integer 16. It should be recalled that Rayleigh publicly called for the verification of 'Prout law' in 1882 and set about his own experiments in 1885. During the interim period, he was busy thinking over and designing the measuring procedure from the beginning to the end and preparing the necessary laboratory equipment. At the same time, Rayleigh had to continue his official duties ³¹ and wrote papers. ³²

Rayleigh carried out all the studies at his own expense, for which purpose he refurbished the old stables at his family's ancestral estate of Terling Place for the use as a laboratory. In 1885, he resigned from his professorship at Cambridge and set about private research at Terling assisted by J Gordon, the former head of the maintenance shop at the Cavendish Laboratory when it was directed by Rayleigh (Fig. 2).

It should be recalled that in order to measure gas density, Rayleigh and Gordon had to make two glass globes of equal external volumes and weights using whatever materials they might have at hand. ³³ When describing this part of the work, Rayleigh simply referred to Regnault, who had been the first to propose this method [24].

Certainly, it was impossible to make two absolutely identical spheres. Therefore, in the Regnault experiment, a skillful glass-blower first made a pair of them looking as much alike as possible. Regnault also proposed a clever scheme to compare their external volumes. He filled one globe with water and weighed it (the accuracy attainable in weighing a total mass of some 10 kg was about 0.1 g, corresponding to the relative accuracy 10^{-5}). Then, he weighed the same globe immersed in water (with the same relative accuracy). Naturally, the difference between the two weights was equal to the mass of water in the external volume of the globe, whence this volume was calculated, knowing the density of water at a given temperature. Thereafter, a glass ampule was hung from the small-volume globe whose external volume practically fully compensated for the difference. Regnault did not describe how he manufactured such an ampule, leaving it to the reader to guess his ways. In all probability, he used a thick-walled ampule finely ground to the desired volume. Finally, to equalize the weights of the two globes, Regnault filled the counterpoise one with mercury and sealed it.

The two globes of equal weights and external volumes thus prepared "remained suspended from the pans of the

³¹ In 1882, Rayleigh was a professor of experimental physics at the Cambridge University and headed the Cavendish Laboratory (with its 62 undergraduate students). Simultaneously, he served as the President of the Mathematical and Physical Sections of the British Association for the Advancement of Sciences. In 1884, Rayleigh was elected President of this Association; in 1885, he became Secretary of the Royal Society and kept this position until 1896.

³² Rayleigh published more than one paper per month, on the average, during 30 years. Moreover, he issued a two-volume monograph 'Theory of Sound,' and his article under the title of 'The Wave Theory of Light' written for Encyclopedia Britannica is actually another monograph [25]. ³³All those visiting Rayleigh at Terling Place noted that he used very simple and even crude equipment. Rayleigh was reputed as hating superficial gloss and being thrifty and reluctant to pay extra expenses. All most important details of the equipment he used in his experiments were made and gauged to be thoroughly precise, whereas the remaining ones were manufactured from all sort of improvised materials. At Terling, "wax, ropes, pieces of wood, and glass tubes put together in the most clumsy and unsightly combinations stroke the eye here, there, and everywhere" [18, p. 155].



Figure 2. Lord Kelvin (right) visiting Lord Rayleigh's laboratory at Terling Place (July 1900).

balance for fourteen days; during this time, the equilibrium was strictly maintained although air temperature varied from 0°C to 17°C and barometric pressure from 741 to 771 mm" (Hg) [24]. According to Regnault, an additional advantage of the method (as we might put it today) was that the absorption of water on the glass surface (depending on air temperature and humidity) no longer affected the results of weighing: "At the final stage of the weighing procedure, the observer does not come close to the balance and watches the beam swinging from afar through a spyglass" [24]. Regnault also noticed a subtle effect with which Dumas and Boussingault had been concerned when they measured gas densities prior to him: "wiping the balloons with a dry rag is apt to strongly electrify them. I was surprised to see how much time it took this electricity to disperse; the globe wiped with a dry rag was at first 0.75 g heavier than its baseline weight and still remained 0.1 g heavier after a lapse of 5 hours. Effect of electrization was even more pronounced when the walls of the box were coated with lead and the balloon was placed close to the floor. The electricity was gone after the balloon had been wiped with a wet cloth. As a precaution against this undesirable effect in my experiments, I wiped the globes with a cloth slightly wetted with distilled water and used a gold-leaf electroscope to be sure that there was no electricity left on them. Not infrequently, I left the balloons suspended from the pans of the balance overnight to be sure that their weight remained unaltered" [24].

In accordance with Regnault's description, Rayleigh made globes approximately 1800 ml in volume and 200 g in weight and started taking measurements in 1885. It is difficult to say how long it would have taken him to obtain the results, had his work not been given, quite unexpectedly, a new impetus by a publication that appeared in the proceedings of the American Academy of Natural Sciences in 1887. It was the paper by J P Cook ³⁴ and his co-author entitled "The Relative Values of the Atomic Weights of Hydrogen and Oxygen." Cook attempted to verify the 'Prout law' using the same approach as was chosen by Rayleigh and outstripped him! Evidently, this publication spurred Rayleigh's activity and he submitted his communication "On the Relative Densities of Hydrogen and Oxygen. Preliminary Notice" to the Royal Society on February 2, 1888.

After a brief account of the incentives for his experiments, Rayleigh moved straight to the description of the procedure borrowed from Regnault's article. In modern terminology, the reproducibility of balance readings was 0.1 mg; that is, the results of consecutive weighings (without displacement of the globes) differed by not more than 0.1 mg. Therefore, Rayleigh emphasized that each weight value cited in his communication was an average over several readings.

The balance was placed in the basement where air temperature was practically constant. However, periodic air flows sometimes caused the pans to swing overnight. In the absence of air flows, the beam remained fairly steady.³⁵

Rayleigh modified the Regnault procedure of filling one of the globes with the gas to be weighed. When filling the sphere, Regnault placed it in melting ice, thereby automatically keeping its temperature at 0 °C.

This, however, required that the outer surface of the globe be wiped dry after the filling was completed. This introduced an uncertainty as regards the amount of adsorbed water, which might markedly affect the results of weighing a light gas such as hydrogen. Rayleigh resolved this uncertainty by placing the globe being filled with the gas into a wooden box equipped with two thermometers that measured temperature to the nearest 0.1 °C. The average over the readings of the two thermometers was taken to be the gas temperature (in the absence of uncontrolled effects on the globe surface). The two globes were manipulated in a similar way, that is, they were transferred from the basement to the laboratory and back as cautiously as possible in gloved hands, even though only one globe was filled with the gas.

The complexity of the hydrogen weighing procedure was combined with the necessity of obtaining chemically pure samples of hydrogen and oxygen. In his first experiments of 1885, Rayleigh produced gases by electrolysis of acidified water³⁶ in a U-shaped tube in the hope of obtaining

³⁴ J P Cook was educated at Cambridge.

³⁶ It is well known that electrolysis of a weak sulfuric acid solution with the use of passive electrodes leads to the release of hydrogen bubbles on the cathode and oxygen bubbles on the anode, with the amount of sulfuric acid in the solution remaining unaltered. The complicated process of electrolysis comprises a few intermediate stages, but its outcome is described by the integral formula of the so-called current-generating (current-consuming) reaction: $2H_2O = 2H_2 + O_2$. This means that in the above case, electrolysis results in the chemical decomposition of the solvent rather than electrolyte; in the course of this process, the concentration of sulfuric acid increases near the anode and decreases near the cathode.



Figure 3. Sprengel's mercury pump.

virtually pure hydrogen slightly contaminated with oxygen and vice versa. Rayleigh wanted to remove the oxygen from the hydrogen by forcing the gas mixture through a red-hot tube (to the oxidize oxygen) and drying the purified gas by passing it through phosphoric anhydride. This approach failed and the hydrogen still contained impurities from water, such as dissolved nitrogen. Rayleigh then devised an electrolytic cell in which water had no contact with the atmospheric air and took special measures to purify sulfuric acid in order to improve the hydrogen purification procedure.

The reader must know how a vacuum was created in the XIXth century. Rayleigh used the then standard mercury pumps devised by Töppler and Sprengel. By way of example, Fig. 3 shows the sketch of the Sprengel pump. The principle of its action is very simple: mercury flows down from the top funnel into the vessels at the bottom of the device through the regulator tap and the rubber hose. The flow of mercury captures and carries away gas bubbles from the volume being pumped out, with which it is connected through a tube entering the upper part of the hose from the right. Mercury is periodically poured from the vessels back into the funnel.

The pump operates slowly. It is a Sprengel pump with the funnel for mercury at the top that appears to be pushing the figure of Rayleigh into the background in the photo above (see Fig. 2). Rayleigh wrote that he pumped out the gas until its pressure fell at least 20,000 times compared with the baseline value. This allowed him to neglect the presence of the gas that might still remain in the globe when he repeated

³⁵ Rayleigh noticed that the air flows resulted from a temperature gradient. In winter, the floor of the cellar was warmer than the ceiling, which made the air ascend; in summer, however, the floor was cooler than the ceiling and the air remained close to it, leaving the balance at rest. Rayleigh tried to eliminate excessive moisture in the cellar by bringing in a blanket welldried in front of a fireplace. The blanket absorbed as much as 800 g of moisture within 24 hours. Thus, Rayleigh's cellar was really wet!

the weighing. ³⁷ In other words, Rayleigh estimated the mass of the gas contained in the globe from the weight difference between the filled and the empty globe.

Rayleigh repeatedly filled and emptied the globe, weighing hydrogen after the completion of each procedure. He represented the results of this work as the weights (in grams) of hydrogen produced by electrolysis of a weak sulfuric acid solution corrected for the following combination of parameters: pressure of 30 inches Hg (i.e., P = 762 Torr) and T = 12 °C [26, p. 361).

Novemb	er 5	 0.15811
"	8	 0.15807
"	10	 0.15798
"	12	 0.15792
	Mean	 0.15802

Rayleigh found that the substitution of hydrochloric acid for sulfuric acid in the same apparatus resulted in the release of heavier hydrogen; its weight was 0.15812 g and Rayleigh did not take it into consideration in his further work.

He encountered fewer problems with oxygen. It was obtained by electrolysis of potassium chlorate or its mixture with sodium chlorate. There was practically no dispersion of balance readings (given the pressure and temperature were taken into account), and the weight of oxygen in the globe under identical conditions was found to be 2.5186 g.

It seemed easy to calculate the gas density ratio by dividing the weight of oxygen by the weight of hydrogen. But Rayleigh introduced a correction that had not been made by Regnault, on the assumption that the volume of the globe decreased after the removal of the gas under the effect of compression due to a pressure difference of approximately 1 atmosphere.

The empty globe having been weighed, the counterpoise one was subjected to a stronger expulsive force and the measured weight of the empty globe became smaller than the real one. In other words, any weight value needed to be increased by the expulsive force of the atmospheric air in a volume corresponding to the compression of the globe at the pressure difference of 1 atmosphere.

Rayleigh wrote: "By filling the globe with carefully boiled water, it is not difficult to determine experimentally the expansion per atmosphere." He estimated the correction at 0.00056 g, in excellent agreement with his calculations made in conformity with the theory of thin elastic spherical shells taking the properties of the glass into consideration.

Thus the 'apparent weight' of hydrogen that Rayleigh assumed to be 0.15804 became the 'real' weight after he introduced a correction of 0.00056 g; the corresponding weight of oxygen was 2.5192 g. The real weight ratio 15.884 was smaller than the 'apparent' weight ratio 15.938. Interestingly, by correcting the result (the currently accepted density ratio is 15.90), i.e., reducing it, Rayleigh underestimated the real value by approximately as much as the uncorrected result was overestimated.

Consequently, the oxygen-to-hydrogen density ratio decreased from 15.963 (Regnault, 1845) to 15.884 (Ray-leigh, 1887). Rayleigh was disappointed with his findings,

hence, probably, his desire to designate the result as 'preliminary.' Nevertheless, Rayleigh arrived at the following ratio of the atomic weights of oxygen and nitrogen [with the correction for the deviation from ideal gas behavior, see Eqn (1)]³⁸:

$$\frac{m_{\rm O}}{m_{\rm H}} = \frac{2 \times 15.884}{1.9965} = 15.912\,. \tag{2}$$

Thus, the first step Rayleigh made to verify 'Prout's law' confirmed that Berzelius, Stas, and many other researchers were right: there was no hope of affirming 'Prout's law' by measuring the oxygen-to-hydrogen density ratio. Moreover, Rayleigh himself emphasized, concluding his communication, that even more thorough measurements would increase the value in (2) by at most one or two thousandths.

However, the 'a priori conviction in favor of simplicity' was so deeply rooted in Rayleigh's mind that he decided to recheck Scott's data that he had already taken into consideration in Eqn (2). In other words, he set to determine anew the completely reacted volumes of hydrogen and oxygen. In 1889, Rayleigh published a paper "On the Composition of Water" [28] that opened with the description of his failed "hope of being able to prepare lighter hydrogen than was then possible." Because measurements of water weight composition have no bearing on the subsequent discovery by Rayleigh, it is enough to simply indicate the final result: Rayleigh reduced the oxygen-tohydrogen atomic weight ratio from 15.91 to 15.89. Despite slight variances in the results of different researchers, ³⁹ they must seemingly have put an end to further attempts to confirm 'Prout's law' and led to the discontinuation of any work along this line.

But Rayleigh still believed in 'Prout's law' and tried to recheck the 'preliminary' value of the oxygen-to-hydrogen density ratio! Seven years after his first experiments (in 1892), he published another paper "On the Relative Densities of Hydrogen and Oxygen. II" [29]. Having performed even more thorough studies (not described here), Rayleigh found that the density ratio of oxygen to hydrogen was equal to 15.882 or practically the same (15.884) as he had obtained four years before.

Concluding his report [29], Rayleigh reviewed 11 articles devoted either to the determination of the density ratio of gaseous oxygen and hydrogen or to the direct measurement of water weight composition (from which the oxygen-to-hydrogen atomic mass ratio can be deduced straightforwardly). Nine of these studies carried out between 1888 and 1892 were doubtlessly initiated in response to the call Rayleigh made in 1882. The results of these studies are presented in Table 3, supplemented by the respective current values borrowed from Ref. [12].

We note with reference to this table that Rayleigh, first, stimulated the interest of many researchers in the problem being considered and, second, provided motivation for a more active participation in its development by North American scientists at the end of the XIXth century (Keiser, Cook and Richards, Morley). All of them (with the exception of Keiser) determined the weight composition of water (i.e., the atomic weight ratio of oxygen and hydrogen) more accurately than their European colleagues

³⁷ The pumping out of gases was largely performed by Gordon, Rayleigh's assistant. See Ref [27] for details about Töppler and Sprengel mercury pumps.

³⁸ The current value is 15.8734.

³⁹ See table 3 below.

Table 3.

Author	Date	Atomic weight	Density
Dumas	1842	15.96	_
Ragnault	1845	_	15.96
Reyleigh	1888	_	15.884
Cook and Richards	1888	15.869	_
Keiser	1888	15.949	—
Rayleigh	1889	15.89	_
Noyes	1890	15.896	
Dittmar	1890	15.866	—
Morley	1891	15.879	_
Leduc	1891	_	15.965
Reyleigh	1892	_	15.882
Current values	1991	15.8734	15.90

and reported values practically coincident with currently accepted ones. $^{\rm 40}$

"The work has been unusually tedious" [29, p. 463] during the seven years that had elapsed before Rayleigh published his results in 1892.⁴¹ He stopped further attempts to verify experimentally disproved 'Prout's law' even though seemingly continuing to believe in it as follows from his statement that the measured values might have been underestimated because the hydrogen was contaminated by mercury vapor.

For all that, Rayleigh did not give up the 'tedious' measurements of gas density altogether. He exhibited his inborn talent of an experimenter by using the acquired experience to accurately measure the absolute densities of principal gases. For this, he had to know the weight of a gas in a globe relative to the weight of water in the same globe. Water density was measured by many researchers both before and after 1893 (see footnote 40). Rayleigh published a paper "On the Densities of the Principal Gases" in 1893 [31]. The results of this work are briefly expounded below without many details, reported as usual by the author, who again referred to Regnault's method.

Rayleigh found the gas-to-water density ratios under normal conditions and T = 4 °C to be as follows: ⁴² 1.4295 (1.4290) for oxygen, 0.09001 (0.08988) for hydrogen, and 1.25718 (1.2506) for nitrogen. Comparison of these figures with current values indicates that the relative error of Rayleigh's estimates was of the order of $0.0005/1.429 \approx$

⁴¹ Rayleigh called 'tedious' the procedure of weighing gases to an accuracy of 0.1 mg and numerous breakdowns that now and then brought to naught large volumes of preparatory work.

⁴² For convenience, the gas-to-water ratios are multiplied by 1,000; the currently accepted values (from [32]) are given in parentheses.

 $\approx 3 \times 10^{-4}$ (as shown below, there was some systematic error).

Rayleigh prepared nitrogen following the advice of Ramsay by blowing air through liquid ammonia and then through a tube containing red-hot copper. The copper absorbed the oxygen, the ammonia partly decomposed releasing nitrogen, the hydrogen reacted with the oxygen, and excess ammonia and water vapor were absorbed by sulfuric acid. Having obtained some consistent results, Rayleigh was about to stop working with nitrogen. Had he done so, he would have never made his greatest discovery. However, Rayleigh was a first-class experimenter. As he said in his Nobel lecture, he was aware that Regnault had obtained nitrogen by a different method. Therefore, to be able to correctly compare his results with those of Regnault, he decided to reproduce Regnault's procedure, that is, to simply pass air over red-hot copper and thus have oxygen (and, naturally, water and carbon dioxide) absorbed from it.

To give an idea of the statistical error, Rayleigh as usual reported the results of a series of weighings. Having prepared nitrogen by Regnault's method and weighed it in a sphere on different days, Rayleigh obtained the following results⁴³ (in grams) reduced to T = 14.85 °C and P = 762.511 Torr [31, p. 145]:

1892,	August	8	 2.31035
	"	10	 2.31026
	"	15	 2.31024
	M	ean	 2.31028

In other words, statistical absolute dispersion of gas weights measured in different days was of the order of 0.00007, corresponding to the relative precision 3×10^{-5} .

In the end, Rayleigh's many years of effort and unprecedented conscientiousness were rewarded: he documented the difference between the densities of nitrogen prepared by two methods, which was significantly higher than the statistical accuracy of the measurements.⁴⁴ Rayleigh began to search for the cause of the discrepancy. He excluded contamination of 'light' nitrogen with hydrogen, ammonia, and water vapor because his experiments preceding the discovery of the 'nitrogen anomaly' had demonstrated that hydrogen added to the air during isolation of nitrogen had no effect on gas density. Contamination of 'heavy' nitrogen with oxygen was equally unlikely because the weights of the two gases were rather similar and the oxygen content in 'heavy' nitrogen must have been very high (hence, easily detectable). Unable to account for the 'nitrogen anomaly,' Rayleigh wrote a "Letter to the Editor" entitled "The Density of Nitrogen" and sent it to the journal *Nature*, then popular among researchers. The paper was submitted on September 24, 1892 and published on September 29 [33].

When informing the scientific community about his surprising finding, Rayleigh demonstrated a rare example of a researcher looking for help to elucidate the problem of nitrogen density: "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.

⁴⁰ At about the same time, D I Mendeleyev, then Director of Russia's Main Chamber of Weights and Measures, was also engaged in weighing studies. In 1896, he determined the weight of 1 liter of water at 4° C as 999.847 g instead of 999.973 g (an error of 126 mg) [30], although the attainable weighing precision during his time was 0.1 mg per 1 kg. For comparison, all five groups of French researchers who measured the weight of 1 liter of water in 1899–1909 obtained values that differed by less than 2 mg from the currently accepted one, i.e., 60-100 times more accurate than Mendeleyev's result [23, p. 265].

⁴³ The reader is sure to remember that each value in the table is an average of many weighings.

⁴⁴ Rayleigh prepared oxygen in different (three) ways, but the oxygen density was independent of the method employed, within the experimental accuracy.

According to two methods of preparation I obtained 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" [33, p. 512].

At the same time, Rayleigh expressed his own opinion as to the cause of the discrepancy: "Is it possible that the difference is independent of impurity, the nitrogen itself being to some extent in a different (dissociated) state?" [33, p. 513].

Rayleigh's address aroused the criticism of some chemists [20, p. 17]. In all likelihood, their opposition reduced to the fact that a chemically pure substance, be it nitrogen or any other element, must not change its properties depending on the way it was obtained by a researcher. In his book "Life of John William Strutt, Third Baron Rayleigh,"⁴⁵ Rayleigh's son mentions some letters addressed to his father containing some useful advice that, however, failed to answer the question [34, p 89]. One of the letters was from professor W Ramsay of the London University College, dated November 20, 1892, which contained comments on Rayleigh's experimental findings and mentioned Ramsay's interest in the problem. Ramsay "asked for and obtained the permission to make some experiments with the purpose of explaining, if possible, the unusual behaviour of the atmospheric air. He abstained from publishing on this subject for a year" [20, p. 18].

Rayleigh continued to investigate the nitrogen problem seeking to increase the discrepancy! Two years later, he wrote explaining his decision: "In the beginning, it was an instinctive drive to try and avoid this discrepancy, but the experience showed that it was the wrong choice. It was in fact necessary to enhance this small discrepancy to find an explanation" [20, p. 17].

In his paper on the densities of principal gases published in 1893 [31], Rayleigh reported that the use of chemically pure oxygen instead of the air to obtain nitrogen from liquid ammonia (with subsequent absorption of oxygen by red-hot copper) resulted in a five-fold larger discrepancy, i.e., 0.5% versus 0.1%. In other words, chemically pure nitrogen proved 0.5% lighter than the 'atmospheric' gas! Reporting this result as 'preliminary,' Rayleigh put forward the hypothesis of the dissociated state of lighter nitrogen.

From this time on, Rayleigh focused on the 'nitrogen problem.' In February 1894, he submitted a paper "On an Anomaly encountered in Determinations of the Density of Nitrogen Gas" to the Royal Society. The paper immediately appeared in the *Chemical News*⁴⁶ published by Crookes and thereafter was published as usual in the "Proceedings of the Royal Society" [35].

In this paper, Rayleigh confirmed the 0.5% difference between the densities of 'atmospheric' and chemically pure nitrogen but rejected the explanation of this anomaly as a result of contamination of 'atmospheric' nitrogen by oxygen or chemically pure nitrogen with light gases, such as hydrogen or water vapor. Rayleigh obtained pure nitrogen by several different methods including the reaction between ammonia and oxygen in the presence of red-hot copper or carbon-free iron and the decomposition of NO and NO_2 over red-hot iron. Each time, the density of chemically pure nitrogen was 1/200 times smaller than that of the 'atmospheric' gas (the weight of the sphere was 11 mg smaller).

Rayleigh's results are illustrated by tables presenting gas weights (in grams) in a sphere corrected for pressure and temperature [35, p. 343].

Nitrogen from air by hot iron:

1892,	December	r 12	 2.31017
	"	14	 2.30986 (H)
	"	19	 2.31010 (H)
	"	22	 2.31001
		Mean	 2.31003

The symbol H on the right indicates the presence of a hydrogen admixture in the air, which had no substantial effect on the results of weighing.

Nitrogen from N₂O by hot iron:

1892,	December	26	 2.29869
	"	28	 2.29940
	Ν	lean	 2.29869

To check the natural suggestion that the heavy weight of nitrogen might be due to the formation of N_3 molecules, Rayleigh exposed pure nitrogen to the action of a weak electric discharge in an apparatus in which he produced ozone O_3 from oxygen. This, however, had little effect on the weight of chemically pure nitrogen, as can be seen from the table below [35, p. 344].

Nitrogen from N₂O by hot iron, electrified:

Rayleigh stored chemically pure nitrogen for eight months and then weighed it again. The result was the same, that is, chemically pure nitrogen remained 0.5% lighter than the 'atmospheric' gas. Rayleigh made no comment but his thought was perfectly clear: had light chemically pure nitrogen been present in a dissociated state, its atoms would have combined into heavier molecules during the storage and it would have become heavier.

Rayleigh's paper [35] was presented at the meeting of the Royal Society at Oxford on April 19, 1894. The meeting was attended by Ramsay, who discussed the 'nitrogen anomaly' with Rayleigh and first thought some technical mistakes by Gordon (Rayleigh's assistant) to be its probable cause. However, neither Gordon nor Rayleigh had made a mistake. There was practically no doubt that the air contained an unknown heavy component, "although the question of whether it was an element or a compound remained open." Rayleigh's paper contains no indication as to the possible source of the discrepancy. It may be supposed that he did not want for a time to make even a preliminary note of a discovery because the amount of the residual gas was not necessarily proportional to the amount of the air needed for its production. Later, it was shown that this discrepancy resulted from water absorption by argon. Apart from this and other facts, Rayleigh was cautious about a premature

⁴⁵ Unfortunately, the author had no opportunity to look through this book, unlike all other references cited in this review.

⁴⁶ The full title of the Journal: *The Chemical News of Physical Science*. *With which incorporated the "Chemical Gazette". A Journal of Practical Chemistry in all its Applications to Pharmacy, Arts, and Manufactures.*

publication of his data (as Schuster witnesses) not only because he was very particular about what appeared under his name but also because, in his words, 'mockers would be encouraged' [20, pp. 19, 20]. Moreover, Rayleigh knew about the will of Godkins "under which a prize of 10,000 US\$ was established for the most important discovery in the atmospheric sciences. The nominees had to submit a manuscript of the scientific work to the prize-awarding-committee" [34, p. 98]. To make a long story short, suffice it to mention that the work of Rayleigh and Ramsay was nominated for the Godkins prize (together with 217 others) and the authors received the award in 1895 [20, p. 25].

On the next day after Rayleigh delivered his work, Crookes, a co-member of the Royal Society and the publisher of *Chemical News*, wrote to him to give valuable advice "to prepare nitrogen from the air and measure its density. In fact, you have already done it. Now, it is necessary to mix up identical amounts of nitrogen and oxygen, pass an electric spark through this mixture, and absorb the products of the reaction on caustic soda.⁴⁷ Then, you should remove oxygen and measure density. I presume that another gas does not combine with oxygen when the spark is passed through the sample.... Anyway, one should have something in view when searching for the unknown" [34, p. 91].

In other words, this letter of Crookes mentioning 'another gas' gives evidence that Rayleigh had told at least Crookes about his suspicion of 'another gas' being present in the atmosphere and accounting for the 'nitrogen anomaly.' Crookes also advised Rayleigh to bind nitrogen from the 'atmospheric nitrogen' as Cavendish had done in 1785. As mentioned earlier, the eminent English physico-chemist⁴⁸ Cavendish described in his paper 'Experiments on Air' the method of nitrogen oxidation⁴⁹ by which he actually isolated pure argon from the air.

Cavendish placed a mixture of air and oxygen together with a small amount of potash 50 over a layer of mercury in an overturned U-shaped tube (about 2.5 mm in diameter) and passed sparks generated in an electrophorus through a gas column for two weeks. The discharges produced oxides including nitrogen dioxide (a reddish-brown gas with a characteristic smell) that formed nitric and nitrous acids when reacting with water. As a result, the volume of the air/ oxygen mixture gradually decreased as nitrogen was oxidized and the oxides dissolved in water. ⁵¹ At the end of this process, Cavendish discarded the mercury, evaporated the remaining solution to dryness, and obtained a salt precipitate. Burning a sheet of paper wetted with the solution of this salt left potassium nitrate as a residue.⁵² Indeed, anyone studying chemistry at school now knows that nitric acid reacts with potash yielding potassium nitrate KNO₃.

However, Cavendish was not satisfied with the result obtained. He emphasized that nitrogen was a poorly known gas and thought that phlogisticated air (nitrogen) might actually be a mixture of gases. He wrote: "I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest which would refuse to undergo that change." 53 The results of the experiments described in a preceding paragraph indicated that when the mixture contained five parts oxygen and three parts atmospheric air, it practically disappeared even if it was impossible to say whether the residue had the properties of nitrogen. Cavendish addressed this problem by markedly reducing the volume of the air-oxygen mixture and adding more oxygen to the residue while continuing a discharge of electric sparks through the mixture until its volume stopped decreasing. After he removed oxygen from the residue, he was left with a bubble, the volume of which was not more than 1/120 of the initial nitrogen volume. He therefore concluded: "... if there is any part of the phlogisticated air in our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than 1/120 part of the whole" [37, p 194].

For some unknown reason, the outstanding work of Cavendish, who had actually isolated argon from the air as early as 1785, did not attract the attention of any chemist during the next one hundred years. As mentioned above, it was an accepted dogma that the principal constituent elements of atmospheric air were nitrogen and oxygen (with a minor impurity of some known gases, such as water vapor, hydrogen, carbon dioxide, ammonia, and a few others). After a lapse of 110 years, Rayleigh, guided by advice of Crookes, ⁵⁴ repeated Cavendish's experiment.

Instead of an electrophorus, Rayleigh used a more powerful source of alternating voltage, an inductor or Ruhmkorff coil (named after a Paris-based inventor who began devising large high-voltage generators in 1850). The primary coil of his inductor (in fact, a set-up transformer) was excited by a battery of several volts and the current in the primary circuit was frequently interrupted automatically; the oldest type of circuit breaker, a hammer breaker, was used for the purpose, i.e., a relay that disconnected the primary circuit from time to time as current passed through it.

The air mixed with oxygen was enclosed in tube A (Fig. 4) positioned over a large amount of weak alkaline solution B.

Wires sealed in two glass U-shaped tubes C placed in an alkaline solution delivered voltage to tube A. The ends of inner platinum electrodes D were sealed in glass and the downward bends of tubes C were filled with mercury for better insulation of the electrodes from the ambient air. Electric sparks were roughly 5 mm in length, and the volume reduction rate (in correct proportion) was approximately $30 \text{ cm}^3 \text{ hr}^{-1}$, i.e., 30 times that in the Cavendish experiment.

Rayleigh started from an air volume of 50 cm³ to which portions of oxygen were added in succession until the volume was reduced within one hour. Following the removal of oxygen from the residual volume of 1 cm³ (using alkaline pyrogalate as an absorber), the remaining 0.32 cm³ was again transferred to tube A together with a new 50 cm³ portion of air; the new residue had the volume 2.3 cm³ (0.76 cm³ after the removal of oxygen). Generally speaking, the amount of nonoxidizable residue was only approximately (rather than strictly) proportional to the initial air volume, which confused

⁴⁷ Caustic soda is NaOH (note by A.A.M.).

⁴⁸ Cavendish is largely known to physicists for determining the gravitational constant with the help of a torsion balance.

⁴⁹ Cavendish did not use such terms as oxygen and nitrogen, which he called 'de-phlogisticated' and 'phlogisticated' air, respectively.

⁵⁰ Potash is $K_2CO_3(+2H_2O)$.

⁵¹ As shown by Rayleigh and Ramsay [37, p 195], the gas volume during continuous work of the electrophorus used by Cavendish and his assistant decreased at a rate of about 1 cm³ hr⁻¹.

⁵² Potassium nitrate is still used to manufacture fuse paper.

⁵³ Cited from [37, p. 194].

⁵⁴ There is reason to believe that Rayleigh received similar advice from J Dewar [18, p. 157].



Figure 4. Apparatus for the removal of nitrogen from the air by the method of Cavendish (Rayleigh, 1894).

Rayleigh. However, his hypothesis of high solubility of the new gas in water (as the cause of deviation from strict proportionality) was soon confirmed.

In the end, Rayleigh had an amount of the gas sufficient for spectral analysis, which demonstrated that the new gas isolated from the atmospheric air was not nitrogen. This is how Ramsay, Rayleigh's co-author, described the spectrum generation procedure using a gas-discharge tube (Fig. 5):

"Such a tube called a Pflücker's tube, after its inventor, contains wires of platinum sealed through at each end, where it is about half an inch in width; the middle portion of the tube is about 3 inches long, and its bore is a fine capillary. When the platinum wires are connected with the secondary terminals of a Ruhmkorff's coil, and the tube is partially exhausted, a brilliant glow appears in the capillary portion. If viewed through a glass prism, different gases show different sets of coloured lines crossing the usual gradation of colours of the spectrum. Thus, hydrogen exhibits three striking lines, one bright red, one peacock-blue, and one violet; nitrogen shows a large number of somewhat hazy bands, red, orange, yellow, and yellow-green in colour; but the new gas, while exhibiting the bands characteristic of nitrogen, showed in



Figure 5. Gas-discharge or Pflücker's tube.

addition certain groups of red and green lines which did not appear to belong to spectrum of any known gas" [38, p. 162].

William Ramsay, an experienced chemist, started his nitrogen-binding experiments in April 1894, i.e., simultaneously with Rayleigh. Ramsay and his co-workers not only knew the Cavendish method for nitrogen oxidation but were also aware of the ability of magnesium shavings to absorb it.⁵⁵

Ramsay decided to heat to redness fine magnesium shavings that loosely filled a tube of fire-proof glass in the presence of atmospheric nitrogen. The nitrogen was thoroughly purified from oxygen that would otherwise also bind to metallic magnesium (Fig. 6). The very first attempt produced a 40 cm³ residue.

Despite the small amount of gas, Ramsay expected that the rise in its weight would be significantly greater than the accuracy of the weighing procedure. The first weighing in May 1894 demonstrated that the density of the residual gas increased and it became 15 times heavier than hydrogen (rather than 14 times as would have been the case if it were pure nitrogen).

"The result was encouraging, and led to the probability of the nitrogen being altered in some way, or of the presence of some new component of the atmosphere. An experiment was therefore begun on a larger scale, the atmospheric nitrogen being passed backwards and forwards from one large glass gasholder A to another B, through a tube filled with magnesium heated to redness G, to absorb nitrogen; over red-hot copper oxide (a) (b), so that any carbonaceous matter such as dust should be oxidized to carbon dioxide and water; and these, if produced, were absorbed by placing in the train of tubes, one filled with a mixture of soda and lime F and I, to absorb any carbon dioxide which might possibly be formed, and two filled with pentoxide of phosphorus D and H, to dry the gas, so that water-vapour, carried along with the gas from the gasholders (which contained water) might be removed before the gas passed over the red-hot magnesium; for water acts on hot magnesium, forming oxide of magnesium and hydrogen, and the gas would have become contaminated with the latter had this precaution not been taken.

"The process was continued for ten days, by which time most of the nitrogen had become absorbed. The apparatus was then somewhat altered, so as to make it possible to work with a small quantity of gas; but the tubes destined to absorb nitrogen, hydrogen, etc., were filled with the same material as before. In a few days more the volume was reduced to oneseventh of what it had been when the transference to the smaller apparatus was made, or about one-eightieth of the original volume of the atmospheric nitrogen taken.

"The gas was then weighed, this time in a larger bulb, the weight being 0.2190 gram; and such is the possibility of precision in weighing on a good balance, that a difference of one two-thousandth of the whole weight was detectable. The density of the gas was now found to be 16.1. At this stage it was still believed that the new gas was ozone-like modification of nitrogen, difficult to attack by magnesium.... Hence, it was resolved to continue the absorption with fresh magnesium for a still longer time, in the hope of its being possible to isolate three-atom nitrogen molecules. But it became apparent that the bright metallic magnesium was now not much

⁵⁵ A few years before, Ramsay had tried to synthesize ammonia from a mixture of hydrogen and nitrogen passed over red-hot metals and found that magnesium shavings absorbed nitrogen fairly well.



Figure 6. Diagram of experimental setup for nitrogen absorption from the air (Ramsay, 1894).

attacked; and on estimating the total amount of nitrogen absorbed, by treating the compound of nitrogen and magnesium with water, and liberating the nitrogen as ammonia, it appeared that only a small quantity of magnesium nitride had been formed. The density of this further purified gas was again determined, when it was found that a litre now weighed 1.7054 gram, corresponding to a density of 19.086.

"A portion of this gas was mixed with oxygen and exposed to a rain of electric sparks in the presence of caustic soda; in fact, Cavendish's old plan of causing nitrogen to combine was now resorted to. Contraction occurred, and on removing the excess of oxygen, the diminution of volume was found to amount to 15.4 per cent of the original volume taken. Making the supposition that the gas of density 19 still contained



Figure 7. Ramsay in his laboratory.

nitrogen, and allowing for its influencing the density, it followed that the pure gas should be twenty times as heavy as nitrogen."

Having completed the experiment on nitrogen absorption by magnesium on August 3, 1894, Ramsay sent a sample of the gas to Crookes for spectroscopic analysis. On August 4, he wrote a letter to Rayleigh informing him about the result of the experiment. "At last, I isolated the new gas. Its density is 19.075 and it is not absorbed by magnesium. The density of gas X was growing continuously in the course of the absorption process; as you can see, the results are not occasional and go beyond possible experimental errors" [34, p. 94]. Two days later, Rayleigh answered: "I suppose I have also isolated the gas even if in a negligible quantity.... As regards publication, I was about to send some results of the work to Oxford, but they are so closely connected with yours that it seems difficult if not impossible to present them separately. In my opinion, the only fair decision that may be taken is a joint publication" [35, pp. 94, 95]. Ramsay gave his consent on August 7: "I believe that joint publication would be the best option and I am grateful for the offer" [34, p. 97].

In his letter, Rayleigh alluded to the then forthcoming meeting of the British Association for the Advancement of Sciences to be held at Oxford in August 1894. Rayleigh and Ramsay decided that they had rather convincing evidence of the presence of an unknown gaseous element in the air and Rayleigh reported the discovery (as made jointly with Ramsay) at the meeting of the Chemical Section on August 13. The information about this report appeared in The Times and Crookes, editor of Chemical News, published a note about the claimed discovery of a new gaseous element in the atmosphere in the issue that came out on August 24 [40]. The accompanying note said that, according to Rayleigh, the purification of atmospheric nitrogen from all known gases left about 1% of a previously unknown gaseous material more inert than nitrogen. The density of this new gas referred to hydrogen was 18.9-20.0 and the characteristic spectrum was different from that of nitrogen.

The report by Rayleigh aroused interest, surprise, and skepticism bordering on impudence. O Lodge, a physicist, asked Rayleigh after he ended his lecture: "Have you not, gentlemen, discovered the name of this gas either?" [34, p. 97]. In fact, Lodge hinted that Rayleigh and Ramsay had isolated a known gas but described it as something new. Rayleigh's comember of the Royal Society, Dewar, professor of chemistry at the Royal Institute, immediately sent two letters to *The Times* at an interval of only one day (August 15 and 16) that were also published in the *Chemical News* [40]. In the first letter, Dewar called the unknown gas new nitrogen and categorically stated that the content of an unknown component in the atmosphere, if any, must be negligibly small and by no means amount to one per cent. In other words, Dewar, by hastily sending his letter before he promptly looked into the essence of the matter, likened himself to a character from Chekhov's short story who asserted that there can be no spots on the sun just because there can be no such thing at all [41, p. 14].

On the next day, Dewar sent another letter, as an afterthought, in which he did not so indiscriminately refute the discovery of a 1% impurity in nitrogen by Rayleigh and Ramsay but expressed an opinion that these authors had obtained triatomic molecules of 'ozone-like' nitrogen N_3 (rather than a new element) as they were removing usual nitrogen from the air, in analogy with the creation of ozone by exposing oxygen to the action of electric discharges. Dewar thought that the interaction between nitrogen and red-hot magnesium produced 1% of N_3 molecules nonexistent in the air under the normal condition.

"The journal *Electric Review* launched a campaign against the 'myth of the new gas' and suggested that researchers 'should study the new gas by well-known analytical methods and cease to mislead public opinion by alluding to 'spectral analysis'" [34, p. 98].

Setting aside insolent attacks, the constructive criticism aroused by the first report by Rayleigh on the discovery of an unknown gas was quite appropriate taking into consideration that this verbal presentation was too short and of a preliminary character; moreover, it was not followed by a written publication. Now, the co-authors of the discovery had to disprove Dewar's opinion of that they had obtained the new gas (i.e., triatomic nitrogen) as they isolated nitrogen from the air, that is, to confirm its constant presence in the atmosphere, accurately measure its density, and determine its physical and chemical properties. The next four months were devoted to intense work, with Rayleigh bearing responsibility for the physical part of the study and Ramsay for its chemical aspects.

The results of the joint work were summarized in a detailed report delivered by Ramsay at a meeting of the Royal Society, the highest attended to that date (over 800 listeners) and chaired by Lord Kelvin, its president. This presentation was followed by a paper entitled "Argon, a New Constituent of the Atmosphere" [37], published on 54 full-size pages in *The Philosophical Transactions*, an official edition of the Royal Society. This time, Rayleigh and Ramsay presented comprehensive proofs for the existence of a new atmospheric gas, leaving not a single chance for sneering. The paper by Rayleigh and Ramsay comprised 16 paragraphs.

The first paragraph, "Density of Nitrogen from Various Sources," described different methods for obtaining nitrogen from chemical compounds, including the method of nitrogen preparation from urea, besides others mentioned earlier in this review. Also described was the procedure for the isolation of nitrogen from the air. Nitrogen in the air was first bound by red-hot magnesium and thereafter converted to ammonia by the treatment of magnesium nitride with water. The resulting ammonia served as a source of nitrogen having a density identical to that of the chemically pure gas. The authors presented final absolute densities of atmospheric and chemically pure nitrogen under normal conditions as 1.2572 and 1.2511 g l⁻¹, respectively, with the latter value differing by only 0.0005 g from the currently accepted density 1.2506 g l⁻¹.

The second paragraph had the title "Reasons for Suspecting a hitherto Undiscovered Constituent in Air." It argued against the thesis that the 'nitrogen anomaly' was a consequence of contamination of chemically pure nitrogen with light gases or its dissociation, which had long ago been disproved by Rayleigh. Chemically pure nitrogen could hardly be a component of a mixture because all nitrogencontaining substances, such as nitric acid, would then be mixtures too. This line of reasoning led the authors to the simplest supposition that 'atmospheric nitrogen' must contain a heavy impurity. They indicated that if the impurity had a weight twice that of nitrogen, the addition of 0.5% of it would be enough; if its weight were 1.5 times that of nitrogen, 1% would be sufficient. Hence, the surprising fact that this admixture surrounding us in such a huge amount remained unnoticed until 1894.

To prove that they were right and to disprove the Dewar's statement that the new gas was created during nitrogen removal from air, the authors referred to the phenomenon of diffusion successfully employed to separate mixtures in the absence of chemical reactions. However, they postponed the description of relevant experiments until paragraph 6 as performed later in the course of their work. Before this, they deemed it necessary to remind their readers that pure argon had actually been obtained by Cavendish as early as 1785 (as mentioned in the foregoing) and that they themselves just reproduced the Cavendish experiment to prepare this gas.

The third paragraph, entitled "Methods of Causing Free Nitrogen to Combine," contained the description of all known nitrogen compounds.

The fourth paragraph, "Early experiments on sparking with Oxygen in presence of Alkali," was devoted to the Cavendish experiment as reproduced by Rayleigh (see above).

The fifth paragraph, "Early Experiments on Withdrawal Nitrogen from Air by means of Red-hot Magnesium," contained the account of the first successful attempt of Ramsay (described earlier in the present paper) to remove nitrogen from the air.

The sixth paragraph was entitled "Proof of the Presence of Argon in Air, by means of Atomolysis" and provided direct evidence that argon was an inherent constituent component of the atmosphere and not a by-product of nitrogen removal from the air. Indeed, this section was designed to reject Dewar's unconvincing objection cited above.

Rayleigh constructed his apparatus for the separation of a gaseous mixture by arranging 12 long clay chibouques of tobacco-pipes into three groups, each containing four seriesconnected chibouques. All three groups were enclosed in a glass tube in which low pressure was maintained with the help of a water pump. One end of each chibouque passed through the sealed outlet to be enclosed in a glass vessel containing bars of caustic soda (usually used to dry the air) and the opposite end to enter a bottle initially filled with water that served as the aspirator (a pumping-out device).

The air from the vessel went into chibouques, through which lighter fractions, i.e., nitrogen and oxygen, were the first to diffuse; the heavier argon-rich mixture entered the aspirator. It took 16 hours to collect 4 liters of the gas. The mixture thus obtained was then used to remove (by a routine procedure) 'atmospheric nitrogen' that turned out to be much heavier than the usual 'atmospheric nitrogen' isolated without diffusion. The result of the experiment indicated that the 'atmospheric nitrogen' was a mixture that could be partly separated by means of diffusion. Any chemical reaction in the course of this process was out of the question. Thus, Dewar's opinion was refuted.

The seventh paragraph had the title "Negative Experiments to Prove that Argon is not derived from Nitrogen or from Chemical Sources." It is worthwhile to note that this issue was a matter of disagreement between Rayleigh and Ramsay. The latter maintained that the available data provided enough evidence of Dewar's error and further work in the same direction would be a waste of time. In the end, however, he consented to continue investigations to meet Rayleigh's stricter requirements.⁵⁶ The researchers used 3 liters of pure ammonia that was, as usual, absorbed by magnesium in Ramsay's laboratory, with no residual material left after the procedure was completed. While the diffusion experiment demonstrated that argon was an indispensable component of the air, the complete absorption of pure nitrogen in the process that, according to Dewar, 'created' the new gas from nitrogen, gave indisputable evidence that argon was not a derivative of nitrogen. This conclusion was confirmed several times by varying the conditions of absorption

Rayleigh and Ramsay needed large amounts of argon to elucidate its physical and chemical properties. Therefore, they devised a few apparatuses that they described in the eighth paragraph of their communication under the title "Separation of Argon on a Large Scale."

The ninth paragraph, "Density of Argon prepared by means of Oxygen," dealt with the first calculation of argon density (that did not require large quantities of the gas) by comparing the densities of chemically pure and atmospheric nitrogen taking into account the volume of the residue left after the removal of nitrogen from the air by Cavendish's method. The elementary computation on the assumption that argon was the sole impurity in nitrogen gave its exaggerated density of 20.6 because the real content of argon in nitrogen was higher than the measured one due to its high solubility in water. The authors arrived at the necessity of directly determining the argon density.

This issue was treated in the tenth paragraph, entitled "Density of Argon prepared by means of Magnesium." The authors concluded that the density of argon under normal conditions was 19.88 (based on hydrogen as one). Naturally, Rayleigh and Ramsay could not determine the parameter of interest with absolute precision because their argon contained traces of all the other noble gases. Nevertheless, their result was not significantly different from the currently accepted value 19.85 (in the same units) [32].

In the eleventh paragraph, "Spectrum of Argon," the spectrum of the new gas was described with reference to the results of similar investigations carried out by the physicist Arthur Schuster, but first and foremost to the thorough spectral studies by Crookes, a recognized expert in this field.⁵⁷ The publication by Rayleigh and Ramsay was followed in the same issue of the journal by a detailed paper by Crookes, "On the Spectra of Argon" [42]. Interestingly,

the investigations into the argon spectrum provided grounds for the assumption that argon itself may be a mixture of different gases. Specially emphasized was the identity of the spectra of gases prepared 'by means of red-hot magnesium' and 'on sparking with oxygen.' The spectrum of sufficiently purified argon displayed no nitrogen lines.

The twelfth paragraph, "Solubility of Argon in Water," provided an explanation why argon disappeared when a small amount was placed in a large volume of water. The cause was its high solubility, estimated at 3.94 gas volumes per 100 water volumes at 12 °C, i.e., almost 2.5 times that of nitrogen. It led to the conclusion that argon had to be concentrated in rain water. Special studies demonstrated that the concentration of argon in the gaseous fraction dissolved in rain water was actually higher than in atmospheric air. Simultaneously, the argon content in certain mineral sources was determined.

The thirteenth paragraph, under the title "Behaviour at Low Temperatures," was devoted to the measurement of the argon boiling and melting points. Rayleigh and Ramsay had no equipment for the liquefaction of argon. Therefore, a sample of the gas was sent by Ramsay to K Olszewski of Krakov, a then reputed expert on the behavior of substances under low temperatures. Forestalling the report by Olszewski in the same journal [43], Rayleigh and Ramsay presented his measurements of the argon boiling and melting temperatures (made at normal pressure) as $-186.9 \,^{\circ}\text{C}$ ($-189.6 \,^{\circ}\text{C}$), respectively (for comparison, figures in parentheses represent the currently accepted values).⁵⁸ These data hardly need any comment.

The fourteenth paragraph, "The ratio of the Specific Heats of Argon," investigated the important question of the molecular composition of the gas. Today, any good undergraduate student knows that in the framework of classical physics (in conformity with the Boltzmann principle of equipartition of energy by the degrees of freedom), the ratio of specific heats of a gas at constant pressure and volume, C_p/C_v , depends on the number *i* of the degrees of freedom of the molecule: $C_p/C_v = (i+2)/i$. Numerous measurements of this ratio for air under the normal conditions yielded the value $C_p/C_v \approx 1.4$, which suggested the presence of five degrees of freedom (three translational and two rotational) in diatomic molecules of oxygen and nitrogen. It was known that for mercury vapor at a sufficiently elevated temperature, $C_p/C_v \approx 5/3$. This meant that mercury was monoatomic at a high temperature. At the same time, the C_p/C_v ratio could not be used to find an integer number of the degrees of freedom in the molecule, despite its decrease with increasing complexity of the molecules. As is known, the explanation for such behavior of gases came only with the development of the quantum concept. Nevertheless, the classical Boltzmann concept worked fairly well for mono- and diatomic gases.

Ramsay determined the C_p/C_v ratio for argon by measuring the velocity of sound in the gas. It is known [44, p. 29] that the velocity of sound in a gas was first determined by Newton (not quite correctly); his findings were supplemented by Laplace, who derived the well-known formula for the velocity of sound v in gases:

$$v = \sqrt{\frac{p}{\rho}} \frac{C_p}{C_v},\tag{3}$$

⁵⁸ K Olszewski also determined the critical pressure and temperature of argon.

⁵⁶ In the book *Life of John William Strutt, Third Baron Rayleigh*, his son wrote: "One could hardly expect that the partnership of these two people [Rayleigh and Ramsay — *A.A.M.*] would last longer than a few months. However, the scientists had a profound respect for each other even if one was from time to time annoyed with the obstinacy of the other" [34, p. 100]. ⁵⁷ As mentioned above, Crookes is credited with the discovery of thallium by spectral analysis in 1861.



Figure 8. Measuring the sound wave length by Kundt's method.

where p is the pressure and ρ is the density. Knowing that $v = f\lambda$, where f is the frequency and λ is the length of the sound wave (other conditions being equal), the ratio for two gases (argon and air) could be written with the experimentally measured C_p/C_v ratio for the latter taken into account:

$$\frac{(\rho\lambda^2)_{\rm air}}{(\rho\lambda^2)_{\rm argon}} = \frac{1.408}{(C_p/C_v)_{\rm argon}}.$$
(4)

Thus, the problem of finding $(C_p/C_v)_{argon}$ was reduced to measuring the ratio of wavelengths of acoustic oscillations of identical frequencies in argon and air at the same pressure. The authors of the paper simply referred to the known method of determining the length of the sound wave; however, Ramsay later described the device used for the purpose in greater detail in his book [38, pp. 204–206] (Fig. 8):

"The simple apparatus with which such determinations are made is due to the physicist Kundt. It consists of a glass tube, through one end of which a glass rod passes, so that half the rod in enclosed in the tube, while the other half projects outside it. ⁵⁹ In the experiments on argon, the rod was sealed into the tube; in other cases, it is better to attach it with indiarubber, or to cause the rod to pass through a cork.

"The open end of the tube is connected with a supply of the gas, so that, after the tube has been pumped empty of air, the gas, in a pure and dry condition, can be admitted. Some light powder (and for this purpose lycopodium dust - the dried spores of a species of fungus — is best ⁶⁰) is placed in the tube, and distributed uniformly throughout it, so that when the latter is in horizontal position, a streak of the powder lies along it from end to end. The portion of the rod outside the tube is rubbed with a rag wetted with alcohol, when it emits a shrill tone squeak, due to longitudinal vibrations; the pitch tone depends, naturally, on the length of the rod, a long rod giving a deeper tone than a short one. The vibrations of the rod set the gas in the tube in motion, and the sound-waves are conveyed from end to end of the tube through the gas. As the tube is closed at the end through which the gas admitted, these waves echo back through it; and a great deal of care must be taken to make the echo strengthen the waves, ⁶¹ so that the compressions produced by the back waves are coincident in position with the compressions produced by the forward waves travelling onwards from the rod."

Having measured C_p/C_v for air, carbon dioxide, and hydrogen by the above method, Ramsay compared the results with numerous data obtained by other researchers. For triatomic carbon dioxide, he determined the ratio as 1.276, while the average over ten different measurements made prior to his experiment was 1.288. The accuracy was fairly satisfactory and, in five series of measurements, Ramsay found that $(C_p/C_v)_{argon} = 1.644$ at the temperature 17.5 °C. Because the theoretical C_p/C_v ratio for a monoatomic gas was 1.677, Rayleigh and Ramsay came to an absolutely correct conclusion that molecules of argon contained one atom each.

In the fifteenth paragraph, entitled "Attempts to induce Chemical Combination," Ramsay described his numerous experiments designed to obtain an argon compound. The following quotation from Ramsay's book briefly lists his attempts to reach the goal and illustrates a great deal of work behind these efforts [38, pp. 190, 191]:

"Many attempts were therefore made to induce argon to enter into combination. And the consistent failure of these attempts led to the choice of the name 'argon' or 'idle' for the newly discovered element. The methods employed to prepare argon free from nitrogen, namely, by exposing the mixed gases to the action of oxygen in a discharge of electric sparks, and by passing them over red-hot magnesium, show that it cannot be induced to combine with one of the most electronegative of elements, oxygen, and one of the most electropositive, magnesium. It also refuses to combine with hydrogen or with chlorine when sparked with these gases; nor is it absorbed or altered in volume by passage through a red-hot tube along with vapours of phosphorus, sulphur, tellurium, or sodium. Red-hot caustic soda, or a red-hot mixture of soda and lime, which attacks the exceedingly refractory metal platinum, was without action on argon. The combined influence of oxygen and alkali in the shape of fused potassium nitrate or red-hot peroxide of sodium was also without effect. Gold would, however, have residual such action, but it would have been attacked by the next agent tried, viz. persulphide of sodium and calcium. This mixture was exposed at a red-heat to a current of argon, again without result. Nascent chloride, or chlorine at the moment of liberation, obtained from a mixture of nitric and hydrochloric acids, and from permanganate of potassium and hydrochloric acid, was without action." 62

The sixteenth and last paragraph, "General Conclusions," summarized the results of the experiments that had brought the discovery of the new gas named argon (or even gases, for the authors foresaw that the isolated argon contained the entire group of noble gases; very soon, Ramsay's unusually intense and fruitful activity created a basis for the discovery of helium, neon, krypton, and xenon).

Setting aside the reasons given by the two authors, suffice it to mention their seven indisputable arguments in favor of the presence of argon in the air (as opposed to the opinion that it was created in the course of preparation).

The results presented in the fourteenth paragraph brought the authors to the assumption of the elemental nature of argon having monoatomic molecules. This conclusion totally disproved the interpretation of argon as triatomic nitrogen and allowed its atomic mass to be roughly calculated as equalling 40 (the currently accepted atomic mass of argon is 39.948 in the carbon-based scale). The co-authors of the discovery showed their unprejudiced thinking by assuming that the isolated argon might be a mixture of gases. However, they were unable to prove it, and argon was considered to be a

 $^{^{59}}$ The total length of the rod was 30 cm (*note by A.A.M.*).

 $^{^{60}}$ Club moss is a genus of evergreen herbaceous plants of the family Lycopodiaceae (*note by A.A.M.*).

 $^{^{61}}$ In other words, a standing wave can arise in a tube sealed on both sides if the tube length equals an integer number of wave lengths. In order to satisfy this condition, a thin-walled rubber tube was put on one end of the glass tube and clamped where necessary (*note by A.A.M.*).

⁶² As is known [45], the first chemical xenon compounds were synthesized only in 1962, while true chemical compounds of argon are still unavailable. It was possible to synthesize only compounds (clathrates) in which argon is trapped among molecules of other substances.

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newly discovered element with the atomic weight 40. However, there was no place for it in the periodic system, as was shown by Rayleigh and Ramsay, who listed a number of other known elements with atomic masses close to 40, such as

Chlorine	 35.5,
Potassium	 39.1,
Calcium	 40.0,
Scandium	 44.0.

Having proved that the new element was argon, Rayleigh and Ramsay correctly noted that the periodic classification of chemical elements was incomplete and proposed a place for it ⁶³ in group 8 comprising silicon Si (a four-valent element), phosphorus P (tri- and five-valent element), sulfur S (di- and six-valent element), and chlorine Cl (mono- and seven-valent element). Argon could be the last element in this row having no valence, (i.e., a zero-valent element unable to combine with others into chemical compounds). It should have been followed by potassium K, a monovalent element.

Concluding their publication, the two co-authors emphasized the striking chemical inertness of argon, which explained why it had so long remained undiscovered. Also, they proposed the chemical symbol for the new element, A.

The reported discovery of argon received much enthusiastic comment. At the meeting of the Royal Society held on November 30, 1894, Lord Kelvin, its president, stated: "The greatest scientific event of the past year is, to my mind, undoubtedly the discovery of a new constituent of our atmosphere. If anything could add to the interest which we must all feel in this startling discovery, it is the consideration of the way by which it was found" [47, p. 291]. It should be noted, however, that Kelvin argued against the proof of the monoatomic nature of argon at the historic meeting of the Royal Society specially convened on the occasion of the discovery of this gas on January 31, 1895.

The eminent German chemist Wilhelm Ostwald, who was later awarded the Nobel Prize, expressed a desire to publish the complete version of the large paper by Rayleigh and Ramsay in the Zeitschrift für physikalische Chemie (Journal of Physical Chemistry) that he edited at that time. The paper was out in the same year of 1895.

The famous French chemist Marcellin Berthelot, one of the founders of modern organic chemistry, wrote in the letter of congratulations that he sent to Ramsay on February 5, 1895 [34, p. 103], "Yesterday, I announced your outstanding discovery to the members of the French Academy and it was received favourably and applauded, a rare and unusual manifestation of enthusiasm at our meetings. I compiled a brief summary of the discovery that is due to appear in our reports next Sunday. I tried, to the best of my ability, to convey your thought as precisely as possible.

"Monsieur Moissan whom I told about your wish places himself entirely at your disposal and says that experiments with fluorine can be easily made because his apparatus is in good operational conditions now. Moissan will create vacuum in a tube with fluorine and introduce argon into it; this will even heat argon a little. But the sample will be unfit for other experiments for the difficulty to handle it.

"I take the liberty to ask you whether you checked up the law of compressibility of argon and also the law of its expansion because the calculation of specific heat is based on these two laws.

"You have probed so deeply into physical properties of argon that I think you will not find this note of mine too bold.... Give my best regards to Lord Rayleigh. Yours respectfully. M Berthelot."

In this letter, Berthelot answered the request of Ramsay for combining fluorine and argon addressed to another eminent French chemist Henri Moisson, a future Nobel Prize winner, who was the first to purify fluorine as mentioned in a foregoing section.

Moissan quickly responded to Ramsay's request in a letter dated February 23, 1895 [34, pp. 104, 105]: "Dear Sir and Colleague, to begin with, I would like to cordially congratulate you and also Lord Rayleigh on the remarkable discovery with which you enriched the scientific world. Monsieur Berthelot was so kind as to inform you that I am at your disposal and ready to start investigations of the action of fluorine on argon."

The studies were conducted and demonstrated once again that argon was inert.

Ramsay also sent the full text of the report of January 31 to Mendeleyev and received congratulations from his Russian colleague. Mendeleyev wrote in the cable dated February 12/24 1895 [46, p. 143]: "Congratulations on the discovery of argon. Believe the molecules to contain three nitrogens due to heat release. Mendeleyev."

In other words, Mendeleyev told Rayleigh and Ramsay that they had discovered triatomic 'ozone-like' nitrogen (rather than the monoatomic gas argon), the formation of which was accompanied by the release of energy; that is, Mendeleyev believed that triatomic nitrogen was more stable than diatomic. In the sixth edition of his Principles of Chemistry (March 1895), Mendeleyev expounded this view at greater length: "If argon is (as it thus far should be) regarded as a new element, the weight of its atom must be close to 40, i.e. to the atomic weights of K = 39 and Ca = 40, in disagreement with the available data on periodicity of the properties of elements arranged in order of their atomic weights; these data give no reason to assume the existence of intermediate elements, and all places in the periodic system above potassium are occupied (italicized by myself — A.A.M.). This calls for a new check-up of the velocity of sound in argon" [48, p. 463].

This quotation shows that the faultless results of the measurement of the velocity of sound in argon reported by two outstanding experimenters, Rayleigh and Ramsay, were publicly doubted by Mendeleyev, who was a far less skillful experimenter and, besides, did not promptly look into the essence of the matter.⁶⁴

It was noted in the foregoing that Dewar also hastened to question the conclusions of Rayleigh and Ramsay in August 1894. Had he withheld from negating the existence of the 1%

⁶³ They rejected as unlikely the proposition that argon is a mixture of elements with atomic masses other than approximately 40.

⁶⁴ As mentioned above, in 1896 Mendeleyev determined the weight of 1 liter of water at 4°C as 999.847 g compared with the current value of 999.973 g (an error of 126 mg or 126 millionths). At about the same time, French researchers obtained the following results [23, p. 265]: Macé de Lépinay, Fabry, Pero (1899) — 999.974; Buisson, Macé de Lépinay, Benoit (1905) — 999.971–999.974; Chappuis (1906) — 999.974; Benoit (1907) — 999.972; Guillaume (1909) — 999.973. The comparison is not to the credit of Mendeleyev; also, the results of his work as Director of Russia's Main Chamber of Weights and Measures were obviously at variance with his ambitious plans "to improve the accuracy of weighing from millionths to billionths of a unit" (! — *A.A.M.*) [48, p. 286].

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impurity in atmospheric nitrogen without adducing any proof to the contrary, his statement at that stage of the study could have been regarded as correct and constructive criticism offering an alternative explanation to the experimental results. However, his interpretation of the discovery was convincingly refuted by Rayleigh and Ramsay (see above for details), who showed that the density of argon could not be the density of triatomic nitrogen, the ratio of specific heats of argon could not be the ratio of specific heats of a triatomic molecule, and the spectrum of atomic argon (displaying prominent lines) could not be confused with the molecular spectrum of nitrogen with its diffuse lines.

Now, in April 1895, even tactful Rayleigh (although not a chemist) objected in sharp words to the peremptory interpretation of argon as triatomic nitrogen. He wrote: "The majority of chemists whom I had consulted on this issue are of opinion that N_3 must be highly explosive or, at least, very unstable.... I am not an advocate of dogmatism" [20, p. 35].

It was not by chance that Rayleigh mentioned dogmatism when defending his discovery from shameless attacks. Indeed, the only reason for which Mendeleyev obstinately rejected the conclusions of Rayleigh and Ramsay was his incorrect formulation of the 'periodic law' that did not recognize the existence of argon with a mass of 40. Mendeleyev continued to dispute the discovery of Rayleigh and Ramsay for another five years (until March 1900). Mendeleyev dogmatically interpreted his continuously rearranged table as an absolute 'law' admitting no exception rather than a more or less successful generalization of empirical data. However, the major premises on which Mendeleyev's 'periodic law' was based (all atoms of a given element are identical; atoms of different elements have nothing in common; the strength of the chemical affinity depends on the mass) were false. Here, everything is incorrect. Indeed, by the incorrect formulation of the 'periodic law,' Mendeleyev put his adherents on the wrong trail.

Moreover, Mendeleyev's concept is contradictory in itself because it is lacking in the periodicity of chemical properties of lanthanides and actinides; also controversial are the reciprocal positions of the three pairs of elements: A (39.95) — K (39.10), Co (58.93) – Ni (58.70), and Te (127.60) — I (126.90).⁶⁵

Even before the discovery of argon, Mendeleyev denied two latter anomalies. In 1871, he 'corrected' (i.e., wrongly predicted based on the 'periodic law') the atomic weight of tellurium as being 125 [49, p. 160]; this wrong prediction was immediately 'confirmed' by the 'faithful mendeleyevist' B Browner⁶⁶ [7, p. 328]. Also, Mendeleyev rejected the cobalt-nickel anomaly and asserted, until 1902, that the atomic weight of nickel is larger than that of cobalt; in his table, the two elements had the same value of 59 units [49, p. 362]. Accordingly, argon having been discovered, Mendeleyev stated that there is no place in the periodic system for an element with such properties.

It should be noted, in addition, that the wrong interpretation of the 'periodic law' inevitably made Mendeleyev oppose almost all new physical concepts emerging on the eve of the XXth century. Suffice it to say that he categorically denied the theory of electrolytic dissociation developed by S Arrhenius, for which this scientist was awarded the Nobel Prize in 1903. Five years after the discovery of the electron by J J Thomson in 1902, Mendeleyev talked about the "incomprehensible hypothesis of electrons" [49, p. 513]. He also rejected the interconversion of atoms (after the discovery of radioactivity) and their divisibility and insisted on the "individual originality of chemical elements" [49, p. 479] in the belief that atoms cannot contain common parts; in other words, he adhered to Dalton's view going in fact back to Democritus.⁶⁷

To sum up, Mendeleyev categorically denied the rational kernel (common matter of different elements) of Prout's hypothesis that turned out to be much closer to the truth than the views of Democritus, Dalton, and himself about "individual originality of chemical elements." As a result, the idea of isotopy of chemical elements made its way with great difficulty over a few decades. A S Russell, a co-worker of Rutherford, raised the question "why did inorganic chemistry so slowly assimilated the concepts of isotopes and atomic numbers?" at the memorial conference held in Manchester in 1950 [50, pp. 157, 158]. Russell wondered how "strikingly long chemists hesitated to arrange some 40 radioactive elements in the periodic table." 68 He justly attributed it to the fact that the classification of elements "was not wholly periodic: rare-earth elements refused to 'go in,' atomic weights of argon, potassium, and other pairs of neighbouring elements posed difficulty, and, worst of all, there was no criterion for the restriction of the number of elements heavier than lead and lighter than hydrogen.... In the course of development of Mendeleyev's classification, it never kept up abreast with new discoveries.... For this reason, its critics always regarded it as ...a mnemonic device for crammers rather than a true principle in embryo...." [50, p. 159].

The denial of the elemental nature of argon by Mendeleyev and some other scientists seriously discouraged Rayleigh, who "gave up argon studies and chemistry at large" and concentrated on physical problems" [1, book 1, p. 248, 249]. His son recollects that Rayleigh once said: "I want to turn back from chemistry to physics. A person of second sort should know his place better" [20, p. 36].

Rayleigh concluded his chemical studies by publishing the article "On Some Physical Properties of Argon and Helium" [51], in which he again determined the density of argon and measured its index of refraction and viscosity.

Meanwhile, his co-author Ramsay continued strikingly laborious and productive investigations. By an irony of fate, it was Ramsay, not Mendeleyev with his denial of the discovery of the new element argon, who predicted the existence of noble gases and undertook to purposefully seek them. Although not without mistakes (for he was quicker in reaching conclusions than Rayleigh), Ramsay discovered helium in 1895 and neon, krypton, and xenon (jointly with his assistant M W Travers) in 1898.

The factual aspect of the discovery of the entire group of noble gases (extending far beyond the scope of the present review) was described by Ramsay himself in his book [38].

⁶⁵ Figures in parentheses are the currently accepted values.

⁶⁶ B Browner, professor of chemistry at the Bohemian University, Prague, called himself so.

⁶⁷ For all that, Mendeleyev commented on some utterances by Democritus, permitting himself the following harsh words: "I think nothing of the kind could occur, even in a delirious dream, to any modern naturalist or even most radical materialist of the new times" [49, p. 471].

⁶⁸ It is worth noting in addition that chemists were equally hesitant when putting lanthanides in proper positions, and no periodic law would have been of any help to them had not Moseley demonstrated that X-ray spectra of chemical elements monotonically rather than periodically change with increasing charge of the nucleus (*note by A.A.M.*).

Ramsay's biography published in Russian contains a detailed account of his remarkable works [34]. In what follows, there is a brief 'first-hand' treatment of the history of Ramsay's discoveries.

Some time after the discovery of argon, Ramsay continued to search for its chemical compounds. When informed that Hillebrandt of the US Geological Service had liberated large amounts of a gas (probably, nitrogen) by heating the mineral clevèite, Ramsay decided to try and isolate argon from the same source and thus to discover some elements with which "an attempt to cause argon to combine might be successful" [38, p. 233]. He wrote: "A sample of clevèite was produced, and heated with sulphuric acid; and a gas was collected, which, after purification by sparking with oxygen in presence of caustic soda, was examined with the spectroscope. The chief characteristic of the spectrum was a brilliant yellow line, much overpowering the others in intensity; and the first idea was that it must have been due to the discharge making the soda in the glass of the vacuum-tube incandescent. The position of the line was not coincident, however, with that of the sodium lines thrown into the field of vision for purpose of comparison; the preconceived idea that the line was due to sodium was hard to eradicate; and the spectroscope was dismantled, the prisms readjusted, and the spectra again compared. This time there could be no doubt; the lines were not coincident. Reference to a table of solar spectrum soon made the matter clear, and terrestrial helium was discovered. Like argon, it is a gas, with no pronounced tendency towards combination; it is, like argon, nearly insoluble in water; while 100 volumes of water at atmospheric temperature (15°C) dissolve 4.1 volumes of argon, they dissolve only 1.4 volumes of helium; for the solubility of helium is nearly the same as that of nitrogen, the least soluble of gases. Attempts made induce helium to enter into combination failed, like those made with argon; and it is therefore reasonable to place it in the same class of elements as argon, especially as the ratio between its specific heats shows it to resemble argon in being a monoatomic gas. Its density is nearly 2.0, that of oxygen being taken at 16.0; next to hydrogen, the density of which is 1.007, it is the lightest gas known" [38, p. 233-235]

Having discovered helium, Ramsay understood that other gases similar to the discovered ones must be present in the atmosphere. He argued in favor of this hypothesis in his address delivered to the meeting of the Chemical Section of the British Association for the Advancement of Sciences held in Toronto in 1897:

"Not long after John Dalton, in 1803, had reintroduced the old Greek hypothesis of the atomic constitution of matter, and had made his somewhat unsuccessful attempt to determine the relative weights of the atoms of the elements, speculation began as to some possible relationship between the weights of these atoms. These speculations finally, as has already been remarked, culminated in the periodic table The last column of that table contains the elements helium and argon. The elements of preceding groups show approximately regular differences between their atomic weights; thus; for example, the difference between the atomic weights of nitrogen, 14, and phosphorus, 31, is 17; that between oxygen, 16, and sulphur, 32, is 16, hydrogen and fluorine show a difference of 18, and fluorine and chlorine of 16.5; and lithium, sodium, and potassium have differences of 16 and 16.1 respectively. It was highly probable, therefore, that an

element should exist, having an atomic weight about 16 units higher than that of neon⁶⁹ and about 17 or 18 units lower than that of argon. It should have a brilliant spectrum; it should be a gas with a boiling-point when liquefied higher than that of helium, yet lower than that of argon; like them it should be monoatomic, and it should display inactivity in resisting combination with other elements. Similar arguments would lead to the conclusion that other two elements of higher atomic weights should also to be found, one with an atomic weight somewhat higher than that of bromine, 80, but somewhat lower than that of rubidium, 85.4; and that a third should succeed iodine, with the atomic weight greater than 127, but less than 133. As no elements are known in the chlorine or sodium column with still higher atomic weights, it was imagined that it would be unlikely that any element with a higher atomic weight than, say, 130 would be discovered belonging to the helium column" [38, pp. 239-241].

"But where were these elements to be sought? A very large number of minerals were heated in a vacuum, and the gases they gave off extracted by pumping; some few yielded no gas whatever; but the majority evolved carbon monoxide and dioxide, and hydrogen, in small quantity, while a considerable number evolved helium, and one, a mineral named malacone, containing zirconium, evolved both helium and argon. The spectra of the inactive gases were carefully examined, but showed no unknown lines. The helium from mineral waters, too, was introduced into vacuum-tubes, but its spectrum likewise failed to show the presence of a new constituent. The diffusion of helium, which might have been expected to separate a light from a heavy constituent of the mixture, was also unsuccessful in revealing any impurity, except a trace of argon; the only clue, and that not a very hopeful one, was that argon, when systematically diffused, gave two portions, one slightly heavier, the other slightly lighter, than the original gas. But the difference was extremely minute, and was probably to have been accounted for by experimental error.

"However, as all other possible sources had been examined, it appeared to be the only one left untried; and after an examination of sea-water, which proved fruitless, a large quantity of argon was separated from the atmosphere, with the view of its liquefaction and distillation ⁷⁰; a process which would separate small quantities of light and heavy constituents more perfectly than any other method" [38, p. 241, 242].

The last idea brought Ramsay and Travers, his assistant, to the discovery of neon, krypton, and xenon in 1898. It is clear today that these gases were liquefied together with argon liberated from the air and then separated from argon by multiple distillation; in the course of this process, the first portions of the gas evaporated during the boiling of argon were enriched with helium and neon and the last ones with krypton and xenon. The light gases were finally separated hosing their different solidification temperatures. Travers constructed an apparatus for liquefaction of hydrogen that was used to cool a mixture of helium and neon; "the neon froze solid, while the helium remained gaseous; the helium was removed by the help of a pump, and the solid neon was allowed to warm up, gasified, and collected separately" [38,

⁶⁹ Misprint in Ramsay's text; the word neon should be substituted by helium (*note by A.A.M.*).

⁷⁰ Distillation is a process involving the purification of a liquid from soluble volatile impurities or the separation of a liquid mixture into fractions by means of heating or boiling of the initial product (*note by* A.A.M.).

p. 249]. Argon, krypton, and xenon were separated by multiple fractionation. Eventually, Ramsay and Travers collected 15 cm³ of krypton and one quarter of this quantity of xenon. It took two more years to study their properties. In conclusion, Ramsay suggested that helium, neon, argon, krypton, and xenon, to the discovery of which he had made such an important contribution, should comprise group 8 of the periodic system.⁷¹

4. Conclusion

The dramatic discovery of argon in 1894 was the first in the next series of breakthroughs including X-rays (1895), radioactivity (1896), the electron and divisibility of the atom (1897) that marked the advent of the quantum era. All the listed discoveries, which laid the cornerstone of modern physics, have much in common, namely they were made accidentally by very inquisitive, skillful, and conscientious experimenters who obtained results quite different from those they had expected to have when they started their work.

It is universally known that Roentgen had studied cathode rays for a year and a half before he discovered X-rays due exclusively to his keenness of observation. Becquerel, on the contrary, sought X-rays but discovered radioactivity only because he decided to make a control experiment that included the development of an unexposed photographic plate. Thomson studied cathode rays without knowing that atoms were divisible and that he had to deal with a universal constituent of all atoms, the electron. The authors of all these discoveries were awarded Nobel Prizes for physics: Roentgen was the first to win it in 1901, followed by Becquerel (jointly with the Curies) in 1903, Thomson in 1906, and Rayleigh in 1904.

However, some of the above discoveries met with opposition. While X-rays and radioactivity were recognized unanimously, argon and electrons had to force their way through the resistance of dogmatists, including Mendeleyev, who treated atoms as incognizable entities differing from one another, for no obvious reason, in mass and chemical properties. Therefore, Bohr was hardly right when he wrote in his recollections of Moseley "about tremendous intuition of Mendeleyev who, in some places of his table, diverged from the regular recurrence of increasing atomic weights" [50 p. 171]. As is clear from the foregoing, Bohr's opinion reflects the poor knowledge of the history of the natural sciences by physicists⁷² and is based on a myth. Indeed, Mendeleyev denied the proposed some corrections for the atomic

weights of certain elements, which, however, do not substantially interfere with the "regular periodicity of increasing atomic weights."

The voluminous panegyric literature devoted to Mendeleyev, especially the works of B M Kedrov, contains no allusions whatever to the fact that the 'periodic law' as formulated by Mendeleyev is simply incorrect. Apologists of Mendeleyev do not usually mention his wrong predictions, his denial of the existence of argon, and other fogey ideas. The author of the present review thinks that, while praising to the skies Mendeleyev's successful predictions, ⁷³ it is necessary to adequately assess the large number of his wrong ones, including tactless criticism of the discovery of argon by Rayleigh.

The sensational discovery of argon crowned by the discovery of the remaining noble gases was promptly and deservedly recognized by the Nobel Prize Committee, which gave the 1904 award for physics to Lord Rayleigh "for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies" ⁷⁴ and the award for chemistry to Ramsay "in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system."

It remains to be added that Rayleigh donated a large part of his Nobel prize (7,000 pounds sterling) for the construction of a new building of the Cavendish Laboratory [18, p. 159].

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⁷³ The well-known German chemist C Winkler called three successful predictions by Mendeleyev 'bold speculation' in his speech on "The Discovery of New Elements During the Last Twenty Five Years" in 1897 [34, p. 136].

⁷⁴ The authors of Rayleigh's biography decided, for an unknown reason, that the Nobel Prize for physics had been awarded to Rayleigh for the studies of vibrational and wave processes [34, p. 87].

⁷¹ No sooner had Ramsay proposed to expand the periodic table as Mendeleyev 'distinguished' himself again. Striving "in the first place to derive as much benefit from the periodic law as possible," he wrongly predicted (in the paper "Attempt at the Chemical Understanding of the World Ether" published in 1903 [52]) the existence of two new noble gases: ether (a hypothetical carrier of the electromagnetic field reckoned by Mendeleyev as a chemical element!) with the atomic weight A < 0.00000096, which Mendeleyev wanted to name newtonium, and a certain coronium with the atomic weight $A \sim 0.4$. At the same time, Mendeleyev predicted the existence of new elements with 1 < A < 4 (including a halogen with the atomic weight A = 3).

⁷² It is worthwhile recalling the opinion of another Nobel Prize winner, H A Lorentz, on this sore subject: "Physicists are often reproached for the complete lack of interest in the history of their science devoting all the time to the solution of current problems. Be that as it may, when speaking about this, I, like my colleagues, feel deeply ashamed and regretful because none of us can deny the truth of this reproach."

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