The History (and Pre-History) of the Discovery and Chemistry of the Noble Gases

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The existence of the then-so-called inert gases was discovered over a short period of time in the 1890s; the demonstration that they were in fact not inert took place during an even shorter period of time, in 1962. This paper surveys the key events, as well as some of the earlier work that led up to them, of those two crucial episodes in the history of chemistry.

X.1 Introduction

Mendeleev's periodic table, initially proposed in 1869, was improved and generally accepted over the ensuing quarter-century — a period of "prediction and accommodation" [1] that did *not* include any thought of the noble gases. And why should it have? Predictions made by Mendeleev and others were aimed mainly to fill in a missing single member of a group, such as Ga between Al and In; some less-than-perfectly-regular atomic weight sequences also caused some concern. But there was nothing to suggest that an *entire* group might be missing! Well, not quite *nothing*: a couple of earlier observations — one almost a century earlier — might have started chemists down the right track sooner. As it happened, though, it was a project with a quite different goal that led to the discovery of the first of the "inert" or "noble" gases in the early 1890s. Characterization of the entire group was completed in less than a decade, a remarkably short period for such a far-reaching development.

The chronology of the chemistry of the noble (*not* inert, therefore) gases is somewhat analogous. After their discovery there was an extended period of unsuccessful — or at best ambiguous — experimentation to establish reactivity, accompanied by argumentation for and against. But when the dam finally broke in 1962, a vast flood of positive findings followed quickly, such that most of the principles of noble gas chemistry were established in fairly short order.

I will focus here on the work preceding and comprising the discovery of the elements, as well as some of the more important studies leading up to the

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demonstration, in 1962, that they *do* have chemistry. I will not say much about subsequent developments of noble gas chemistry; exhaustive surveys may be found in the *Comprehensive Inorganic Chemistry* series [2, 3].

X.2 The Pre-History of the Discovery

X.2.1 Cavendish's Residual Air

In a paper read to the Royal Society on June 2, 1785, and subsequently published [4], Henry Cavendish described some experiments carried out to test his proposal — based not on his own work but that of others — that the volume decrease seen upon "phlogistication" of ordinary air by sparking was not due to the generation of "fixed air" — CO_2 — as had previously been suggested, but rather to the "burning of some inflammable matter in the apparatus." The first such experiment he described was simply to pass a spark through "common air" contained in a small tube in contact with an aqueous solution of litmus; he found, as Priestley had previously observed, that the amount of air diminished, and the water took on a red color, indicating the formation of an acid.

Several additional experiments found that if the gas was "confined" by an alkaline solution — lime-water or (better) "soap-lees" (primarily KOH?) — the "diminution" of air was more pronounced; and the extent of that in turn depended strongly on the nature of the air; "perfectly dephlogisticated air" (O_2) showed no such decrease at all. On trying various proportions, he found that "when five parts of pure dephlogisticated air were mixed with three parts of common air, almost the whole of the air was made to disappear." In an earlier paper he had found that "when nitre is detonated with charcoal, the acid is converted to phlogisticated air" (in modern language, $NO_3^- + C$ gives N_2), whence he concluded that "phlogisticated air is nothing else than nitrous acid united to phlogiston." Accordingly he deduced here that "phlogisticated air ought to be reduced to nitrous acid by being deprived of its phlogiston," and that is what is happening in these experiments: $N_2 + O_2$ gives "nitrous acid" (actually a mixture of oxides of nitrogen). Of course, what he meant by "reduced" was completely different from our present usage!

Being appropriately cautious, however, Cavendish acknowledged that our knowledge of "the nature of the phlogisticated part of our atmosphere" is limited, and hence "though it was reasonable to suppose, that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it might fairly be doubted whether the whole is of this kind, or whether there are not in reality many different substances confounded together by us under the name of phlogisticated air." To investigate that possibility, he repeated the exhaustive sparking of the 5:3 mixture, then added a little more dephlogisticated air (O_2),

continued sparking until no further change could be observed, and added some "liver of sulphur" (a mixture of sulfides, polysulfides, etc. obtained by fusing K_2CO_3 with sulfur) to absorb any remaining O_2, "after which only a small bubble of air remained unabsorbed, which certainly was not more than 1/120 of the bulk of the phlogisticated air let up in the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest…we may safely conclude, that it is not more than 1/120 part of the whole." He refrained from speculating about what that residue might be, or even whether it was really there, or just represented the limited precision of his measurements. His observation attracted little attention over the next century.

X.2.2 An Extraterrestrial Element?

The solar eclipse of August 1868 provided an opportunity for spectroscopic examination of solar prominences. One observer, Jules Janssen, has been given credit by many for the discovery of helium during the course of this eclipse, but that is untrue [5]. English astronomer Norman Lockyer had ordered a new, powerful instrument, which was not ready in time to use on the eclipse; but in October of the same year he found that a yellow line in the solar spectrum close to, but not identical with, the well-known sodium "D" line was bright enough to be seen even without an eclipse [6, 7]. Initially he thought it was a new feature in the spectrum of hydrogen, too weak to be observed by any concentration of the gas that could be achieved under laboratory conditions; but on further consideration (in collaboration with chemist Edward Frankland) he changed his mind, noting that it did not move in parallel with known hydrogen lines [8]:

> I found that the orange line behaved quite differently…so then we knew that we were not dealing with hydrogen; hence we had to do with an element which we could not get in our laboratories, and therefore I took upon myself the responsibility of coining the word helium.…I did not know whether the substance…was a metal like calcium or a gas like hydrogen, but I did know that it behaved like hydrogen and that hydrogen, as Dumas had stated, behaved as a metal.

This proposal was apparently not published anywhere at the time of the observation, but must have circulated informally, since Thomson mentioned it in in a footnote to the published version of his presentation to the 1871 meeting of the British Association for the Advancement of Science [9]. Kragh has provided a detailed account of the early history of helium [10].

As with Cavendish's finding, there was no follow-up with respect to possible implications for the periodic table until the 1890s — although someone came close. Lockyer relates his correspondence with American geochemist William Hillebrand, who in 1888 dissolved a uranium ore called uraninite in sulfuric acid and observed evolution of a gas, which he characterized by spectroscopy and concluded it was

nitrogen, although he and a collaborator *did* find some extra unaccountable lines [11]. But Hillebrand comments "The well-known variability in the spectra of some substances…led me to ascribe similar causes for these anomalous appearances, and to reject the suggestion made by one of us in a doubtfully serious spirit, that a new element might be in question [12]." There is an object lesson here: pay attention to those not-so-serious suggestions!

X.3 The History of the Discovery

X.3.1 Rayleigh's Anomaly

In the late 1880s and early 1890s Lord Rayleigh (né John William Strutt) embarked on a program of measuring gas densities, aimed at a more reliable and precise set of atomic weights. This may *seem* like a confirmation of the common "wisdom" around the turn of the century: that there was not much left to discover in science beyond the next figures after the decimal point. But one commentator suggests that would be unfair: Rayleigh was inspired by "the numerical coincidences that had led much earlier to the formulation of Prout's Law" and hence had a much more fundamental aim [13]. In any case, the eventual outcome of his work amply contributed to the soon-to-be-obvious correction of that drastic misconception. All went smoothly until he came to nitrogen, as he wrote in a letter to *Nature* [14]:

> I am much puzzled by some recent results as to the density of *nitrogen*, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to two methods of preparation I obtain quite distinct values. The relative difference, amounting to about 1/1000 part, is small in itself; but it lies entirely outside the errors of experiment, and can only be attributed to a variation in the character of the gas.

The first method involved removing O_2 from air by passing it through a hot copper tube, the "ordinary way." For the other (a suggestion from William Ramsay, about whom we will hear much more shortly), air was bubbled through liquid ammonia, followed by exposure to hot copper to both oxidize the ammonia to N_2 and scavenge the remaining O_2. The latter procedure gave "N_2" that was lighter by one part in a thousand. Rayleigh considered explanations based on contamination: either "the first nitrogen would be too heavy, if it contained residual oxygen;" or "can the ammonia-made nitrogen be too light from the presence of impurity?" — most probably H_2. But additional experiments ruled those out (mostly) to his satisfaction, and he ended by wondering "Is it possible that the difference is independent of impurity, the nitrogen itself being to some extent in a different (dissociated) state?"

In a full paper the following year [15], Rayleigh described his experimental methodology in considerable detail, reporting densities for O_2 and N_2; the latter value was obtained using the method of removing O_2 from air. But he inserted a comment, beginning with "Although the subject is not yet ripe for discussion…" about the discrepancy reported in the *Nature* letter. He further noted that if pure O_2 instead of air were used to oxidize the ammonia, the difference could be as large as 0.5%, and repeated his belief that "everything suggests that the explanation is to be sought in a dissociated state of the nitrogen itself."

By the next year the subject *had* ripened, sufficiently to merit a paper in its own right [16]. There Rayleigh elaborated upon the experiments he had carried out to exclude the possibility of contamination (in either direction). He also carried out the chemical preparation of N_2 by additional methods: reduction of NO or NO_2, and decomposition of NH_4NO_3. All gave the same density as the NH_3-derived preparation, about 1/200 smaller than that from air. He reported two further studies to test his proposal of an alternate state of N_2: exposing both air- and NH_3-derived samples to electric discharge; and storing (what he took to be) the anomalous NH_3-derived version for 8 months. Neither had any detectable effect.

X.3.2 The Discovery of Argon

As mentioned in Rayleigh's 1892 letter in Nature, Rayleigh and Ramsay had been corresponding on the problem. Ramsay replied to the call for ideas in the *Nature* letter, at some point calling Rayleigh's attention to the century-old Cavendish result, which he had read about in a text [17]. Having previously found that N_2 reacts with hot magnesium turnings, Ramsay thus repeatedly treated the air-derived N_2, and found a steady increase in the density of the residual gas. At the end he obtained a gas sample of about 1/80 of the original volume, which no longer attacked hot Mg, exhibited a density of 19.086 (relative to $H_2 = 1$), showed no reactivity upon sparking with O_2 or Cl_2, and exhibited novel spectral lines [18]. Ramsay seems to have been open to the possibility of a new element more quickly, as he wrote to Rayleigh in May 1894) (Fig. 1) [19]:

Has it occurred to you that there is room for gaseous elements at the end of the first column of the periodic table? Thus

Li	Be	B	C	N	O	F	XXX
—	—	—	—	—	—	Cl	—
—	—	—	—	—	—	Mn	Fe Co Ni
—	—	—	—	—	—	Br	—
—	—	—	—	—	—	?	Pd Ru Rh

etc. Such elements should have the density 20 or thereabouts, and 0.8 pc (1/120 about) of the nitrogen in the air could so raise the density of nitrogen that it would stand to pure [chemical] nitrogen in the ratio 230:231.

He was referring to a form of the periodic table in which the halogens lined up with Mn, so that the postulated new elements would lie above the group VIII metals. Of course, the proposal of density 20 implies that they would all (like N, O and F) be diatomic gases, not metals; but once one accepts the halogens and manganese being placed in the same column, this doesn't seem such an insurmountable obstacle.

Fig. 1 Letter from Ramsay to Rayleigh of 24 May 1894. (Reproduced from ref. [19])

By August of 1894 Rayleigh and Ramsay were convinced that they had in fact discovered "a new Gaseous Component of the Atmosphere," as Rayleigh reported (but making it clear these were joint findings) at the annual meeting of the British Association for the Advancement of Science in Oxford. This new species

comprised around 1% of air, was more inert than N_2, and exhibited a density between 18.9 and 20 as well as new spectral lines (the latter determined by William Crookes). They refrained from proposing a name for the substance, or even definitively identifying it as an element. Disagreement ensued almost immediately. James Dewar opined (in a letter to the London *Times*: not the sort of forum in which we would expect such a scientific dispute today!) that it could not be an entirely new species, since he was confident that he would have noticed an unsuspected one-per-cent constituent during in his work with liquid air; he felt it must be an allotrope of nitrogen generated by the separation processes used by the two researchers, and suggested they test this possibility by exposing "pure" samples to their conditions [12, 20]. (As we have seen, Rayleigh had already done so.) Note that if this new allotrope were N_3, its density would be 21 — not quite within the experimental range reported, but not too far off.

At a special meeting of the Royal Society in January 1895, the full story to date was presented (by Ramsay) [21], and subsequently published at considerable length [22]. It is worth going through the contents in some detail. They summarized the evidence for the discrepant densities, including a new study on N_2 generated by oxidizing urea with NaOBr (which after additional treatment to remove some contaminant "smelling like a dead rat" eventually gave a consistent result). Perhaps in allusion to Rayleigh's original motivation, they commented that the ratio of densities between "chemical nitrogen" and oxygen was almost precisely integral (14.003:16), which was not the case for "atmospheric nitrogen."

They described experiments (mentioned in Rayleigh's 1894 paper) that addressed the possibility (Dewar's theory) that one or more of their procedures could have chemically changed N_2, by exposing "pure" chemical N_2 to the same conditions, and again reported no effect. As a further check, they constructed a device for diffusing air through a series of clay pipes ("atmolysis"), a process that was known to afford a gas mixture enriched in a heavier component but should not cause any chemical change, and found that the gas thus obtained (after removal of O_2) was indeed denser than ordinary atmospheric nitrogen.

From all this they concluded with confidence that there is in fact another chemically inert component of the atmosphere, no artifact of experimental procedures, which they called argon. The name appears not only in the title but *many* times in the body of the paper before they explain the choice, near the very end (it was taken from the Greek α–εργον, meaning no-work or idle).

Then they turned to the isolation of a large-scale sample of pure argon, both for further study and to establish as precisely as possible its concentration in the atmosphere. Using Cavendish's "oxygen method" (Fig. 2) proved problematic from a quantitative point of view (although they were *highly* complimentary about Cavendish's work). They observe: "In all the large-scale experiments, an attempt was made to keep a reckoning of the air and oxygen employed, in the hope of obtaining data as to the proportional volume of argon in air, but various accidents too often interfered." Their best estimate was that Ar comprises between 0.986 and 1.11 percent of what had previously been thought to be atmospheric nitrogen; they

determined that Ar is fairly soluble in water, and discussed how that would affect the conclusion. But they were able to obtain samples of mostly pure Ar (some N_2 was still present, by spectroscopy) in amounts of 75 cc or more. They did not have enough to completely fill the gas bulb used to determine density, so they used Ar-O_2 mixtures for that purpose, and calculated (after correcting for the residual N_2) a density of 19.7. Using Ramsay's method of removal of N_2 by hot Mg (Fig. 3), which was perhaps more reliable and faster but presented its own problems, they *were* able to produce samples large enough to fill the bulb, allowing a direct measurement of density; they took the best value to be 19.88.
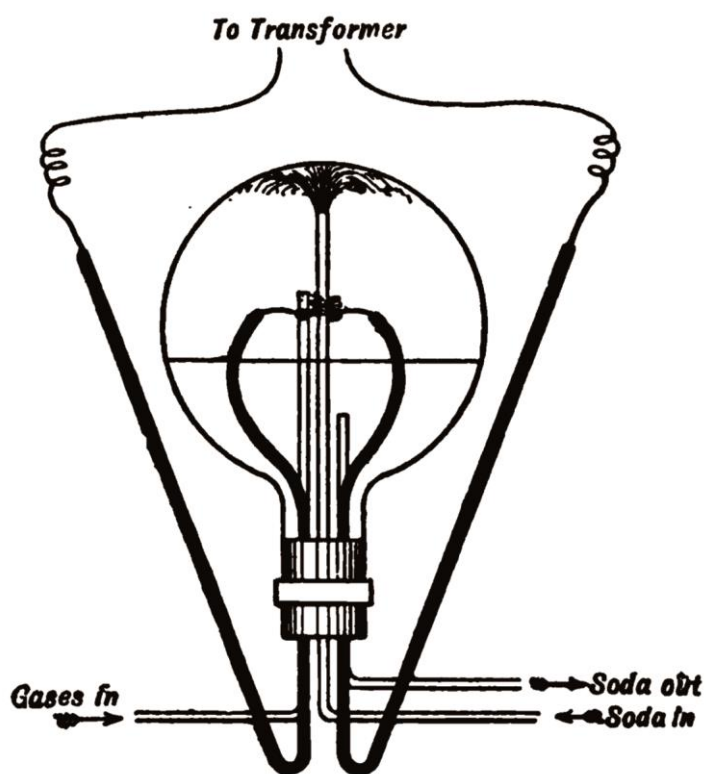

Fig. 2 Apparatus for isolating Ar by the sparking method. A mixture of air and O_2 in the proper proportions for complete consumption of N_2 is fed into a bulb equipped with Pt electrodes; the NO_x produced is removed by the continuously circulating solution of caustic soda. Excess O_2 is subsequently removed from the residual gas by passage over hot Cu. (Reproduced from refn [23])
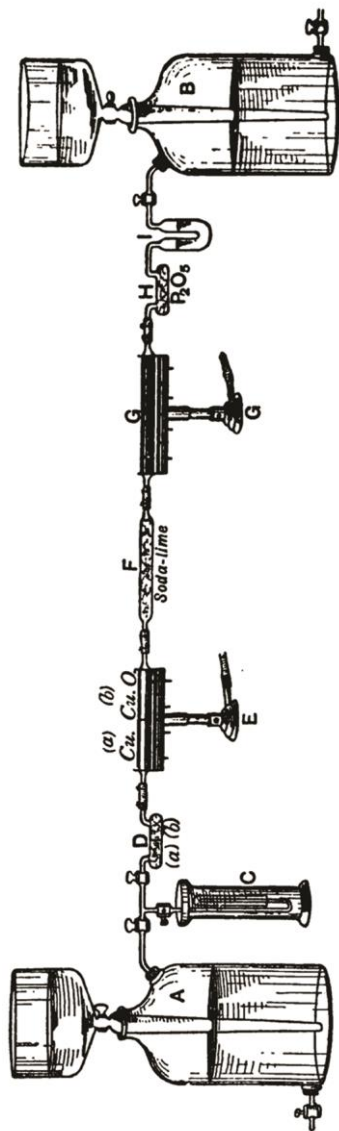
Fig. 3 Apparatus for isolating Ar by the Mg method. N_2 (obtained from air by passage over hot Cu) is passed back and forth between reservoirs **A** and **B** over hot Mg in tube **G**. Additional tubes contain hot CuO to oxidize any carbonaceous impurities, a soda-lime mixture (**F** and **I**) to adsorb the resulting CO_2, and P_2O_5 (**D** and **H**) to remove water. (Reproduced from refn [24])

These preparations were used to determine spectroscopic properties (a full account was given by Crookes in a paper immediately following [25]); the boiling, freezing, and critical points (also detailed in a companion paper, by K. Olszewski

[26]); and — perhaps most importantly — the specific heat ratio (determined from the velocity of sound), which was virtually exactly that expected for a *monatomic* gas. They attempted to demonstrate reactivity with a wide variety of chemicals, with no success — although they did mention that working with F_2 was too challenging for them, and recommended that experiment be carried out. (Which Moissan did, later the same year, and again found no reaction [27].)

Summing up, they claimed strong evidence that a hitherto unrecognized species is a natural component of the atmosphere, at a level around 1% that of N_2; that it is chemically inert; that it has a density around 20 relative to hydrogen; and that it is monatomic, implying an atomic weight around 40. They did allow for the possibility that what they called argon might still be a mixture of two or more species, but felt that the melting/boiling/critical behavior all argued strongly for a single substance. If so, they argued, "there is reason to doubt whether the periodic classification of elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed." If argon was a mixture, the lighter component could come after Cl (and the heavier after Br) as part of the eighth group (as in Fig. 1 above), suggesting that by extension, the series Si-P-S-Cl-? "might be expected to end with an element of monatomic molecules, of no valency, *i.e.*, incapable of forming a compound."

Not surprisingly, the report elicited considerable controversy (a more detailed exposition of which may be found in ref. [28]), both at the meeting itself and shortly thereafter. Much of it focused on the fact that a new element of atomic weight 40 *wouldn't* fit right after Cl, given the then-accepted values of Cl = 35.5, K = 39.1, Ca = 40.1. It was suggested by some that the correlation of atomicity and specific heat ratio might not be all that universal (the only known monatomic gas at the time was vaporized Hg). Perhaps argon could be diatomic, with the absence of chemistry signaling an abnormally strong bond, such that it could effectively behave almost like a spherical molecule? Mendeleev — who was *most* reluctant to accept irregularities of atomic weight progression in his table— speculated on "an inverse correlation between the magnitude of the specific heat ratio and the chemical reactivity of a given gas; the extreme inertness of argon might be responsible for a specific heat ratio higher than would otherwise be expected for a molecule containing two or three atoms." His first choice was that "argon" was actually N_3, as Dewar and others had previously proposed, but he was also open to the idea that it was a new species, diatomic with atomic weight 20, or even hexatomic (!) with atomic weight 6.5 [10, 29].

Later the same year Rayleigh gave a lecture to the Royal Institution, replete with actual demonstrations of some of the experimental procedures. The conclusions were essentially the same as in the full paper; he specifically addressed the N_3 proposal, arguing that it was inconsistent with their observations, as well as being highly unlikely to be a stable molecule; but (generously) ended with "The balance of evidence still seems to be against the supposition that argon is N_3, but for my part I do not wish to dogmatize." [30]. In his full-length book on "The Gases of the Atmosphere" which appeared the following year, Ramsay considered the atomic

weight issue at length [31]. On the one hand, he argued that this was not necessarily a real problem: "If the numbers in the tale actually showed regular intervals…argon might be regarded as of wholly exceptional behaviour. But this is not so….similar divergences, though not of equal magnitude, are common." He did speculate — we might now say rather wildly — on the possibility that atomic weight or mass might somehow depend on properties such as reactivity. Nonetheless, the book includes a periodic table showing argon to the right of chlorine with an atomic weight of 39.9 [32].

X.3.3 The Discovery of the Others

Still in 1895, Ramsay learned of Hillebrand's observation of gas from uraninite (described above), as well as the fact that a related mineral, cleveite, exhibited similar behavior. He thought it exceedingly unlikely that the gas could be N_2, as Hillebrand had proposed, and repeated the experiment on cleveite. Crookes carried out spectroscopy on the resultant gas, finding "a brilliant yellow line…identical with the line D_3, to which Mr. Lockyer many years ago gave the name 'helium,' from its occurrence in the spectrum of the sun's chromosphere." Ramsay reported the density of the gas to be no higher than 3.9; the specific heat ratio to be consistent with monatomicity (although he was not entirely happy with the quality of the data); and chemical inertness similar to that of argon, which "makes the inference probable that they belong to the same natural group." But he also noted that, assuming the atomic weight of argon to be 40, that of He would be 8 on the same basis; whereas an atomic weight of 4, more consistent with placing it before Li, would suggest that $Ar = 20$, "a supposition which may be supported by some lines of argument," ending with "Which of these views is correct time must decide." [33]

In a subsequent 1895 paper [34] Ramsay measured the density of gases similarly obtained from a large number of minerals, and got a rather large range of results, from around 2.04 to as high as 3.75. While the last was most consistent with the previous report, he was able to show that the higher numbers were due to contamination. He settled on a lower limit of 2.13, implying an atomic weight of 4.26 (assuming monatomicity), thus obviating the dilemma expressed in the preceding paragraph. The periodic table in his 1896 book includes He above Ar — with a space marked "?" between them, and several more question marks below argon. The atomic weight of He is given as 4.2 [32].

That first question mark was highlighted in a talk Ramsay gave to the British Association for the Advancement of Science meeting in 1897, held in Toronto, with the title "An Undiscovered Gas" [35]. Ramsay must have had something of a sense of humor: he began by asking to be "excused if I take this opportunity of indulging in the dangerous luxury of prophecy….The subject of my remarks to-day is a new gas. I shall describe to you later its curious properties; but it would be unfair not to put you at once in possession of the knowledge of its most remarkable property —

it has not yet been discovered." He briefly recounted the history of the periodic table, beginning with Döbereiner's triads and ending with Mendeleev and Lothar Meyer (to whom he gave pretty much equal credit), followed by summarizing his and Rayleigh's work on argon — with the interesting revelation that they had at first thought it "was probably a mixture of three gases, all of which possessed nearly the same atomic weights, like iron, cobalt and nickel. Indeed, their names were suggested, on this supposition, with patriotic bias, as Anglium, Scotium and Hibernium." But the strong evidence for monatomicity, along with the subsequent findings for helium, convinced them to postulate a new periodic group. By analogy to the pervasive appearance of triads in the table, "There should, therefore, be an undiscovered element between helium and argon, with an atomic weight 16 units higher than that of helium, and 20 units lower than that of argon, namely 20….And pushing the analogy still farther, it is to be expected that this element should be as indifferent to union with other elements as the two allied elements." Ramsay went on to describe some attempts to find the new gas — mostly as a component of helium samples — but admitted failure; and he ended with a discussion of the problem of atomic weight irregularities, which he also felt unable to resolve.

All but one of the remaining (naturally occurring) noble gases were discovered by Ramsay and Travers in fairly short order, during the first part of 1898, by cryogenic experiments on liquid air. In June Ramsay read a paper to the Royal Society on their preliminary results: after evaporating all but 10 cc of a 750 cc sample of liquid air, followed by removal of O_2 and N_2 in the usual manner, they obtained a gas that exhibited new spectral lines (in addition to those of argon), was monatomic according to the speed of sound, and had a measured density of 22.5. That they felt must be a minimum value, since there was certainly some Ar still present; they argued for a most likely density around 40 and hence an atomic weight of 80. They proposed to call it "krypton", for "hidden" [36]. Shortly thereafter they reported more careful fractionation studies, which led to a *more* volatile species, again with new spectral lines, and an upper limit on the density estimated to be 14.7. They named it "neon" or "new," and predicted the density would turn out to be 10; thus it would correspond to the "undiscovered gas" predicted by Ramsay in 1897. (He refrained from congratulating himself on that score!). They also noticed that a solid condensed out at low temperatures; on warming it turned into a gas with the same density but *not* the same spectrum as Ar, so they believed it must be a new element which they called "metargon" [37]. The latter was eventually recognized to be due to contamination, although the realization took some time [16].

Xenon ("stranger") was announced later that year [38], and in November 1900 a paper on the full group was presented to the Royal Society [39]. After acknowledging their blunder with metargon, they described the experimental apparatus and procedures used to isolate and characterize each of the gases in considerable detail; the latter studies include extensive pressure-volume-temperature data. At this point their best density values were given as: He, 1.98; Ne, 9.96; Ar, 19.96; Kr, 40.78; Xe, 64.0. From those they showed how the elements are well placed as a new group, following the halogens, with atomic weights

respectively 4, 20, 40, 82 and 128. All this impressive success notwithstanding, they remained rather modest about their accomplishment in their general conclusions, excerpts of which are worth quoting. (It seems a bit ironic that they now give credit for the periodic table to *three* inventors, since their work could be viewed as the final nail in the coffin of Newlands' "Law of Octaves." But surely nobody was taking seriously the idea of an analogy between chemistry and music long before the discovery of an 8th group.)

> The great value of Newland's (*sic*), Mendeleef's, and Lothar Meyer's generalisation, known as the periodic arrangement of the elements, is universally acknowledged. But a study of this arrangement, it must be allowed, is a somewhat tantalising pleasure; for, although the properties of elements do undoubtedly vary qualitatively, and, indeed, show approximate quantitative relations to their position in the periodic table, yet there are inexplicable deviations from regularity, which hold forth hopes of the discovery of a still more far-reaching generalisation….When we began the search for the elements of which the physical properties are described in the foregoing pages, we were not without a strong hope that their discovery would solve the problem….But our hope has been fruitless. While the same rough quantitative correspondence between the order in the periodic table and the physical properties is manifest, as with other similar series of elements, we have failed to trace any simple mathematical expressions which would make it possible to predict with accuracy the physical properties of any one of these elements, from a knowledge of those of its congeners. It is possible that such expressions exist; we venture to hope that others, more mathematically gifted than we are, may succeed where we have failed.

The sixth member of the noble gases was discovered in a different manner. In 1899, the American physicist Robert Bowie Owens had discovered that thorium salts steadily generated a radioactive material that could be removed from the containing vessel by passing air through it [40]. Three years later, Rutherford and Soddy, reinvestigating the radioactivity of thorium compounds, observed that they "continuously emit into the surrounding atmosphere, under ordinary conditions, something which, whatever its real nature may be, behaves in all respects like a radioactive gas" [41]. They tried passing it through various solutions and over hot solids, and found no evidence for reactivity, commenting "It will be noticed that the only known gases capable of passing in unchanged amount through all the reagents employed are the recently discovered gases of the argon family." It took some time — not surprisingly — to obtain it in sufficient quantity and purity for full characterization. A lengthy paper by Ramsay [42] summarized some earlier efforts and then described their own, which required particular ingenuity to deal with the complication that the radioactive decay continually generates He. They concluded that the "molecular weight" (later in the paper they refer to it as atomic weight) of the new gas, which they called "niton," was 218.

By 1915 Ramsay's *Gases of the Atmosphere* was up to a fourth edition [43]. There the periodic table (p 221) showed all six members of the last column; the atomic weights were essentially unchanged from the 1901 paper discussed above, with the addition of (still called) niton at 222.4. (A question mark was inserted between xenon and niton, presumably the consequence of not yet understanding how the lanthanides fit into the table, but there was no discussion thereof.) The

group was simply called "the inactive elements" (p 259); the name "noble gases" has been credited to German chemist H. Erdmann [13]. "Radon" was finally chosen for its heaviest member in the 1920s. In 1904 both Ramsay and Rayleigh were Nobel laureates — but not by sharing a single prize: Ramsay won for chemistry "in recognition of his services in the discovery of the inert gaseous elements in air," while Rayleigh's physics prize was "for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies." And that pretty much completes the story.

X.3.4 But Wait, There's (One) More!

The extension of the periodic table into the trans-uranium region of entirely synthetic elements proceeded at a fairly constant rate over the last half of the 20th century [44], so it must have seemed just a matter of time until atomic number 118, which would fall in the noble gas group, was reached at the end of the next period. The first such claim was reported in 1999, when a group at the Lawrence Berkeley lab claimed [45] to have produced three atoms of element 118 by bombarding a lead target with krypton (atomic numbers 82 + 36); but it was retracted the following year, and later found to be not just erroneous but fraudulent [46]. The successful synthesis required fusion of two less common isotopes — ^{249}Cf + ^{48}Ca — to get an isotope of element 118 whose atomic weight was closer to the "Island of Stability." A report was issued in 2002, co-authored by a large team at the Joint Institute for Nuclear Research in Dubna (Russia), led by Yuri Oganessian, and several scientists from the Lawrence Livermore Laboratory, but the first "real" publication [47] appeared a few years later, in 2006. Final acceptance of the discovery took another nine years and some additional results; on 12/30/2015 IUPAC's website [48] announced "the verification of the discoveries of four new chemical elements: The 7th period of the periodic table is now complete," crediting the Dubna/Livermore group. In 2016 the group held a conference call to decide on a name, and — after asking Oganessian to hang up — proposed to name it after him: oganesson [49].

The half-life of ^{294}Og is less than a millisecond, and only a handful of atoms have ever been produced, so clearly there is no experimental evidence available as to whether it in fact *does* have the chemical and physical properties expected for a noble gas. Relativistic effects become increasingly important with atomic weight, so that expectation is by no means a given. Calculations (carried out before it was definitively synthesized!) suggest that Og should be considerably more reactive than Rn, due in part to the magnitude of spin-orbit coupling [50]; others, that it might well be a liquid or even a solid at room temperature [51]. Those of us who like to see experimental confirmation before buying into computational predictions are not likely to be satisfied anytime soon.

X.4 The Pre-History of the Chemistry

The unreactivity of argon towards all common reagents had of course been recognized during the course of the experiments leading to its isolation, and (as already noted) Moissan quickly extended that to the most reactive known species, F_2. Generally similar behavior (or, rather, the absence of any) was established for the other members of the group as they became available. There *was* one positive report: dean of French chemists Marcellin Berthelot sparked Ar with benzene vapor and observed formation of a yellow solid, which he believed to be a compound of Ar [52], but that was soon discredited. One explanation is that no "Ar" was present at all: there is evidence suggesting that the vessel which Ramsay had sent to Berthelot had been opened at French customs, so it would have contained air instead [13]. Nonetheless, H. G. Wells was quick to postulate a compound of argon — and maybe another of the new gases? — as a weapon used by the invading Martians in his 1898 *War of the Worlds*: "Spectrum analysis of the black powder points unmistakably to the presence of an unknown element with a brilliant group of three lines in the green, and it is possible that it combines with argon to form a compound which acts at once with deadly effect upon some constituent in the blood." (That wasn't the only reference to the recent discovery: elsewhere it appears Wells believed the atmosphere of Mars to be rich in argon.)

Laszlo and Schrobilgen [53] discuss some further attempts, referring to a correspondence between Italian chemist Giuseppe Oddo and Ramsay. Oddo suggested that the heavier elements should be more reactive than Ar [54]; Ramsay agreed but was dubious about being able to obtain enough for meaningful experimentation. W. Kossel proposed, on electronegativity grounds, that fluorides of Kr and Xe should exist [55]. German chemist A. von Antropoff offered a similar argument in 1924, and then tried to confirm it by sparking Kr with Cl_2 and Br_2; initially they claimed a new red solid [56], but subsequently found it was an artifact, and retracted their claim.

In the same year Fritz Paneth wrote a short essay on the periodic table [57] in which he mentioned Antropoff's work, but concluded "Die Sonderstellung der nullwertigen Edelgase im periodischen System gehört zu den sichersten Ergebnissen des chemischen Experimentes und der physikalischen Interpretation, und es scheint mir ein Anachronismus, sie der äusserlichen Gleichförmigkeit der acht Gruppen zuliebe preiszugeben." Or: "The special position of zero-valued noble gases in the periodic system is one of the safest results of chemical experimentation and physical interpretation, and it seems to me anachronistic to give them up for the sake of the uniformity of the eight groups." (That was obtained from Google Translate; the only important change needed is "zero-valued" to "zerovalent." Not bad for a machine translation: they must have gotten much better since I last tried one!)

A 1933 paper by Linus Pauling, ostensibly about antimonates, proposed that XeO_6^{4-} should form isolable silver salts, based on ionic radius considerations and

analogy to known species. He also "predicted formulas KrF_6 and XeF_6, with XeF_8 as an unstable compound which might be capable of existence." [58] But Pauling was already pushing beyond predictions: the previous year he had written to his former teacher Fred Allen, now at Purdue, asking for a sample of xenon [59]:

> I should like to do some work (with Professor Yost) in an attempt to prepare certain compounds of Xenon suggested by theoretical arguments. No doubt your xenon is precious; if, however, you could lend us 10 cc. or so (of not necessarily pure stuff), we would try to return it to you either as such or in some compound (I hope), and we would be properly grateful. If this is asking too much, or if you can't lend it, could you give us advice as to where we might possibly obtain some?

The sample was duly received, and given to Pauling's colleague Don Yost. Working with his graduate student Albert Kaye, they carried out a series of studies of sparking mixtures of Xe with either F_2 or Cl_2, using an old Ford coil (photoirradiation was also tried with Cl_2, but not F_2). Unfortunately, they saw nothing beyond some attack on the quartz vessel, and submitted an account of their efforts to *JACS* — where it was published, perhaps surprisingly, considering they had only negative findings [60].

The version of this attempt in the Laszlo and Schrobilgen essay — which was based in large part on an interview with Kaye, whom they managed to track down many years after the event — is quite different. According to Kaye (presumably) it was *Yost* who took the initiative, with Pauling nothing more than "a most interested on-looker." Kaye was not even aware that Pauling had obtained the Xe sample: when he gave a departmental seminar on his work, he was surprised at how much Pauling seemed to know about the subject [53]! This is pretty much diametrically opposed to all other accounts of the episode — both those of Pauling himself and other commentators — and I have to believe that the latter are much closer to the truth. True, Pauling was often ready to reconstruct stories to put himself in a better light. For that matter, so was Yost: his own retrospective, in a collection of articles published shortly after Bartlett's breakthrough (see below), omitted any mention of Pauling whatsoever. It is well known that Pauling and Yost came to detest one another, but exactly when that began is not so clear [61]. But Kaye's version, as recounted by Laszlo and Schrobilgen, just doesn't ring true — whether due to his own faulty and/or selective memory, or because Yost misled him about Pauling's role, or both. It is notable that Kaye described — and "drew from memory" — the "copper reaction vessel" used for the study, whereas the original *JACS* article explicitly refers to "an all-quartz apparatus provided with copper electrodes." Laszlo and Schrobilgen seem to cast some doubt on the latter, noting that "Pauling and Kaye both recall the use of metal" (but according to Pauling, many years later, it was a *nickel* reactor), but it seems far more probable to me that the contemporaneous report was correct.

In any case, success was not achieved. After Bartlett's 1962 paper, a number of people (including Pauling) offered possible reasons for the failure. I have discussed these in detail elsewhere [62], including my own interpretation — that they would

have succeeded had they used a higher pressure of Xe and/or longer reaction times (Laszlo and Schrobilgen have a different opinion here too) — and will not repeat them here. Over the next three decades there were a few more claims and predictions, but none of those stood up either [53]. Pauling in particular ceased to be an enthusiast, whether because of Yost and Kaye's failure or for other reasons. The 1947 edition of his general chemistry textbook has the following language [63]:

> Helium, the second element, is a gas with the striking chemical property that it forms no chemical compounds….The congeners of helium — neon, argon, krypton, xenon, and radon — are also chemically inert. The failure of these inert elements to form chemical compounds is similarly due to the great stability of their electronic structures.

And so things (mostly) remained, until 1962.

X.5 The History of the Chemistry

The story of Bartlett's discovery is well known, and needs little elaboration here. As he reports in a very short (three paragraphs!) communication, having previously found that O_2 is oxidized by PtF_6 to give a salt, and recognized that O_2 and Xe have almost the same ionization potential, he predicted the analogous reaction, $Xe + PtF_6 = Xe^+PtF_6^-$, and indeed found the two substances reacted to give a solid that evolved gaseous Xe (along with O_2 and HF) upon hydrolysis [64]. Subsequently it has been recognized that the formula was not correct; a later study indicated the *presence* of $XeF^+PtF_6^-$ in a complex mixture whose composition depends on initial stoichiometry [65].

Bartlett's paper was received on May 4, and was published in June. A huge amount of work quickly ensued; indeed, some of it was already underway. Rudolf Hoppe had begun trying to react Xe with F_2 the previous year — using almost exactly the same methodology as Yost and Kaye had tried nearly 30 years earlier — and "in the last week of July 1962…were already certain that they had pure, crystalline XeF_2 in hand," as told in a letter [66] (Figs. 4-6) from Hoppe's crystallographer colleague W. Klemm to Herbert Hyman (who led a group of noble gas chemistry researchers, inspired by Bartlett's paper, at Argonne National Laboratory). Hoppe's paper [67] — like Bartlett's, only three paragraphs long — was received on October 8 and appeared in the November 21 issue of *Angewandte Chemie*. That *followed* a report of XeF_4 (from the Argonne group) which had a received date of August 20 [68]; another preparation of XeF_2, by a different procedure, was published in a paper received on October 29 [69]. Klemm notes "The American work in this field was…first begun on August 2nd, when Professor Hoppe already had prepared xenon difluoride. These results were not immediately published…because they had to wait for the mass spectrometric studies. In Münster there were at that time no mass spectrometers, and moreover because August is the holiday month, this research was considerably delayed." So Hoppe lost priority for the discovery of binary noble gas compounds due, in large part, to European

vacation practices! In any case, though, there appears to be no question, from the chronology of receipt and publication dates, that Bartlett's demonstration of reactivity was indeed the first, in terms of both when it was carried out and when it was published.

By April of the following year so much had already been accomplished that the Argonne group felt a conference was in order; the proceedings, published in book form [70], contained over 50 papers on xenon fluorides, oxyfluorides, and oxides, including several theoretical treatments (one of them oxymoronically titled "Theory of Binding in Inert-Gas Molecules"!), and prefaced by "Historical Remarks on the Discovery of Argon" (by Erwin Hiebert) and Don Yost's afore-mentioned reminiscences. One paper reported a radon fluoride [71], and another claimed the isolation of KrF_4 [72]; the latter work proved irreproducible, and it is believed that KrF_2 was actually obtained [73].

In the half-century since, the chemistry of the noble gas elements has been greatly expanded. Compounds of the lighter noble gases still exist only in the gas phase or in matrices, but those of the heavier ones are no longer limited to combinations with strongly electronegative elements such as F and O, the rationale that governed most of the early work. These so-called "atypical" compounds [74] include organoxenon species such as $[Xe(C_6F_5)]^+$ (a quite electronegative carbon-centered bonding partner, to be sure). Quite a number of compounds — some quite stable — involve noble gas centers acting as ligands to transition metal centers; for example, square-planar $[AuXe_4]^{2+}$ and linear $[(F_3As)AuXe]^+$ have been isolated and crystallographically characterized [75]. A review [76] calls these coordination compounds "perhaps the most surprising, interesting and thought provoking observations" in the history of the field; but given that noble gas atoms are isoelectronic to halide ions — among the most common ligands —in retrospect perhaps we should not have been all that surprised. It will be interesting to see whether greater surprises still await us.

Herrn Prof.Dr. Bailar zur Kenntnisnahme!

Anorganisch-Chemisches Institut der Universität
44 Münster (W)
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10. Juni 1964

Prof.Dr.W. Klemm

Herrn
Professor Dr. H.H. H y m a n
Argonne National Laboratories
9700 South Cass Avenue
A r g o n n e / Illinois 60440

Sehr geehrter Herr Hyman!

Ich möchte heute kurz in einer Angelegenheit an Sie schreiben,
die mich schon seit längerer Zeit beschäftigt. Es handelt sich
um den Anteil, den Herr Professor Hoppe an der Entdeckung von
binären Edelgasverbindungen, insbesondere Xenondifluorid
gehabt hat. Sie schreiben auf Seite 34 Ihres Buches 'Noble
Gas-Compounds' darüber einiges, wobei Sie am Schluß schreiben:

> "On learning of the Argonne discovery of xenone tetra-
> fluoride, the München group proceeded with their own
> approach and published some inadequately established
> preliminary observations. Their contribution to this
> volume is a revised and somewhat enlarged version of
> this earlier communication."

Bei München ist wohl gemeint Münster.

Diese Darstellung gibt ohne Zweifel den Sachverhalt nicht
richtig wieder und mit Rücksicht darauf, daß die Gefahr
besteht, daß bei einer späteren historischen Darstellung
die Verhältnisse unrichtig wiedergegeben werden, möchte ich
Ihnen kurz schildern, wie sie wirklich gewesen sind.

1.) Wie Sie richtig schreiben, bestand der Plan, Fluoride
des Xenons darzustellen, bei Herrn Professor Hoppe schon
sehr lange[1]. Die Schwierigkeit bestand in der Beschaf-
fung des flüssigen Fluors, das in Deutschland indu-
striell nicht hergestellt wird. Ein Versprechen der
Allied Chemical Coorporation (im August 1961!), Herrn

---

[1] Die Arbeiten von Herrn Professor Hoppe sind also nicht
durch die schönen Untersuchungen von BARTLETT über $XePtF_6$
angeregt worden, denn die Pläne zur Darstellung von
Xenonfluoriden sind viel älter und gehen bis 1949 zurück,
wie ich bezeugen kann.

Fig. 4 Letter from W. Klemm to H. Hyman of June 10, 1964, page 1. (Kindly provided by G. Girolami [66]). See the Appendix for the translation.

- 2 -

Professor Hoppe einige Bomben flüssigen Fluors zu schicken, konnte nicht realisiert werden, da die amerikanischen Ventile in Deutschland nicht zugelassen waren und die deutschen Ventile nicht in Amerika. Herr Professor Hoppe mußte daher mit Laboratoriumsmethoden zunächst einmal flüssiges Fluor herstellen und hat dann Anfang Juli 1962 - wie durch viele Zeugen belegt werden kann - das erste Xenondifluorid hergestellt und analysiert; in der letzten Juliwoche war man bereits sicher, reines, kristallines XeF$_2$ in Händen zu haben. Dieses Ergebnis wurde nicht sofort veröffentlicht, da noch die massenspektrometrischen Untersuchungen abgewartet werden sollten. In Münster befand sich damals kein Massenspektrometer, und daß der August zudem Ferienmonat ist, verzögerten sich diese Untersuchungen erheblich. Außerdem war ja auch nicht bekannt, daß von anderer Seite Arbeiten auf diesem Gebiet in Angriff genommen werden würden.

2.) Die amerikanischen Arbeiten auf diesem Gebiet sind, wie sich aus Ihrem Buch, Seite 31, ergibt, erst am 2. August begonnen worden, als Herr Professor Hoppe bereits Xenondifluorid dargestellt hatte. Die Veröffentlichung der Darstellung von Xenontetrafluorid ist aber schneller erfolgt (H.H. Claassen, H. Selig, and J.G. Malm, J.Am.Chem.Soc. 84, 3593, 1962). Diese Mitteilung wurde hier etwa am 1. Oktober bekannt.

3.) Am 8. Oktober hat dann Professor Hoppe in der Zeitschrift ANGEWANDTE CHEMIE 74, 903 (1962) das Xenondifluorid beschrieben. Bald darauf hat dann auch D.F. Smith in der Zeitschrift J.Chem.Physics 38, 270, 1963, das Xenondifluorid beschrieben - Eingangsdatum 29. Oktober 1962 - Bei der Darstellung des durch Herrn Professor Hoppe beschriebenen Xenonfluorids handelt es sich um ein anderes Verfahren.

Fig. 5 Letter from W. Klemm to H. Hyman of June 10, 1964, page 2. (Kindly provided by G. Girolami [66]). See the Appendix for the translation.

- 3 -

Aus dem Vorstehenden ergibt sich, daß die erste Publikation über Xenontetrafluorid und damit über binäre Edelgasverbindungen überhaupt durch die amerikanischen Forscher erfolgt ist, daß aber Xenondifluorid von Herrn Professor Hoppe dargestellt worden ist, ehe diese ihre Arbeiten begonnen haben, und daß Herr Professor Hoppe über die Darstellung von XeF_2 publiziert hat, ehe die erste amerikanische Mitteilung über XeF_2 erfolgte.

Eine geschichtlich korrekte Darstellung müßte also hervorheben, daß praktische gleichzeitig und unabhängig die Darstllung von binären Edelgasverbindungen erfolgt ist, und daß das XeF_4 zuerst angeregt durch BARTLETT's Arbeit von den Amerikanern, XeF_2 dagegen zuerst von deutscher Seite (unabhängig von BARTLETT's Untersuchung) dargestellt und publiziert worden ist.

Wie Sie sehen, entspricht dies nicht der Darstellung, die Sie in Ihrem Buch[x) geben, und ich darf der Erwartung Ausdruck geben, daß Sie bei einer Neuauflage die Verhältnisse richtig wiedergeben.

Ich weiß, daß unsere amerikanischen Kollegen größten Wert darauf legen, Fragen persönlicher Verdienste in fairer Weise zu behandeln. Ich möchte Ihnen die korekte Darstellung des zeitlichen Ablaufs, den Sie infolge der etwas verwickelten Verhätlnisse nicht übersehen konnten, natürlich nicht zum Vorwurf machen, umso weniger, als auch in einem deutschen Buch von WIBERG (1964) der Name HOPPE nicht einmal erwähnt ist.

Ich bin aber überzeugt, daß es Ihnen angenehm ist, daß ich den historischen Ablauf korrekt dargestellt habe.

Mit verbindlichen Grüssen
Ihr sehr ergebener

M. Klemm

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x) In einer späteren Arbeit (J.Chem. Education **41**, 174, 1964) wird bei der Besprechung von XeF_2 der Name HOPPE nicht einmal erwähnt.

Fig. 6 Letter from W. Klemm to H. Hyman of June 10, 1964, page 3. (Kindly provided by G. Girolami [66]). See the Appendix for the translation.

X.6 Acknowledgment

X.7 Appendix

The following is a translation of the letter from W. Klemm to H. Hyman of June 10, 1964, provided by G. Girolami [66].

June 10, 1964

Herr Professor Dr. H. H. Hyman
Argonne National Laboratories
9700 South Cass A venue
Argonne, Illinois 60440

Dear Mr. Hyman:

I wanted to write briefly to you about a matter that has occupied me for some time. It concerns the share which Herr Professor Hoppe had in the discovery of binary noble gas compounds, especially xenon difluoride. You write on page 34 of your book "Noble Gas Compounds" concerning this, and at the end you write:

"On learning of the Argonne discovery of xenon tetrafluoride, the München group proceeded with their own approach and published some inadequately established preliminary observations. Their contribution to this volume is a revised and somewhat enlarged version of this earlier communication."

By München is actually meant Münster.

This account without doubt does not give the correct facts, and in this regard there is a risk that later historical accounts of the circumstances will again be incorrectly given. I would like to describe to you briefly how it really was.

1.) As you correctly write, Professor Hoppe had long had a plan to prepare fluorides of xenon.[1] The difficulty existed in the procurement of liquid fluorine, which was not prepared industrially in Germany. A promise by Allied Chemical Corporation (in August 1961!) to send Professor Hoppe several bombs of liquid fluorine could not be realized, because the American valves were not permitted in Germany and the German valves were not permitted in America. Therefore, Professor Hoppe had to prepare some liquid fluorine via laboratory methods, and by the beginning of July 1962 - as many witnesses can attest - had prepared and

---

[1] The work of Professor Hoppe was not stimulated by the beautiful investigations of Bartlett on $XePtF_6$, because the plans for the preparation of xenon fluorides were much older and go back to 1949, as I can testify.

analyzed the first xenon difluoride; in the last week of July 1962 they were already certain that they had pure, crystalline XeF_2 in hand. These results were not immediately published, but instead because they had to wait for the mass spectrometric studies. In Munster there were at that time no mass spectrometers, and moreover because August is the holiday month, this research was considerably delayed. Also it was not known that on the other side [of the Atlantic] work attacking this field was being undertaken.

2.) The American work in this field was, as you prove in your book on page 31, first begun on August 2nd, when Professor Hoppe already had prepared xenon difluoride. However, the publication of the preparation of xenon <u>tetra</u>fluoride took place more quickly (H. H. Claassen, H. Selig, and J. G. Maim, J. Am. Chem. Soc. 84, 3593, 1962). This communication became known here about October 1st.

3.) On October 8th, Professor Hoppe described xenon <u>di</u>fluoride in the journal Angewandte Chemie 14, 903 (1962). Soon thereafter, D. F. Smith also described xenon difluoride in the journal J. Chem. Physics, 38, 270, 1963 - receipt date October 29, 1962. It concerns a different procedure for the preparation of xenon difluoride than that described by Professor Hoppe.

From the preceding it follows that the first publication concerning xenon <u>tetra</u>fluoride, and therewith concerning binary noble gas compounds generally, resulted owing to the American researchers, but that xenon difluoride was prepared by Professor Hoppe before their work had begun, and that Professor Hoppe had published the preparation of XeF_2 before the first American communication on XeF_2 took place.

A historically correct account must also emphasize that the preparation of binary noble gas compounds occurred practically <u>at the same time and independently</u>, and that, stimulated by Bartlett's work, XeF_4 was first prepared and publicized by the Americans, while XeF_2 was first prepared and publicized by the German side (independently of Bartlett's research).

As you see, the account given in your book[2] does not correspond to this, and I should give the expected expression that you will correctly recount the circumstances in a new edition.

I know our American colleagues place great value in treating questions of personal credit in a fair way. I naturally do not wish to blame you for the incorrect account of the past course of events, which you could not survey due to the somewhat complicated circumstances; much less, as also in a German book by Wiberg (1964) the name Hoppe is not mentioned once. I am however convinced that you will accept that I have depicted the historical course of events correctly.

    With obliging greetings
    Yours very devotedly

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[2] In a later work (J. Chem Education 41, 174, 1964) during the discussion of XeF_2 the name Hoppe is not mentioned once.

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[Translated by G. S. Girolami, 26 Dec 1992.]

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