Conclusions

The safest solvent which can be used for testing iodine and bromine is ICI Arklone P but because of its high initial price, the much cheaper tetrachloroethene is highly recommended. Dichloromethane is a third solvent which is technically satisfactory if the preferred tetrachloroethene is not available. All these solvents offer high standards of safety; they are all non-flammable and they are reliable and easy to recover; they are all well established commercial products and are thus excellent links between teaching and everyday life.

The use of tetrachloromethane as a routine general reagent should be abandoned since it is a serious hazard to health and is technically no longer the best product available. Supplies of the recommended solvents are available from the usual suppliers of laboratory chemicals.

Acknowledgements

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The Principal of Pendleton College, Mr W. J. Mills, BA, ACIS, kindly read the text. The work described was carried out in the laboratories of Pendleton College over three years with the help of many students and the College Science Club.

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Noble gas compounds – in the beginning

C. B. Hunt


NEIL BARTLETT

Just 21 years ago, the first true chemical compound of a noble-gas element was prepared in an experiment which swept away years of scepticism. This article describes the circumstances in which this discovery was made.

The discovery of the noble-gas elements stemmed from Lord Rayleigh's observations on gas densities and his suggestion that atmospheric nitrogen contained an inert gas. This suggestion was investigated experimentally in 1894 by Sir William Ramsay who was able to announce his discovery of a new gaseous constituent of the atmosphere, which 'has so long been with us, incognito', at a meeting of the Chemistry Section of the British Association for the Advancement of Science (BAAS) in Oxford on Monday, 13 August, 1894. The gas was named argon, from the Greek *argos* meaning inert.

Shortly after the discovery of helium the following year (although it had been detected spectroscopically in the spectrum of the sun in 1868), Ramsay reflected on the position of these elements in the periodic table and accordingly prefaced his Presidential Address to the Chemistry Section of the 1897 BAAS meeting in Toronto, with the following words:

> . . . perhaps I may be excused if I take this opportunity of indulging in the dangerous luxury of prophecy, a luxury which the managers of scientific journals do not often permit their readers to taste.
>
> The subject of my remarks today 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.

This element was neon, discovered only one year later, and by the end of the century another three elements had been added to the list (Table 1).

Table 1. The noble-gas elements.

Helium	He	from *helios*, sun	1895
Neon	Ne	from *neos*, new	1898
Argon	Ar	from *argos*, inert	1894
Krypton	Kr	from *kryptos*, hidden	1898
Xenon	Xe	from *xenos*, strange	1898
Radon	Rn	from radium	1900

During the course of his work Ramsay had frequent occasion to emphasise the chemical inertness of these elements, a point which continued to be stressed for the next 50 years. A claim by Marcellin Berthelot (1827–1907), professor of organic chemistry at the École de France, made to the Académie des Sciences in Paris as early as March, 1895, that a compound could be formed between argon and benzene proved spurious as his experimental results could not be reproduced: 'though Berthelot must always take high rank as a chemist, no chemist of note has placed on record so many statements which cannot be verified' was the tart judgement delivered by Morris Travers, an erstwhile assistant of Ramsay's.

In contrast, Ramsay wrote in his book *The gases of the atmosphere,* published in 1896, 'It cannot, of course, be stated with absolute certainty that no element can combine with argon, but it appears at least improbable that any compounds will be formed'. With the subsequent development of theories of chemical bonding by G. N. Lewis, W. Kossel, I. Langmuir and others, the chemical inertness of these elements became axiomatic and deeply entrenched in chemical thinking. Only a few sporadic attempts were made to disprove this view although some slight encouragement had been proffered by Linus Pauling who, in 1933, suggested[1] that compounds of xenon and fluorine might be possible and even went so far as to suggest formulae for speculative compounds such as XeF_6 and H_4XeO_6. One important attempt to combine these two elements was recorded in the chemical literature;[2] although it was unsuccessful it is clear, with hindsight, that the workers came very close to success. It seems that chemists remained convinced of the unprofitable nature of such research; perhaps they should have heeded the advice offered to Alice (*Through the Looking Glass*) who, on complaining 'There's no use trying, one can't believe impossible things', was told by the Queen 'I daresay you haven't had much practice'.

It is possible to argue that the fairly ready acceptance of the inertness of the noble-gas elements is an example of the way in which a scientific law or orthodoxy can inhibit or stifle research. Not surprisingly, therefore, the announcement, in 1962, that such an element could form a true compound caused great excitement in the chemical world. At the root of it was a young British chemist called Neil Bartlett.

Super-oxidiser PtF_6

Neil Bartlett was born on 15 September 1932 in Newcastle upon Tyne and entered the then King's College (now the University of Newcastle upon Tyne) to read chemistry in 1951. After graduation he carried out research there under the supervision of Professor P. L. Robinson. In 1958 Bartlett was appointed lecturer in chemistry at the University of British Columbia in Vancouver, where he began research into the fluorides of platinum. His aims were to investigate compounds in which such metals exhibited high oxidation states and to elucidate the relationship between the molecular geometry of these compounds and their electron configurations.

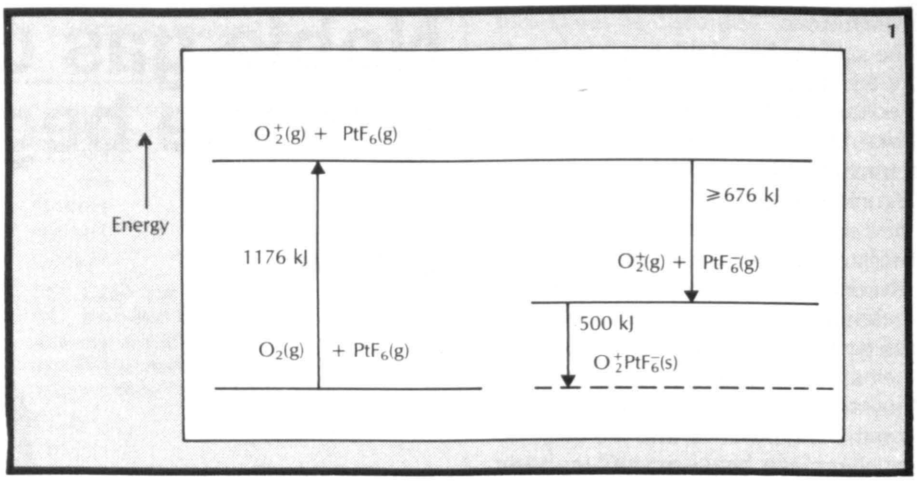

Fig. 1. Energy cycle for the formation of O_2PtF_6.

In 1956, while still at King's College, Bartlett had found that when platinum metal and some of its compounds were treated with fluorine in glass or silica apparatus at moderate temperatures, a deep red solid was formed which could be sublimed under vacuum at less than 100°C. When he arrived in Vancouver, he assigned to his first PhD research student, D. H. Lohmann, the task of analysing this compound and determining its structure. It soon became clear that the compound was an oxyfluoride and that the incorporated oxygen must have originated in reaction of the fluorine with the silica apparatus, according to the equation

$$SiO_2 + 2F_2 \longrightarrow SiF_4 + O_2$$

This suspicion was confirmed when platinum was treated with fluorine in a nickel container and no compound was obtained.

The analysis of the deep red product proved no easy task, particularly for a research student, because the compound reacted violently with water to give a mixture of products affording inconsistent analytical figures. Hydrolysis of the solid with water vapour, however, was more successful and by the time that Lohmann had completed his thesis in October 1961 the formula O_2PtF_6 had been proposed for it.

Evidence suggested that the compound was an ionic salt to be formulated as $O_2^+PtF_6^-$. Says Bartlett:

> The work establishing $O_2^+PtF_6^-$ was the most difficult of my career. The composition had been established as O_2PtF_6 but we were not yet convinced that it was $O_2^+PtF_6^-$. Soon after Lohmann's departure, however, I had the idea of preparing the salts $NO^+OsF_6^-$ (by mixing nitric oxide with OsF_6) and $NO^+SbF_6^-$ (by a more conventional solution method). These compounds proved to be structurally similar to O_2PtF_6 and I was encouraged to work out the structure of the platinum salt on the basis of the salt formulation $O_2^+PtF_6^-$. Quite quickly all of the bits of the puzzle fit into their places with this formulation; the structure fit, the magnetic properties fit and even the chemistry fit. My scepticism (of the energetically bewildering O_2^+ formulation) disappeared. Of course, the major problem with $O_2^+PtF_6^-$ was that the oxidation of O_2 to yield O_2^+ demanded of PtF_6 that it be a better oxidiser than anyone had believed could exist.

Figure 1 shows an energy cycle for the formation of the salt using enthalpy values, rather than free energy values, for simplicity. The first ionisation energy for molecular oxygen O_2 is 1176 kJ mol^{-1}. Calculation of a lattice energy using the Kapustinskii equation gives a value of about 500 kJ mol^{-1}. Thus for reaction to be favoured, *ie* for the reaction to show a negative enthalpy change (ignoring any entropy factors at this stage) it would seem that PtF_6 must have an electron affinity greater than 676 kJ mol^{-1}, nearly twice the value for fluorine or chlorine.

Bartlett resolved to react O_2 with PtF_6 in the hope that they would combine directly. PtF_6 had first been made, in 1957, by a research group headed by Bernard Weinstock at the Argonne National Laboratory in Chicago where research into fluorine chemistry had been conducted ever since World War II. Bartlett had avoided working with it, previously, feeling that the compound 'belonged' to the other group. By the end of 1961, however, that group had not reported any reaction between O_2 and PtF_6 and so Bartlett put aside his objection to working with it, particularly since he could establish precedence with the compound that he had made back in Newcastle in 1956 – 'you see that we were lucky'. When the PtF_6 was mixed with oxygen at room temperature the familiar red solid was indeed formed

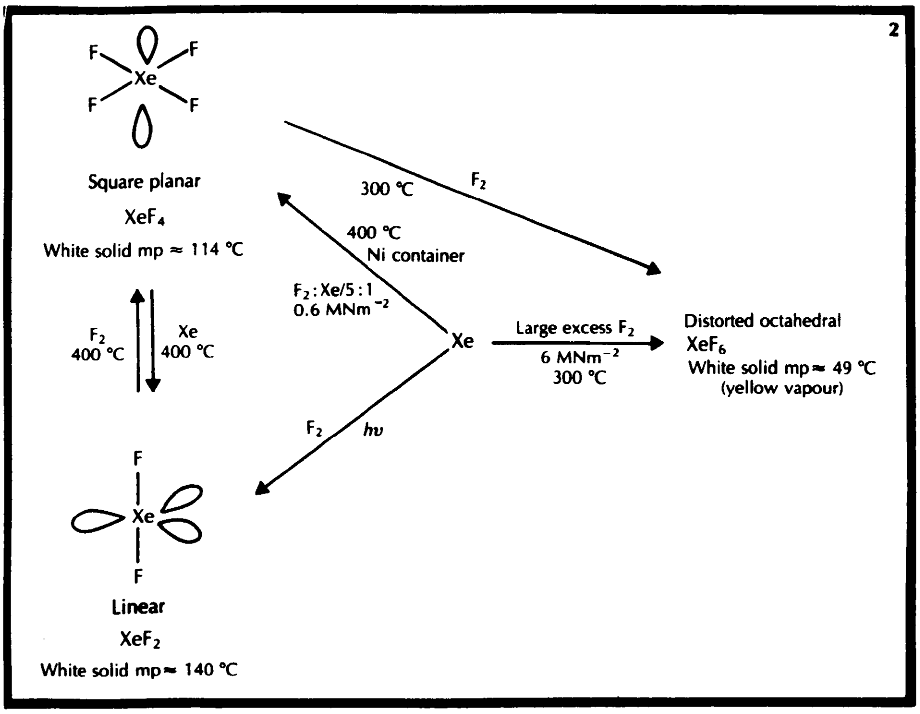

Fig. 2. Xenon fluorides.

immediately and Bartlett's reaction was – 'I was convinced that PtF_6 was the most powerful oxidiser the world has yet known.'

The intriguing observations and results of Bartlett and Lohmann were published[3] in March 1962 but the reaction of the chemical fraternity was not quite what Bartlett had expected:

> Once the $O_2^+PtF_6^-$ report was published the cat was out of the bag and I worried that there would be a rush to PtF_6 chemistry. To my surprise there was not and I met much scepticism about $O_2^+PtF_6^-$, even in the chemistry department at the University of British Columbia, where I had discussed the experimental evidence and demonstrated the $O_2^+PtF_6^-$ reaction to produce the salt. Certainly, I was myself very excited about this remarkable oxidising capability of PtF_6 and I was convinced that it would carry off other spectacular oxidations if applied properly. Naturally, I wanted to find an even more spectacular case than O_2 and this desire was probably fired a little by a wish to prove the super-oxidiser status of PtF_6 to the doubting Thomases about me.

Bartlett's train of thought was being directed slowly towards the noble gases although when the idea first struck him it did not inspire any confidence.

> I knew that PtF_6 would not oxidise N_2 since nitrogen had been used as a carrier gas for F_2 in our early preparations of O_2PtF_6. On one occasion, in late 1961, the noble gases did occur to me, but I happened to know that the first ionisation energy of helium is 2370 kJ mol^{-1} and this knowledge led me quickly to dismiss further conscious thought along these lines.

Oxidising noble gases

But it was by the merest chance that Bartlett's attention was brought back to the noble gases.

> The crucial step occurred in late February, 1962. I was preparing a lecture for sophomores and had occasion to check a textbook. By chance, as I was flicking through the text, the familiar plot of first ionisation energies of the elements as a function of atomic number caught my eye. In an instant the old thought, of the possibility of oxidising the noble gases, returned. A quick check confirmed my immediate suspicion that the heavier gases should be oxidisable by PtF_6. Radon looked a certain bet since the ionisation energy was only 1040 kJ mol^{-1} compared with 1176 kJ mol^{-1} for oxygen. But even xenon looked good since its ionisation energy, 1170 kJ mol^{-1}, was marginally less than that of oxygen. Although I recognised that both Rn and Xe were likely to be bigger than O_2^+, and the lattice energies of the salts therefore smaller than for $O_2^+PtF_6^-$, I estimated that this effect was not likely to be adverse by more than 42 kJ mol^{-1}. Work with radon was out of the question at UBC, but xenon posed no problems.
>
> I still recall leaving my office quickly, after the idea had come to me, to find one of my colleagues who routinely used the heavier noble gases for matrix-isolation spectroscopy. By coincidence, he was in the hallway talking to another colleague. I asked the spectroscopist 'Do you have any xenon you could let me have?' His response was 'No, I'm sorry, plenty of krypton but no xenon–what do you want the xenon for?' To my reply 'to oxidise it' both laughed, although not derisively. Their laughter indicated to me then, that they did not believe, as I did, in the super-oxidiser capability of PtF_6, but I believe now that it probably had more to do with the concept of the inertness of the noble gases. In any case, I was convinced that my reasoning was sound and I ordered the xenon.

Bartlett set up a piece of apparatus which contained a break-seal bulb with a narrow tube by-passing the seal. The deep red PtF_6 vapour was introduced into the bulb by way of the by-pass which was then sealed off to contain the fluoride in the bulb. The xenon gas was separated from it by the thin glass capillary seal. Bartlett well remembers that day, 23 March 1962:

> It had taken the entire day to get everything set up and I wasn't ready to break the glass capillary separating the xenon and PtF_6 until about 6.45 pm. My students had left for supper (they never admitted to scepticism) and I was alone when the capillary was broken. Of course, I was overjoyed when there was an immediate interaction of the gases. Everything had gone as predicted. Everything held together. Naturally, I was conscious of the sceptics and took care to prove that my xenon *was* xenon and also demonstrated that xenon was retained even on sublimation of the $Xe^+PtF_6^-$ material.

When the two gases mixed at room temperature they deposited a yellow-orange crystalline solid rapidly. It was as simple as that – xenon was *not* chemically inert:

$$Xe(g) + PtF_6(g) \longrightarrow Xe^+PtF_6^-\ (s)$$

Subsequent work showed that the reaction did not always follow this course, as illustrated[4] by the results in Table 2. The stoichiometry of the reaction varied between 1 and 2 moles PtF_6 for every mole of xenon which reacted. Explains Bartlett:

> Unfortunately the interaction of xenon with PtF_6 proved to be more complex than a simple 1 : 1 oxidation and only some time later were we able to prepare high-purity $XePtF_6$, by using a large excess of xenon with dilute PtF_6. We got rather tied up on this complex system and with a desire to fix krypton, which I guessed could be done by RhF_6. For these reasons, I missed being the first to synthesise xenon fluorides (this was the consolation prize for the Argonne scientists). Ironically however, we quickly discovered that pyrolysis of the $XePtF_6$ product yielded XeF_4.

Table 2. Some results for the xenon + platinum hexafluoride reaction.[4]

Tensimetric results for gas + gas reaction in a glass bulb		
	(1)	(2)
Pressure of PtF_6 mm	95.0	70.0
Initial pressure of Xe mm	156.5	72.0
Residual pressure of Xe mm	82.0	23.0
Combining ratio Xe : PtF_6	1 : 1.27	1 : 1.42

Tensimetric results for PtF_6 (solid + gas) + Xe (gas) in a glass bulb			
	(1)	(2)	(3)
Initial pressure of PtF_6 mm	93.0	56.0	117.5
Residual pressure of PtF_6 mm	0	12.0	0
Initial pressure of Xe mm	108.0	27.5	117.5
Residual pressure of Xe mm	17.0	0	59.0
Combining ratio Xe : PtF_6	1 : 1.02	1 : 1.60	1 : 2.0

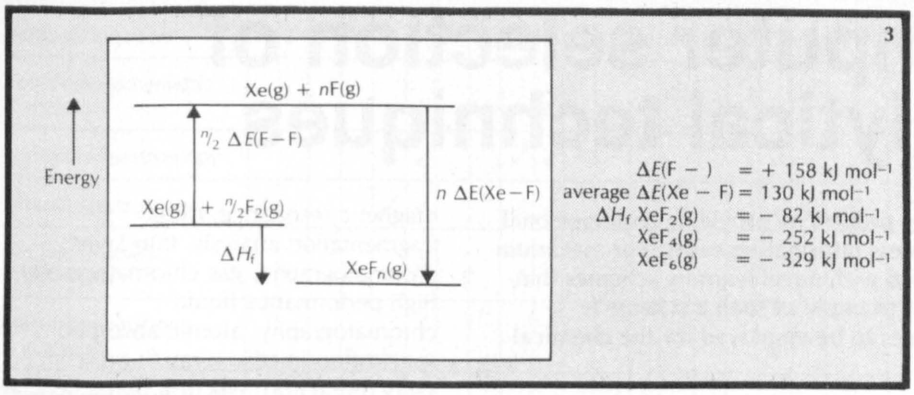

Fig. 3. Thermodynamic cycle for the formation of xenon fluorides.

These reactions described by Bartlett are:

$$Xe + PtF \longrightarrow Xe^{+}PtF_6^{-}$$
$$Xe^{+}PtF_6^{-} + PtF_6^{-} \longrightarrow XeF^{+}PtF_6^{-} + PtF_5$$

His results were published as a short, prosaic note[5] in the *Proceedings of the Chemical Society* to whom he had sent them on 4 May 1962. Bartlett recalls:

> My communication on $XePtF_6$ had first been submitted to *Nature* on 2 April 1962 (I deliberately avoided sending it on 1 April) and since the editors responded to my letters by sea-mail to Vancouver (then 6 weeks delivery time) I eventually and exasperatedly withdrew the communication and submitted it instead to *Proc. Chem. Soc.* where it appeared in the June issue. Many people in Britain knew of $XePtF_6$ as early as late April.

Further work

The conventional format in which the results of Bartlett's experiments were communicated to the scientific world typifies the almost clinical 'depersonalised' accounts which constitute scientific communications and which rob us of so much excitement and interest in chemical research; this is one reason for the present article. Nevertheless, when the note appeared it caused quite a sensation and the claim to have prepared the first true noble gas compound spurred other groups to similar efforts.

Following the publication of Bartlett's note, the team working on fluorine chemistry at the Argonne National Laboratory had no difficulty in reproducing Bartlett's experimental results and they lost no time in trying other metal fluorides in the reaction. Using RuF_6 they found that the molar reacting ratio with xenon was more like 3:1 than 1:1 and that RuF_6 was evidently acting as a fluorinating agent. The direct reaction between xenon and fluorine therefore seemed distinctly possible. On 2 August, less than two months after Bartlett's publication, Howard Claassen, Henry Selig and John Malm, of the Argonne laboratory, carried out their first experiment on the direct combination of xenon and fluorine. By heating five volumes of fluorine with one volume of xenon at 400°C in a nickel container for one hour, followed by rapid cooling they were able to obtain large white crystals of XeF_4. Some unexpected analytical results of their compound delayed the announcement of their findings but it was finally made in a note[6] which was sent off for publication in the *Journal of the American Chemical Society* on 20 August. By varying the proportions of fluorine and xenon a difluoride and a hexafluoride could also be obtained (*Fig. 2*).

Workers in any field of research seldom lack competitors and unknown to the Argonne team xenon difluoride had already been prepared one month earlier at the Anorganisch-chemisches Institut of the University of Münster in Westphalia. A research group was based there under the direction of Dr Rudolph Hoppe who had first contemplated the synthesis of xenon fluorides over 13 years earlier. He had been particularly interested in the synthesis of fluorides since 1951. 'We were convinced' Dr Hoppe has written 'that xenon tetrafluoride and difluoride must be thermodynamically stable to decomposition into their elements'. Efforts to synthesise such compounds had been thwarted, however, by lack of supplies of xenon of sufficient purity and the unavailability of cylinders of compressed fluorine gas.

During the last week of July, 1962, no doubt encouraged by Bartlett's paper which appeared in print in June, the team subjected a mixture of pure xenon and fluorine gases contained in a sealed quartz vessel to electrical discharges from an induction coil. They produced colourless crystals of xenon difluoride. To ensure that they were not criticised for lack of convincing data, they subjected the compound to an extremely thorough investigation which, unfortunately for them, delayed the publication of their results. These were finally submitted for publication in the German journal *Angewandte Chemie* on 8 October. By this time, of course, the Americans had published their work on the tetrafluoride and so had beaten them to it, although in point of fact the work post-dated Hoppe's.

In 1962, Professors Cotton and Wilkinson were able to write in their textbook:[8]

> All of these elements are chemically inert as the group name implies. They form no chemically bound compounds since with high ionization potentials and negligible electron affinities they can neither lose nor gain any electrons in ordinary chemical processes.

Within the space of some six years, there appeared three textbooks devoted solely to the chemistry of the noble gases!

The synthesis of noble gas compounds was thought at first to have important implications for theories of chemical bonding, based on the dogma of the electronic octet, but in fact it has necessitated no radical changes and thermodynamic data are available for consideration and analysis of the formation of various noble-gas compounds (*eg Fig. 3*). Many compounds are now known although it seems unlikely that any compounds of helium, neon or argon will be made.

Acknowledgement: I wish to express my sincere thanks to Professor Neil Bartlett, FRS for the generous help given to me, some time ago, in answering my questions concerning his work.

Clive B. Hunt is chemistry master at Birkenhead School, Birkenhead, Merseyside. He is particularly interested in the more recent history of chemical discoveries.

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