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Preface

The elements of group 18 (the noble gases) are, generally, perceived as only less reactive. Only krypton and xenon form, in fact, isolable compounds (the radioactive and short-lived radon is hardly investigated), and the synthesis of compounds containing helium, neon, and argon still remains an open challenge. Chemistry is, however, also a matter of environment and conditions, and, particularly for noble gas chemistry, a proper choice of these factors may open doors that would remain, otherwise, definitely locked. The HArF detected so far in cold matrices, and the Na_2He recently obtained at the highest pressures (unique compounds of argon and helium, respectively), are two major illustrative examples. But the binding capabilities of the noble gases are greatly enhanced also under the isolated conditions of the gas phase. In this environment, all the elements, including helium and neon, really ‘forget’ to be inert, and form an exceptionally large family of molecular species, ranging from fragile van der Waals adducts to strongly bound covalent species. A variety that is, probably, unique in the periodic table! Interestingly, this richness is, in essence, the daughter of the inertness. Thus, while resistant (especially He, Ne, and Ar) to definitely break their electronic clouds to form true ionic or covalent bonds, the noble gas atoms are still sensitive to the polarisation effects exerted by neutral and ionic binding partners. The stabilising interactions thus range from dispersion forces to electrostatic and inductive interactions, with in case contribution of charge transfer. And the spectrum of the bonding motifs further enlarges under photodissociating or ionising conditions that favour also the formation of true covalent bonds. The simplest HeH^+ was, indeed, first detected in 1925, nearly 40 years before the breakthrough advances in xenon chemistry that officially destroyed the myth of noble gas inertness! And ArH^+ was quite recently detected in the galactic and extragalactic regions as the first naturally occurring species containing a noble gas atom: a connection between Nature and laboratory that, certainly, rejuvenates the interest for the gas-phase chemistry of the noble gases. This is, indeed, the main topic of this book, with emphasis on both neutral and ionic species. The matter is, certainly, of experimental interest, but it enjoys also the major contribution of the calculations that are extensively employed not only to aid the interpretation of the experiments but also to independently explore still unreported molecules and ions. The subtitle of the book ‘Structure, Bonding, and Gas-Phase Chemistry’ wishes also to emphasise the strict relationship in this field between experiments and theory.

The book is divided in two parts. The first one (Chapters 1–3) is intended as an introductory overview of noble gas chemistry, also functional to the second part, more specifically concerned with gaseous neutral (Chapter 4) and ionic species (Chapter 5). Chapter 1 is, in particular, a historical introduction to noble gas chemistry, aimed at emphasising the salient facts that marked the discovery of the elements, the emerging of their reactivity under different experimental conditions, and the subsequent evolution of these fields. Chapter 2 illustrates a classification of noble gas compounds, grouped here in five categories (clusters of noble gas atoms, monocoordinated-, dicoordinated-, polycoordinated compounds, and cage, inclusion, and adsorption compounds) that appeared best suited for gaseous species. Alternative classifications could be, certainly, generally taken, and I could say the same for the selected illustrative examples. Chapter 3 is concerned with the applications of the calculations, with emphasis on issues of major interest in noble gas chemistry, particularly gas-phase chemistry: the structure and stability of noble gas compounds, their bonding character, and the kinetics of their formation and decomposition processes. The methods most extensively employed to perform the bonding analysis of noble gas compounds are also shortly recognised here. The methods most commonly employed for electronic structure calculations were, instead, briefly recalled in Appendix B. Chapter 4 is, mainly, concerned with the structure, bonding, and stability of gaseous neutral species. The first discussed systems are monocoordinated adducts of diverse composition and complexity, examined in terms of a preliminarily outlined interpretative model. Gaseous dicoordinated covalent compounds are also accounted. Chapter 5 is concerned with gas-phase ion chemistry, and illustrates issues of current interest such as the behaviour of the noble gases as ligands of ionic species, the chemistry of protonated noble gases and other related species, and the properties of other ions of potential interstellar interest. Illustrative examples of gaseous ionic reactions involving noble gas atoms are also accounted.

The book is, mostly, built on original research articles published in journals. The various authors and groups are mentioned in the cited references, and I wish to thank the colleagues who kindly provided reprints or preprints of their work. The choice of the covered issues and illustrative examples is, certainly, not exhaustive, and mirrors, to some extent, my own experience in this field. I apologise here to anyone whose contribution may have been missed. A relevant part of the cited articles were accessed through the online library of the Italian National Council of Research, and I am really indebted to this institution for this invaluable support. I greatly appreciated stimulating discussions with the colleagues in Perugia L. Belpassi, F. Pirani, and F. Tarantelli, and I am also grateful to my coworkers in Viterbo S. Borocci, N. Bronzolino, and M. Giordani, who shared with me, over the years, the interest for noble gas chemistry. Finally, this book is, certainly, also the result of the love, patience, and understanding of my family: my wife Franci, and my children Silvia and Simone. To them, my deepest gratitude. The book is also dedicated to my parents, and to the memory of my uncle.

Viterbo, September 2017 *Felice Grandinetti*

Part I

An Overview of Noble Gas Chemistry

1

A Historical Introduction

1.1 The Discovery of the Elements

The discovery of the noble gases is one of the most fascinating episodes in the history of science. It tells about creativeness and intuition, as well as rigour and perseverance. It is also a real showcase of fundamental and applied science working in concert.

All the noble gases (but radon) are natural constituents of air, with percentages in volume which range from c. 0.9% (Ar) to less than $9 \times 10^{-6}\%$ (Xe) (see Appendix A). However, while apparently so accessible, these elements remained unknown until the end of the nineteenth century, when physical methods, particularly spectral analysis and liquefaction of gases, became sufficiently well developed. It was not that chemists and physicists had not previously encountered them. In particular, in 1785, when reporting about his 'Experiments on air', Cavendish (1785, p. 382) wrote:

> Having by these means [exhaustive electric sparking] condensed as much as I could of the phlogisticated air [N_2], I let up some solution of liver of sulphur to absorb the dephlogisticated air [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 into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude, that it is not more than 1/120 part of the whole.

He had actually isolated argon (and, probably, also other noble gases), but he did not recognise this residue as a new element. The official discovery had to wait more than one century, and its announcement was the epilogue of a really intriguing story. In 1892, Lord Rayleigh (born John William Strutt) had observed that the nitrogen obtained from the reaction of ammonia with oxygen was lighter than the nitrogen recovered from common air. The difference was small (nearly one part in 1000), but, as Rayleigh wrote in a letter to *Nature* of September 29 (Rayleigh, 1892, p. 512), it was 'entirely outside the errors of experiment'. He declared to be 'much puzzled' by these findings, 'obliged if any of your chemical readers can offer suggestions as to the cause'. No proposals came at that time, and Rayleigh continued to work on this anomaly. He could thus confirm that,

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irrespective of the preparation method, the ‘chemical’ nitrogen was, invariably, lighter than the ‘atmospheric’ nitrogen (Rayleigh, 1893). In a paper read on 19 April 1894, Rayleigh (1894, p. 340) wrote:

> Upon the assumption that similar gas should be obtained by both methods, we may explain the discrepancy by supposing either that the atmospheric nitrogen was too heavy on account of imperfect removal of oxygen, or that the ammonia nitrogen was too light on account of contamination with gases lighter than pure nitrogen.

He could, actually, safely discard the first alternative, but the contaminant lighter than the ammonia nitrogen remained elusive, and he honestly recognised that ‘the difficulties in the way of accepting the second alternative are hardly less formidable’. After the lecture, Ramsay, who was sitting in the audience, suggested to Rayleigh that the atmospheric nitrogen could be contaminated by a heavier component other than oxygen. The episode was recalled by Ramsay himself in his Nobel Lecture of 1904 (Ramsay, 1904):

> Before leaving Bristol, I had carried out some experiments in connection with the combination of gaseous nitrogen with hydrogen and with oxygen, with the aid of platinum as a catalysing agent; the results of the research were negative, and were not published. But I must have read the well-known account of Cavendish’s classical experiment on the combination of the nitrogen and the oxygen of the air at that date; for in my copy of Cavendish’s life, published by the Cavendish Society in 1849, opposite his statement that on passing electric sparks through a mixture of nitrogen with excess of oxygen, he had obtained a small residue, amounting to not more than 1/120th of the whole, I find that I had written the words “look into this”. It must have been the latent memory of this circumstance which led me, in 1894, to suggest to Lord Rayleigh a reason for the high density which he had found for “atmospheric nitrogen”.

With the permission of Rayleigh, Ramsay started independent work, aimed at isolating the suspected, and still unknown, heavier component of air. After removal of O_2 by reaction with hot copper, he fixed N_2 by repeated reactions with hot magnesium (to form Mg_3N_2), and showed that, after each run, the residual nitrogen became progressively denser. From May to August 1894, Ramsay was in continuing correspondence with Rayleigh, and, on August 4, he communicated to him to have isolated the gas. Two days later, Rayleigh responded that he, too, had isolated the gas, ‘though in miserably small quantities’. The two scientists decided to join the efforts, and asked Sir William Crooks to examine the spectrum of the new gas. The observed lines were definitely different from those of nitrogen. The results were communicated on 13 August to the British Academy for the Advancement of Science. The new proposed element resulted chemically inactive, and was therefore called *argon* (after the Greek ἀργόν, the inactive). The achievement was really astonishing, and prompted some criticisms and debate.

Figure 1.1 Sir William Ramsay and Lord Rayleigh shortly after the discovery of argon. *Source:* Thomas (2004). Reproduced with permission of John Wiley & Sons.

Thus, Rayleigh and Ramsay spent 5 additional months to reinforce the evidence, and, on 31 January 1895, in a crowded theatre of the University of London, they could officially read to the Royal Society (the president Lord Kelvin sitting in the chair) their long-waited paper on 'Argon, a new constituent of the atmosphere' (Rayleigh and Ramsay, 1895). A picture of Sir William Ramsay and Lord Rayleigh taken shortly after the isolation of argon is shown in Figure 1.1.

The independent role in this discovery of this 'non-inert pair' of British scientists (according to a nice definition by Thomas (2004)) was officially recognised in 1904, when the Royal Swedish Academy of Sciences awarded Lord Rayleigh the Nobel Prize in Physics 'for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies', and Sir William Ramsay the Nobel Prize in Chemistry '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'. The latter motivation highlights also that, for Ramsay, the discovery of argon was just the first episode of an exceptional scientific adventure that led him to isolate, within 4 years, an entire new group of chemical elements (a nice account of the salient legs is given by Ramsay (1904)). The second conquered element was helium. In seeking for a clue which would guide to the formation of argon compounds, Ramsay learnt about a report by Dr. Hillebrand, a chemist to the Geological Survey of the United States, on the occurrence of nitrogen in uranium minerals. Hillebrand noticed that compounds such as uraninite and cleveite, when heated with dilute sulphuric acid, gave off a gas, which he identified as nitrogen based on its chemical behaviour and spectral lines. Ramsay doubted on this assignment, and believed that the gas could be argon. He therefore re-examined the spectra (evolving the gas, in particular, from cleveite), and noticed a brilliant yellow line, absent in the argon spectrum, and nearly, but not quite, coincident with the *D* line of sodium. He asked Crooks to examine this line, and the answer was astonishing: the measured wavelength of 587.49 nm was exactly coincident with the D_3 line detected in the solar chromosphere! This emission was, actually, known to the astronomers since 1868, and had been assigned to an element unknown on the earth, named *helium* after the Greek ἥλιος (the sun) (Hillebrand subsequently wrote to Ramsay that, when examining the spectrum of the evolved gas, he noted, indeed, lines that could not be identified with any mapped one. However, taking into account the well-known variability in the spectra of some substances under the varying operating conditions of the discharge tube, he ascribed causes similar to these anomalous appearances, and rejected the considered hypothesis that a new element might be in question). Ramsay communicated the identification of the terrestrial helium on 26 March 1895 (Ramsay, 1895), beating on time the Swedish chemist Abraham Langlet, who shortly afterwards independently isolated the element working in Cleve's laboratory. In a subsequent and more extensive account of his findings (Ramsay, Collie and Travers, 1895), Ramsay, honestly, noted that, in 1882, Luigi Palmieri, on examining a lava-like product ejected by Vesuvius, found a soft substance which gave a yellow spectral line of wavelength 587.5 nm. However, the Italian scientist did not investigate this point in further detail.

The physical and chemical properties of helium and argon were strictly similar, making it evident that they belonged to the same natural family. In addition, their atomic weights of 2 and 40 made evident the necessity of at least one element with the atomic weight of 20 (as a matter of fact, Ramsay was convinced that two other elements awaited discovery). Thus, with the help of his assistant Dr. Travers, he started a wide research programme, and spent nearly 3 years to examine the gases evolved from minerals and meteorites, or collected from hot or mineral springs, and to perform the fractional diffusion of patiently collected samples of helium and argon. The results were sometimes encouraging, but real breakthrough advances were achieved only in the early summer of 1898, when Dr. Hampson, who had invented a machine for the liquefaction of gases, placed at the disposal of Ramsay and Travers about 750 cc of liquid air. As Ramsay reported in the accounting paper of 3 June 1898 (Ramsay and Travers, 1898a), the sample was evaporated almost entirely, and a small residue of 10 cc was slowly boiled off into a gas holder. After removal of oxygen and nitrogen, there remained 26 cc of a gas which showed, besides the spectrum of argon, new lines not seen before. The new element was named *krypton* after the Greek κρυπτόν (the hidden), and its atomic weight was estimated as 80. Only 10 days later, Ramsay and Travers (1898b) announced the isolation of still another gas, contained in the lower boiling portions of a previously collected sample of 18 l of argon. They proposed the name *neon* after the Greek νέον (the new). The element showed a spectrum featuring a brilliant flame-coloured light, consisting of many red, orange, and yellow lines. Its density turned out to be intermediate between that of helium and argon, although it had not yet been isolated as a pure gas. The complete separation of neon and argon was achieved only later.

In September 1898, Ramsay and Travers (1898c) announced the discovery of *xenon* (after the Greek ξένον, the stranger). It was separated from krypton by fractionation, and, indeed, it possessed a still higher boiling point. The pure element was, however, obtained only in the middle of 1900 (Ramsay and Travers, 1900).

The discovery of *radon* is dated 1900, and is attributed (Partington, 1957) to the German physicist Friedrich Ernst Dorn, who reported about the emission by radium of a radioactive material, that he called simply 'emanation' (Dorn, 1901). A similar emission had been, however, observed earlier by Rutherford (1900) as an emanation of thorium, and this raises the question as to who should be actually awarded credit for the discovery of radon (Marshall and Marshall, 2003). The apparatus used by Dorn was, indeed, very like that used by Rutherford, and, in his accounting paper, Dorn (1901) mentioned and confirmed Rutherford's experiments. We currently know that Dorn had stumbled onto the most stable ^{222}Rn isotope, which has a 'long' half-life of 3.823 days, while the isotope emanated from thorium, ^{220}Rn (called also 'thoron'), has a half-life of only 54.5 s. In any case, a major subsequent contribution came from Rutherford, who showed, together with Soddy, that thorium and radium emitted the same material, that it was a gas, and that it was chemically inert and analogous in nature to the members of the argon family (Marshall and Marshall, 2003, pp. 78–79). Rutherford introduced the name 'radium emanation', subsequently changed to 'niton' by Ramsay in 1915, and definitely replaced by radon in 1923 by the International Committee of Chemical Elements (Aston et al., 1923, p. 871). Ramsay was, indeed, deeply involved in the study of the radium emanation, and reported, in particular (in collaboration with Soddy, Collie and Gray) its emission spectrum in 1904 (Ramsay and Collie, 1904), and its density in 1910 (Ramsay and Gray, 1910), showing that it was the densest among the known gases.

1.2 The Emerging of Different Chemistries

In their landmark paper on the discovery of argon, Rayleigh and Ramsay (1895, p. 234) accounted also their attempts to chemically combine the new element. They wrote in the conclusions:

> We do not claim to have exhausted the possible reagents. But this much is certain, that the gas deserves the name "argon", for it is a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very

> opposite character, ranging from sodium and magnesium on the one hand, to oxygen, chlorine, and sulphur on the other. It will be interesting to see if fluorine also is without action.

The reaction with fluorine was actually soon attempted by Moissan (1895), but it was as well unsuccessful. One year later, Ramsay and Collie (1896–1897) had to recognise the likewise inertness of helium, incapable of forming compounds even under vigorous conditions. The amounts of neon, krypton, and xenon available at that time were, instead, too small to assay their reactivity (a somewhat unfortunate circumstance that, probably, delayed the development of noble gas chemistry). Thus, soon after their discovery, argon, helium, and their companions appeared as, essentially, inactive. A challenge for the inventive chemists who never ceased to search for their reactivity. What about the results of these efforts? After more than one century, it is possible to state that, *if one refers exclusively to compounds synthesised in macroscopic amounts under ordinary, or nearly ordinary, conditions*, the challenge was definitely won only for krypton and xenon, several hundreds of *bulk-phase* compounds of these elements (especially xenon) having been already isolated and structurally characterised. Radon chemistry was also assayed, but its study is, generally, hampered by the radioactive character of the element, and by the short lifetime of its isotopes. A first (and, to date, unique) helium compound, Na_2He, was also quite recently obtained (Dong et al., 2017), but only at the highest pressures. The variety of the noble gas-observed species becomes, instead, really impressive if one turns to environments such as *the supercritical fluids, the cold matrices or the gaseous phase*. Under these conditions, all the elements, including helium and neon, exhibit a rich chemistry, typically investigated by spectroscopic, mass spectrometric, and other experimental methods, as well as by theoretical calculations. It is, thus, possible to recognise different noble gas chemistries, and the salient events that marked their beginning are briefly accounted in the subsequent paragraphs.

1.2.1 Bulk-Phase Compounds

The first officially recognised compound of the noble gases is the celebrated 'Xenon exafluoroplatinate(V) $Xe^+(PtF_6)^-$' announced by Niel Bartlett in a short communication dated 23 June 1962 (Bartlett, 1962). Graham et al. (2000) subsequently showed that this compound was, actually, a mixture of $XeF^+PtF_6^-$, $XeF^+Pt_2F_{11}^-$, and PtF_5. The arguments that inspired this synthesis are accounted in most inorganic textbooks, and were often recalled by Bartlett himself. He had previously prepared the solid dioxygenyl hexafluoroplatinate(V), $O_2^+(PtF_6)^-$, by direct combination of O_2 and PtF_6 (Bartlett and Lohmann, 1962). Since the first ionisation potential of O_2 is nearly the same as that of xenon, he speculated that this element also could be oxidised by PtF_6. Here is Bartlett's description of the attempted experiments (Bartlett, 1963, pp. 114–115):

> The predicted interaction of xenon and platinum hexafluoride was confirmed in a simple and visually dramatic experiment. The deep red platinum exafluoride vapor, of known pressure, was mixed, by breaking a glass

> diaphragm, with the same volume of xenon, the pressure of which was greater than that of the exafluoride. Combination, to produce a yellow solid, was immediate at room temperature and the quantity of xenon which remained was commensurate with a combining ratio of 1:1.

Bartlett died on 5 August 2008, and Christe (2008) celebrated him as the 'founder of noble gas chemistry'.

Soon after Bartlett's synthesis, the group of Claassen, Selig, and Malm at the Argonne National Laboratory and the group of Hoppe at the University of Münster announced the preparation, respectively, of the xenon tetrafluoride (Claassen, Selig, and Malm, 1962) and difluoride (Hoppe et al., 1962). XeF_2 was soon prepared also at Argonne (Weeks, Chernick, and Matheson, 1962), and first insights into xenon–oxygen and radon–fluorine chemistry were as well achieved (Chernick et al., 1962). The Argonne group recognised the inspiring role of the first Bartlett report in these terms (Chernick et al., 1962, p. 138, note 6):

> At Argonne National Laboratory the reaction with platinum hexafluoride was duplicated and xenon was shown to react at room temperature with ruthenium hexafluoride, but not with uranium, neptunium, or iridium hexafluorides. When the ruthenium exafluoride system was studied quantitatively, a larger than equimolar consumption of the exafluoride was observed, and some reduction of the ruthenium seemed to occur. This suggested the role of a hexafluoride as a fluorine carrier and led to the studies with xenon and fluorine.

These reports traditionally divide the synthetic chemistry of the noble gases into 'before 1962' and 'after 1962'. The events occurring in the former period are, indeed, generally perceived as a sequence of theoretical predictions and experimental facts, which jointly contributed to establish a *myth of inertness* that resisted up to the early 1960s. A really enjoyable account of the various protagonists and events was reported so far by Laszlo and Schröbilgen (1988). Decisive episodes occurred, in particular, in 1933. In that year, in a paper concerned with the formulas of antimonic acid and the antimonates, Pauling (1933a) predicted the conceivable existence of xenic acid, H_4XeO_6, and of salts such as Ag_4XeO_6 and AgH_3XeO_6, of KrF_6 and XeF_6, and the instability of XeF_8. Stimulated by these suggestions, Yost and Kaye (1933) attempted the combination of xenon with chlorine and fluorine by light irradiation or under electric discharge. We currently know that, under these conditions, xenon fluorides would have to form. The obtained results, while not definitive, were, instead, essentially negative. Yost and Kaye were using the right key, but, for unclear reasons, the door remained closed! The year 1933 saw also the retraction by von Antropoff, Frauenhof, and Krüger (1933) of a previously reported paper (von Antropoff, Weil, and Frauenhof, 1932) that accounted the claimed combination of krypton with chlorine and bromine under an intense electric discharge. Von Antropoff docked at the experimental work based also on own previous theoretical predictions (von Antropoff, 1924) concerning the position of the noble gases in the periodic system, and their ensuing possibility to form bonds with negative elements. The electronegativity of the binding partners as a criterion to search for noble gas compounds had been, indeed, anticipated, for example, by Kossel (1916). In any case, the negative experimental evidence about xenon and krypton reactivity was in line with the already accepted inertness of their lightest congeners, and appeared well consistent with the octet rule, meanwhile formulated by Lewis in his seminal paper (Lewis, 1916). Thus, since 1933, the myth of noble gas inertness seemed established, and was even reinforced by other subsequent events. In 1935, based on thermal analysis, Booth and Wilson (1935) reported the formation at low temperature of complexes between argon and boron trifluoride. Their inspiring arguments were strictly similar to those behind Bartlett's synthesis: since boron trifluoride could form complexes with the closed-shell dimethyl ether, it was legitimate to expect analogue compounds with the noble gases. Their observations were, however, subsequently ascertained to be wrong (Wiberg and Karbe, 1948).

Reinforcing evidence against the capability of the noble gases to form true chemical compounds came from the study of other bulk-phase species such as *clathrates* and *metal compounds*. An argon hydrate was actually prepared soon after the discovery of the element (Villard, 1896), and the krypton and xenon analogues were subsequently reported (de Forcrand, 1923, 1925). However, between 1949 and 1954, von Stackelberg and coworkers (von Stackelberg, 1949, 1954; von Stackelberg and Frühbuss, 1954; von Stackelberg and Jahns, 1954; von Stackelberg and Meinhold, 1954; von Stackelberg and Müller, 1954) demonstrated that these species were *clathrate compounds*. The term *clathrate* was coined by Powell in 1948 to designate 'a structural combination of two substances which remain associated not through strong attraction between them but because strong mutual binding of the molecules of one sort only makes possible the firm enclosure of the other' (Powell, 1948, p. 63). Between 1949 and 1950, Powell himself (Powell and Guter, 1949; Powell, 1950a,b,c) obtained the clathrates of argon, krypton, and xenon with quinol, and, in 1960, Waller (1960) prepared the double hydrates of the heaviest noble gases with acetone, methylene dichloride, chloroform, and carbon tetrachloride as the third component. The limited chemical significance of these species was, however, soon recognised. Powell (1950b, p. 300) wrote that 'no ordinary chemical bonds are needed between quinol and the other molecule', and Waller (1960, p. 430) described, in particular, the noble gas clathrates in these terms: 'they can scarcely be called chemical compounds since the electrons of the inert gas atoms are not involved in the binding forces which are responsible for their existence'. As a matter of fact, this implicitly recognised distinction between *chemical* and *physical* interactions is of key importance in noble gas chemistry, especially that occurring in the gas phase. In any case, the study of noble gas clathrates and other inclusion and cage compounds was further expanded in the subsequent years, and still remains a research area of current interest.

What about noble gas metal compounds? In 1897, Ramsay and Travers reported their unsuccessful attempts to cause helium and argon to pass through red-hot palladium, platinum, and iron. In their accounting paper (Ramsay and Travers, 1897, p. 267), they concluded: 'this would imply their inability to form any compound, however unstable, with these metals, or to dissolve them at a red heat'. Nevertheless, in the subsequent four decades (and, particularly, between

1920 and 1940), tens of reports appeared (nicely accounted, for example by Chernick, 1964), whose authors claimed to have combined by electric discharges not only helium but also argon and neon, with several main-group and transition metals. These findings, however, never received definite credit, and were definitely doubted in 1960, when Waller (1960) re-examined these processes, and concluded that at most some sputtering occurred of the metal of the electrodes, and some occlusion of the noble gas, but no formation of compounds. Whether these findings have some connections with the recently reported Na_2He (Dong et al., 2017) is a point that would, probably, demand further scrutiny.

Overall, yet in 1961, the feeling about the possible preparation of noble gas compounds is clearly expressed by Pauling's sentence (Pauling, 1961, p. 16):

> Xenon is completely unreactive chemically. It has no ability whatever to form ordinary chemical compounds, involving covalent or ionic bonds. The only chemical property that it has is that of taking part in the formation of clathrate crystals.

Only 1 year later, the situation changed dramatically, and the synthetic chemistry of krypton and xenon enjoyed an astonishing and unceasing progress.

1.2.2 Molecules in Cold Matrices

In 1963, Turner and Pimentel (1963) reported the preparation of krypton difluoride, the first and by far most important krypton compound. Despite previous announcements of krypton fluorides, this was the first correct identification of KrF_2, based on infrared (IR) spectroscopy. Turner and Pimentel (1963, p. 974) wrote:

> We now report the preparation of KrF_2 by the photolysis of fluorine suspended in a solid mixture of argon and krypton at 20° K. This experimental method is called the matrix isolation technique.

This sentence marks the beginning of noble gas chemistry in cold matrices. The technique is, typically, employed in conjunction with IR measurements, and is, therefore, also called matrix-IR spectroscopy. In the concluding part of their paper, Turner and Pimentel (1963, p. 975) noticed:

> This work shows that the matrix technique is useful for preparing compounds of inert gases, and it may have unique value for those that are least stable.

As a matter of fact, the xenon halides $XeCl_2$, XeF_2, and $XeClF$ were subsequently reported (Nelson and Pimentel, 1967; Boal and Ozin, 1971; Howard and Andrews, 1974). In 1974, Poliakoff and Turner (1974) studied the reactions of $[Fe(CO)_4]$ induced by ultraviolet (UV) photolysis in xenon and krypton matrices, and wrote (p. 2282) that the experiments 'strongly suggests' the formation of $[Fe(CO)_4Xe]$, and that another band 'was *possibly* due to a very unstable compound [$Fe(CO)_4Kr$]'. Evidence for the interaction of $Cr(CO)_5$, $Mo(CO)_5$, and $W(CO)_5$ with noble gas atoms in low-temperature matrices was also obtained 1 year later (Perutz and Turner, 1975), and these experimental findings stimulated the first theoretical questions about the character of metal/noble gas interactions (Demuynck, Kochanski, and Veillard, 1979); the first hints to the numerous noble gas/metal complexes that were detected in cold matrices over the subsequent years, and extensively investigated by theoretical calculations.

But the field of *cold* noble gas chemistry truly exploded since 1995, when Räsänen and coworkers discovered an entirely new group of somewhat unexpected molecules containing the noble gases (particularly Xe and Kr) bound to a hydrogen and a halogen atom. The evidence about the first reported species was succinctly summarised as follows (Pettersson, Lundell, and Räsänen, 1995a, p. 6430):

> In this paper we have shown that the strong infrared absorbers in Kr and Xe matrices, originating from photodissociation of hydrogen halides and subsequent annealing of the matrix, are *neutral charge transfer species of type* HX^+Y^-. The four compounds observed so far are HXeI, HXeBr, HXeCl, and HKrCl.

This assignment, supported by theoretical calculations, was inspired also by a previous computational study by Last and George (1988), who had predicted the existence of an ionic molecule $(HXe)^+Cl^-$ for impurity centres in rare gases. The family of the HNgY was progressively enlarged to include other related species, and it is, certainly, of major interest in modern noble gas chemistry. The most celebrated member is HArF, reported in 2000 as the first (and to date unique) neutral covalent argon compound (Khriachtchev et al., 2000). In this regard, it is of interest to note the very last sentence of the early paper by Turner and Pimentel (1963, p. 975): 'It is significant, perhaps, that no evidence could be obtained for an argon-fluorine compound by this method'. They were attempting to prepare ArF_2 starting from Ar and the most reactive F_2: a choice no doubt in line with chemical intuition! However, the right (and, probably, counterintuitive) way to solve the problem was to react Ar with the much more stable HF!

1.2.3 Molecules in Liquid and Supercritical Noble Gases

The cold solid matrices are not the only condensed environments which favour the fixation of noble gas atoms. In 1983, Poliakoff, Turner, and coworkers reported the formation of [$Cr(CO)_5Xe$] in liquid xenon, and in liquid krypton doped with xenon. They wrote (Simpson et al., 1983, p. 1356):

> Here, we present evidence which shows that in liquid noble gas solution at $-100^\circ C$ the solvated species [$Cr(CO)_5Xe$] is sufficiently stable to be detected by conventional Fourier-transform i.r. interferometry.

The limitations arising from low temperature were subsequently gone over in 1996 by George and coworkers (Sun et al., 1996, p. 10526):

> In this paper, we report the use of time-resolved infrared measurements in supercritical fluids, a new technique, which offers a general route to studying the interaction of weakly coordinating ligands in solution at, or above, ambient temperature.

The employed supercritical fluids included, in particular, Ar, Kr, and Xe; and, under these conditions, stable complexes of these elements with $Cr(CO)_5$, $Mo(CO)_5$, and $W(CO)_5$ were detected. The chemistry in liquid and supercritical noble gases was pursued in further detail, but it did not enjoy the astonishing progress of the studies performed in cold matrices.

1.2.4 Chemistry Under High Pressures

The synthesis of certain noble gas compounds demands pressures higher than the ordinary one. For example, the quinol clathrates mentioned in Section 1.2.1 are prepared at noble gas pressures of several tens of atmospheres. However, the term *chemistry under high pressures* is, typically, used to denote processes that occur at the ultra-high pressures of (up to) millions of atmospheres (hundreds of gigapascal). Under these conditions, it is possible to open the doors of noble gas chemistry that, otherwise, would remain definitely locked (Grochala, 2007). These studies actually commenced by addressing an intriguing problem lying in between chemistry and physics, namely, the conditions required to convert the solid noble gases from insulators to metals. An inert gas solid has a filled valence band, as well as lowest excited states which are from 8 to 12 eV higher in energy. Thus, a conceivable mode to convert it into a metal is to compress until the energy gap between the valence and the conduction bands become small or disappear, resulting in a transition to a metallic state. This strategy was initially pursued using high temperatures (*shock compression*), and evidence was actually obtained in 1965 (Keeler, van Thiel, and Alder, 1965, p. 1437) 'which could be traced to large-scale thermal excitation of electrons in xenon to the conduction band across a pressure-narrowed energy gap'. A subsequent theoretical paper by Ross (1968) supported this interpretation, and described the phenomenon in chemical terms. Ross (1968, p. 777) wrote:

> The present report will show that as a result of high temperatures and compressions, compressed xenon is converted to a metal-like state in which electrons from the filled 5*p* valence band have been promoted to an unfilled 5*d*-like conduction band, resulting in a material which is similar to cesium at very high pressure.

Breakthrough advances were, however, achieved only in 1979, when the conducting state of xenon was produced by the application of high pressure on a solid sample at 32 K (Nelson and Ruoff, 1979; Yakovlev, Timofeev, and Vinogradov, 1979). This achievement was made possible by the use of the *diamond-anvil cell* that became, since then, the selection device to investigate the noble gas chemistry at the ultra-high pressures. Definite evidence for the metallisation of xenon was simultaneously reported in 1989 by two groups (Goettel et al., 1989; Reichlin et al., 1989), who estimated, in particular, as 132 and 150 GPa, respectively, the previously controversial value of the pressure demanded to achieve the insulator-to-metal transition. The field of noble gas chemistry under high pressure is, currently, enjoying a significant expansion, and promises to offer exciting opportunities of investigation.

1.2.5 Gaseous Neutral Complexes

The group 18 elements have the distinct ability to form gaseous complexes with neutral atoms and molecules. These systems constitute a relevant part of the gas-phase chemistry of the noble gases, and are commonly described as *van der Waals complexes*. This term recognises occurring interactions that are, in general, much weaker than typical 'chemical' bonds, and best described as long-range 'physical' dispersion forces (London, 1936). The bonding situation of neutral noble gas complexes may be, however, more complex than this simplest model, and its description poses challenging problems even to accurate methods of bonding analysis. Various examples in this regard are discussed, in particular, in Chapter 4.

Like other interatomic and intermolecular complexes, the neutral noble gas complexes were, initially, only postulated, and related, in particular, to physical phenomena occurring in gases and liquids. Using the *interaction potential* V as the bridging concept, these systems were initially studied by fitting the parameters involved in the potential, particularly the geometry and the depth of the energy minimum, to benchmark bulk-phase data such as the second virial coefficient, and transport coefficients of the pure dilute gas (shear viscosity, thermal conductivity, and self-diffusion coefficient). For example, already in 1937, studying the equation of state and the critical parameters of different gases, including helium, neon, and argon, Lennard-Jones reported, in the paper accounting the explicit formulation of the celebrated two-terms potential (Lennard-Jones, 1937), the equilibrium distance (R_e) and the interaction energy (ε) of He_2, Ne_2, and Ar_2. The derived values of 2.92 Å and 0.59 meV, 3.05 Å and 3.05 meV, and 3.82 Å and 10.30 meV, respectively, are, indeed, reasonably close to the currently accepted values of 2.97 Å and 0.95 meV, 3.09 Å and 3.64 meV, and 3.76 Å and 12.34 meV! Even higher accuracy was, subsequently, achieved using more flexible potentials, and benchmark data that included experimental results of different types (an approach that is usually referred to as a *multiproperty analysis*). For example, the accurate numerically tabulated potential of Ar_2, obtained in 1969 by Dymond and Alder (1969) from properties of the dilute gas ($R_e = 3.81$Å and $\varepsilon = 12.05$ meV), was also capable of predicting the heat of sublimation, and the atomic separation of its solid phase (Burton, 1970). Meanwhile, between 1965 and 1966, mass spectrometric experiments furnished *direct* evidence for the actual existence of noble gas complexes such as Ar_2, Xe_2, $Ar(CO_2)$, and $Ar(N_2)$ (Robbins and Leckenby, 1965; Leckenby and Robbins, 1966). In their preliminary report, Robbins and Leckenby (1965) wrote:

> We have observed double molecules, for example $(CO_2)_2$, in carbon dioxide, nitrous oxide, nitrogen, oxygen, argon and xenon. It is believed

> that these double molecules exist in all gases at temperatures where the attractive van der Waals interaction is important, and where the pressure is sufficiently high to produce a significant fraction of three-body collisions. Their existence has been predicted for many years.

They could also rule out the formation of these species by the adiabatic cooling of the gas, or as the products of ion–molecule or excited-state reactions in the mass spectrometer. In addition, at least for Ar_2 in argon, the measured concentrations at 300 K and 100 torr agreed reasonably well with the predictions based on a Lennard-Jones potential, thus ascribing the stability of these systems to typically dispersive interactions. Mass spectrometry, however, did not give insights into the structure and stability of the neutral complexes, and bulk-phase data provided only an indirect probe of the interaction potential. Much more information in this regard unravelled – in particular, *spectroscopic measurements* (under various spectral regions) and *molecular beam scattering experiments*. As a matter of fact, during the 1960s and early 1970s, these techniques became established tools to probe the structure, stability, and interaction potential of gaseous complexes, including systems containing noble gas atoms. The first spectroscopic achievements include, for example, the measurement of the vibrational energy levels of Ar_2 in vacuum UV absorption (Tanaka and Yoshino, 1970), the detection of the IR spectrum of $Ar(H_2)$ (McKellar and Welsh, 1971) and $Ar(N_2)$ (Henderson and Ewing, 1974), and the recording of the microwave and radiofrequency transitions of Ar(HCl) (Novick et al., 1973) and Ar(ClF) (Harris et al., 1974). The number of experimentally investigated species soon increased and, already in 1980, in his benchmark review article, Klemperer (1980) could compile all the diatomic Ng_2 and NgNg′ (Ng, $Ng' = He - Xe$), and the complexes of various Ng, particularly Ar, Kr, and Xe, with Na, F, Cl, H_2, N_2, O_2, HX ($X = F, Cl, Br, I$), ClF, I_2, CO_2, COS, N_2O, BF_3, and SO_3. Meanwhile, different groups started to perform high-resolution scattering experiments on systems containing noble gas atoms. Under these conditions, it is possible to measure effects that are highly informative about the interaction potential. The first illustrative reports include, for example, the measurement of the ‘glory’ structure in the integral cross section for the scattering of Li by Xe (Rothe et al., 1962), and the measurement of ‘rainbow’ and ‘diffraction’ oscillations in the differential cross sections for the scattering of Ne by Ar, Kr, and Xe (Parson et al., 1970), of Ar by Ar (Cavallini et al., 1970; Searcy et al., 1971) and of Ar by N_2 (Bickes and Bernstein, 1969).

During the 1960s and 1970s, parallel to the progress made in the experimental investigation, neutral noble gas complexes were also attracting the interest of the theoreticians, who used these simplest systems also as reference tests for developing computational methods and codes. Thus, already in 1976, a review article by Blaney and Ewing (1976) could account the major role of neutral noble gas complexes in the experimental and theoretical study of van der Waals molecules. After 40 years, the field has impressively expanded, and some recent achievements are discussed, in particular, in Chapter 4.

1.2.6 Gas-Phase Ion Chemistry

The gas-phase ion chemistry of the noble gases is a fascinating field of experimental and theoretical research. It features distinct peculiarities that clearly emerge also by studying its origins.

The very first reports date back to 1925. As part of their investigation on the ionisation of hydrogen by electron impact, Hogness and Lunn (1925, p. 50) noticed:

> With mixtures of helium and hydrogen in the tube two particularly interesting intensity peaks of $m/e = 5$ and a less definite one at about $m/e = 6$ were observed repeatedly. Although the small amount of these ions did not permit of a study of their origin, there is little doubt that the $m/e = 5$ ion is the ion of helium hydride, HeH^+, while the other may be $HeH_2{}^+$.

Meanwhile, Lind and Bardwell (1925, 1926) were reporting that, when ionised by added radioactive radon, all the noble gases accelerated the polymerisation of acetylene, cyanogens, and hydrogen cyanide. Whether arising from electron-transfer reactions, or involving the formation of activated intermediate complexes between Ng^+ and C_2H_2, C_2N_2 or HCN, this observed 'catalytic' role of the Ng^+ clearly established the ability of the noble gases to participate in gas-phase ionic processes. As a matter of fact, the $Xe(C_2H_2)^+$ and $Xe(CN)_2{}^+$ were, actually, detected more than 30 years later (Melton and Rudolph, 1960; Rudolph, Lind, and Melton, 1962). In 1933, Pauling (1933b) calculated that the previously reported $He_2{}^+$ (Weizel, 1931, pp. 255–270) was stable by nearly 58 kcal mol^{-1}, and predicted also the conceivable existence of $He_2{}^{2+}$. Thus, already in the early 1930s, while chemists were still debating about the conceivable existence of xenon compounds, various covalent ions containing helium had been detected, and evidence had emerged for ionic reactions involving all the noble gases! But the interest for this chemistry strongly increased during the 1950s and 1960s, when processes involving noble gas atoms emerged as exemplary cases of gas-phase ion–molecule reactions (Stevenson, 1957). In the early studies, particular attention was focused on the diatomic $Ng_2{}^+$. They were first detected by Tüxen (1936), and Hornbeck and Molnar (1951) subsequently established that they formed by electron excitation of Ng, followed by a bond-forming collision:

$$Ng + e \rightarrow Ng^* + e \tag{1.1}$$

$$Ng^* + Ng \rightarrow Ng_2{}^+ + e \tag{1.2}$$

Ten years later, Dahler et al. (1962) unravelled that, under higher pressures, the $Ng_2{}^+$ could be also obtained from the termolecular addition of Ng^+ to Ng:

$$Ng^+ + 2Ng \rightarrow Ng_2{}^+ + Ng \tag{1.3}$$

Meanwhile, it was ascertained that the Ng^+ could participate in different types of ion–molecule reactions, including electron transfer, dissociative electron transfer, and abstraction reactions, even with robust substrates such as CH_4 and H_2. Exemplary processes involving Ar^+ (Melton, 1960; Stevenson and Schissler, 1958) are reported here:

$$Ar^+ + CH_4 \rightarrow Ar + CH_4{}^+ \tag{1.4}$$

$$Ar^+ + CH_4 \rightarrow Ar + CH_3{}^+ + H \tag{1.5}$$

$$Ar^+ + H_2 \rightarrow ArH^+ + H \tag{1.6}$$

The first evidence was also obtained for ion–molecule reactions involving *neutral* Ng atoms. For example (Giese and Maier, 1961):

$$H_2{}^+ + Ar \rightarrow ArH^+ + H \tag{1.7}$$

As a matter of fact, we currently know that Equations (1.1)–(1.7) exemplify the main different modes to activate the Ng atoms by ionic processes, namely, (i) excitation to Ng* followed by bond-forming collisions with a neutral (the Hornbeck–Molnar mechanism), (ii) ionisation to Ng^+ and subsequent charge-transfer or bond-forming reaction(s), and (iii) ion–molecule reactions involving the neutral Ng. As a matter of fact, already in the early 1960s, all these mechanistic routes had been successfully employed to prepare a variety of noble gas ionic species, including, for example, all the heteronuclear $NgNg'^+$ ($Ng, Ng' = He - Xe$) (Munson, Franklin, and Field, 1963), ArN^+ (Kaul and Fuchs, 1960), the $NgN_2{}^+$ and $NgCO^+$ ($Ng = Ar, Kr, Xe$) (Munson, Field, and Franklin, 1962), the ArI^+ and KrI^+ (Henglein and Muccini, 1960) and various Ng–C cations ($Ng = Ar, Kr, Xe$) (Field, Head, and Franklin, 1962; Field and Franklin, 1961). Other interesting bond-forming reactions emerged a few years later by studying the reactivity of the $Ng_2{}^+$ (Bohme et al., 1970; Adams, Bohme, and Ferguson, 1970), that were observed to undergo, in particular, ligand displacement and abstraction reactions. Meanwhile, argon was observed to undergo the termolecular addition to $H_3{}^+$ to form $Ar(H_3{}^+)$ (Fehsenfeld, Schmeltekopf, and Ferguson, 1967), and the study of ion mobility in noble gases had already stimulated interest in the complexes of metal cations with Ng atoms (Dalgarno, McDowell, and Williams, 1958; Mason and Schamp, 1958).

But other strategies were also pursued during the 1960s to prepare gaseous noble gas ions. The first employed route was the electron ionisation of available xenon compounds, used, in particular, as precursors of Xe–F and Xe–O cations (Studier and Sloth, 1963; Svec and Flesh, 1963; Huston, Studier, and Sloth, 1964), and Xe–F anions (Begun and Compton, 1969). Noble gas ions were also obtained by the radioactive decay of molecules labelled with T, ^{82}Br, and ^{131}I. These isotopes undergo β^--decay to form $^3He^+$, $^{82}Kr^+$, and $^{131}Xe^+$, respectively. Starting from a tritiated compound R–T, the ensuing $R - He^+$ is, actually, a $R^+(He))$ complex, which is unstable with respect to the loss of He. Only HT produces an abundant HeH^+ (Snell and Pleasonton, 1958). On the other hand, the $(R\text{–}^{82}Kr)^+$ and $(R\text{–}^{131}Xe)^+$ arising from the decay of $R\text{–}^{82}Br$ and $R\text{–}^{131}I$, respectively, are, in general, more stable, and, in fact, various C–Kr and C–Xe cations were obtained in this way (Carlson and White, 1962, 1963a,b). This mode of preparation, however, did not receive further attention in the subsequent years, and the structure, stability, and reactivity of noble gas ions were typically investigated nearly exclusively by mass spectrometric and spectroscopic techniques. Since the early 1980s, a relevant contribution to noble gas ion chemistry came also from theoretical calculations. The first systematic investigation was performed, in particular, by Cooper and Wilson (1981), who examined noble gas molecular ions of different composition and charges, and also made comparisons with previously reported results. But decisive progress was made, during the 1980s, by Frenking and coworkers, who performed an extensive study of noble gas compounds, and reported, *inter alia*, a deep scrutiny of exemplary noble gas ions, with special attention to species containing helium, neon, and argon (Koch et al., 1987; Frenking et al., 1989a,b). Any current investigation of noble gas ion chemistry is, indeed, typically accomplished by experiments and theory working in concert; numerous illustrative examples await the reader in Chapter 5.

1.3 The Development of the Diverse Fields

Over the years, the diverse fields of noble gas chemistry enjoyed a continuing expansion, marked by countless experimental and theoretical advances. Some salient events, which are also of relevance for the chemistry mainly discussed in this book, are briefly surveyed in this section.

The synthetic advances achieved in the early 1960s suggested that krypton and xenon could combine exclusively with the most electronegative fluorine and oxygen. It took nearly three decades to establish that at least three additional elements, namely, nitrogen, carbon, and chlorine, could form isolable compounds with xenon. The first Xe–N compound, $FXeN(SO_2F)_2$, was reported in 1974 (LeBlond and DesMarteau, 1974), and Kr–N compounds were obtained in 1988 (Schrobilgen, 1988a,b). The first Xe–C compounds were prepared in 1989 as salts of $C_6F_5Xe^+$ and boron anions (Frohn and Jakobs, 1989; Naumann and Tyrra, 1989), and the Xe–Cl compounds C_6F_5XeCl and $[(C_6F_5Xe)_2Cl][AsF_6]$ were prepared in 1999 (Frohn, Schroer, and Henkel, 1999). A Xe–Br compound was also obtained in 2006 (Bock et al., 2006), and novel Xe–Cl and Xe–Br compounds were quite recently synthesised (Goettel, Haensch, and Schrobilgen, 2017). As a matter of fact, more than 50 years after the first achievements, we currently know that, in its typical oxidation states (II, IV, VI, and VIII), xenon combines particularly with fluorine, oxygen, carbon, and nitrogen to form a large variety of compounds and bonding motifs. Compounds of krypton (II) with fluorine, oxygen, and nitrogen are also well established. The reactivity of synthesised noble gas compounds has attracted as well continuing experimental and theoretical interest; the versatility of XeF_2 as a fluorinating agent is an outstanding example in this regard (Betz and Schrobilgen, 2012). Exhaustive accounts of this more 'traditional' synthetic chemistry of xenon and krypton are given in benchmark review articles and book chapters (Holloway and Hope, 1998; Gerken and Schrobilgen, 2000; Frohn and Bardin, 2001; Christe, 2001; Lehmann, Mercier, and Schrobilgen, 2002; Grochala, 2007; Calladine et al., 2009; Brock, Schrobilgen, and Žemva, 2013b; Haner and Schrobilgen, 2015). But xenon can also form isolable compounds with metal atoms, particularly gold and mercury. At the beginning of the millennium, the synthesis of $[AuXe_4][Sb_2F_{11}]_2$, a salt of the square-planar cation $AuXe_4^{2+}$ (Seidel and Seppelt, 2000) was, indeed, one of the most astonishing achievements in noble