

4.7: Noble Gases and their Compounds

In the 18th century, H. Cavendish discovered an inert component in air. In 1868, a line was discovered in the spectrum of sunlight that could not be identified and it was suggested to be due to a new element, helium. Based on these facts, at the end of the 19th century W. Ramsay isolated He, Ne, Ar, Kr, and Xe and by studying their properties demonstrated that they were new elements. In spite of the nearly 1% content of argon Ar in air, the element had not been isolated until then and noble gases were completely lacking in Mendeleev's periodic table. The Nobel prize was awarded to Ramsay in 1904 for his achievement.

Noble gases are located next to the halogen group in the periodic table. Since noble gas elements have closed-shell electronic configurations, they lack reactivity and their compounds were unknown. Consequently, they were also called inert gases. However, after the discovery of noble gas compounds, it was considered more suitable to call these elements "noble gases", as is mentioned in the following chapter.

Although the abundance of helium in the universe is next to that of hydrogen, it is very rare on the Earth because it is lighter than air. Helium originated from solar nuclear reactions and was locked up in the earth's crust. It is extracted as a by-product of natural gas from specific areas (especially in North America). Since helium has the lowest boiling point (4.2 K) of all the substances, it is important for low-temperature science and superconductivity engineering. Moreover, its lightness is utilized in airships etc. Since argon is separated in large quantities when nitrogen and oxygen are produced from liquid air, it is widely used in metallurgy, and in industries and laboratories that require an oxygen-free environment.

(b) noble gas compounds

Xenon, Xe, reacts with elements with the largest electronegativities, such as fluorine, oxygen, and chlorine and with the compounds containing these elements, like platinum fluoride, PtF_6 . Although the first xenon compound was reported (1962) as XePtF_6 , the discoverer, N. Bartlett, later corrected that it was not a pure compound but a mixture of $\text{Xe}[\text{PtF}_6]_x$ ($x = 1-2$). If this is mixed with fluorine gas and excited with heat or light, fluorides XeF_2 , XeF_4 , and XeF_6 are generated. XeF_2 has chain-like, XeF_4 square, XeF_6 distorted octahedral structures. Although preparation of these compounds is comparatively simple, it is not easy to isolate pure compounds, especially XeF_4 .

Hydrolysis of the fluorides forms oxides. XeO_3 is a very explosive compound. Although it is stable in aqueous solution, these solutions are very oxidizing. Tetroxide, XeO_4 , is the most volatile xenon compound. $\text{M}[\text{XeF}_8]$ (M is Rb and Cs) are very stable and do not decompose even when heated at 400 °C. Thus, xenon forms divalent to octavalent compounds. Fluorides can also be used as fluorinating reagents.

Although it is known that krypton and radon also form compounds, the compounds of krypton and radon are rarely studied as both their instability and their radioactivity make their handling problematic.

Discovery of noble gas Compounds

H. Bartlett studied the properties of platinum fluoride PtF_6 in the 1960s, and synthesized O_2PtF_6 . It was an epoch-making discovery in inorganic chemistry when analogous experiments on xenon, which has almost equal ionization energy (1170 kJ mol^{-1}) to that of O_2 (1180 kJ mol^{-1}), resulted in the dramatic discovery of XePtF_6 .

noble gas compounds had not been prepared before this report, but various attempts were made immediately after the discovery of noble gases. W. Ramsay isolated noble gases and added a new group to the periodic table at the end of the 19th century. Already in 1894, F. F. H. Moisson, who is famous for the isolation of F_2 , reacted a 100 cm^3 argon offered by Ramsay with fluorine gas under an electric discharge but failed to prepare an argon fluoride. At the beginning of this century, A. von Antoropoff reported the synthesis of a krypton compound KrCl_2 , but later he concluded that it was a mistake.

L. Pauling also foresaw the existence of KrF_6 , XeF_6 , and H_4XeO_6 , and anticipated their synthesis. In 1932, a post doctoral research fellow, A. L. Kaye, in the laboratory of D. M. L. Yost of Caltech, where Pauling was a member of faculty, attempted to prepare noble gas compounds. Despite elaborate preparations and eager experiments, attempts to prepare xenon compounds by discharging electricity through a mixed gas of xenon, fluorine, or chlorine were unsuccessful. It is said that Pauling no longer showed interest in noble gas compounds after this failure.

Although R. Hoppe of Germany predicted using theoretical considerations that the existence of XeF_2 and XeF_4 was highly likely in advance of the discovery of Bartlett, he prepared these compounds only after knowing of Bartlett's discovery. Once it is proved that

a compound of a certain kind is stable, analogous compounds are prepared one after another. This has also been common in synthetic chemistry of the later period, showing the importance of the first discovery.

✓ problems

4.1

Write a balanced equation for the preparation of diborane.

4.2

Write a balanced equation for the preparation of triethylphosphine.

4.3

Write a balanced equation for the preparation of osmium tetroxide.

4.4

Describe the basic reaction of the phosphomolybdate method used for the detection of phosphate ions.

4.5

Draw the structure of anhydrous palladium dichloride and describe its reaction when dissolved in hydrochloric acid.

4.6

Describe the reaction of anhydrous cobalt dichloride when it is dissolved in water.

4.7

Draw the structure of phosphorus pentafluoride.

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