

第九章 稀有气体

Chapter 9 The Rare Gases

Helium (He) 太阳 Neon (Ne) 新的 Argon (Ar) 懒惰的
Krypton (Kr) 稳定的 Xenon (Xe) 陌生的 Radon (Rn) 发光的
Electronic configuration: ns^2np^6 except He $1s^2$

从 1894-1900 年期间上面稀有气体相继全部被发现，其中 Ramsay 功绩最大，他荣获 1904 年 Nobel 化学奖。1892 年，J.W.S.Rayleigh 发现从空气中分离出来的氮气密度比从化合物中分离出来的氮气密度略重 (1.2565/1.2507)，但不知其原因。W.Ramsay 紧随其后，以敏锐的观察力和高超的实验技术，与合作者经过几年的艰苦努力，终于发现和离析了几乎一整族稀有气体。

一、General Properties:

1. 它们都是单原子分子(monatomic molecular)，在通常条件下，它们都是气体，也称为惰性气体 (noble or inert gases)。
2. 蒸发热、在水中的溶解度以及熔、沸点都很小，并且随着原子序数的增加而逐渐升高。氦是所有气体中最难液化的物质。He 的沸点为 4.2K，H₂ 的沸点为 20.4K。氦冷却至 2.178K，则变成第二种液体 (helium II)，发生无粘度流动，称为超流体 (superfluidity)。He-II 的热传导是 He-I 的 10⁶ 倍，比热传导最优的金属银强得多。
3. 由于稀有气体的最外电子层都有相对饱和的结构 (octet rule)，这种电子结构是相当稳定的，其电子亲合势都接近于零，而且都有很高的电离势，因此它们在化学性质上表现为惰性。
4. 在自然界中的分布：在接近地球表面的空气中，每 1000 升空气中约含 9.3 升氩、18 毫升氖、5 毫升氦、1 毫升氙和 0.8 升氙，所以液态空气是提取稀有气体的主要原料。
5. 用途：氩、氙的同位素在医学上被用来测量脑血流量和研究肺功能，计算胰岛素分泌量。

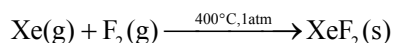
二、Chemical Properties

在稀有气体发现后一段时间内 (1900-1960 年)，把它们作为化学性质上绝对惰性的。直到 1962 年，Bartlett 将 PtF₆ 的蒸气与等摩尔的氙混合，在室温下制得了 XePtF₆ 的橙黄色固体，推翻了持续了近 70 年之久的关于稀有气体完全化学惰性的传统说法。

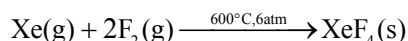
下面我们主要讨论氙的氟化物和含氧化合物。

1. 氙的氟化物 (Fluorides of xenon) XeF₂、XeF₄、XeF₆

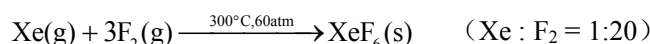
(1) preparation



(由 Xe 在缺 F₂ 情况下加压反应)



较易制得，在如上条件下加入 Xe 和 F₂ (1:5) 混合物，几十小时后便制得。



或 $\text{XeF}_4(\text{s}) + \text{F}_2(\text{g}) \longrightarrow \text{XeF}_6(\text{s})$ (在常压下)

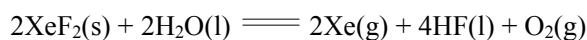
Irradiating a xenon-fluorine mixture with ultra-violet light at ordinary temperature produces XeF₂ (together with some XeF₄)

为什么 Xe 与 F₂ 混合如此容易化合但六十多年间却没有能合成出 Xe 的化合物？主要有这几方面原因：当时拥有的 Xe 的量太少；绝对干燥的玻璃仪器不能获得；实验技术落后，更重要的是思想上有框框。

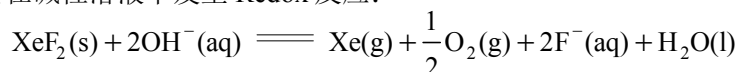
(2) properties:

a. 氙的氟化物都与水发生反应:

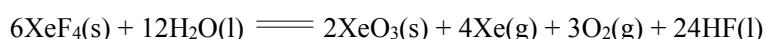
(i) XeF_2 在水中的溶解放出刺激性臭味，在酸性溶液中水解很慢，但在碱性溶液中水解很快:



XeF_2 在碱性溶液中发生 Redox 反应:

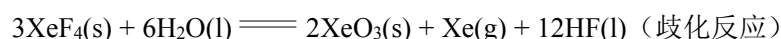


(ii) XeF_4 在水中既发生歧化反应，又发生氧化还原反应:



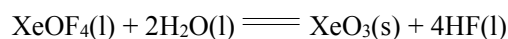
分解成: $3\text{XeF}_4(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightleftharpoons 3\text{Xe}(\text{g}) + 3\text{O}_2(\text{g}) + 12\text{HF}(\text{l})$

(与水的氧化还原反应)

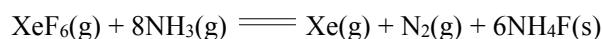
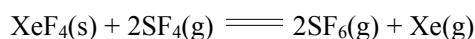


所以上述反应方程式只是 XeF_4 等摩尔参与歧化反应以及与水氧化还原反应的配平结果。实际上这是一个多重配平的方程式。

(iii) $\text{XeF}_6(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{XeOF}_4(\text{l}) + 2\text{HF}(\text{l})$

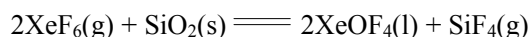


b. 氙的氟化物都是强氧化剂



可以使 $\text{HCl} \rightarrow \text{Cl}_2$, $\text{Ce}^{(\text{III})} \rightarrow \text{Ce}^{(\text{IV})}$, $\text{NH}_3 \rightarrow \text{N}_2$

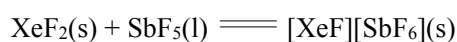
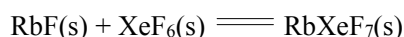
XeF_6 化学性质非常活泼，甚至与石英反应:



XeF_6 在碱性条件下也能发生歧化反应:



c. 氙的氟化物都是良好的氟化剂

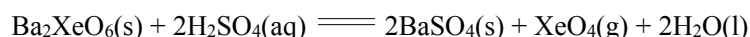


2. 氙的氧化物 (Oxides of xenon)

(1) preparation:

a. XeO_3 由 XeF_4 和 XeF_6 水解制得。

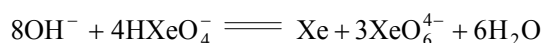
b. XeO_4 由 XeF_6 在 $\text{Ba}(\text{OH})_2$ 中歧化制得的高氙酸钡 Ba_2XeO_6 ，高氙酸钡再与硫酸反应制得:



(2) properties:

a. 稳定性 (stabilization)

无色无味 $\text{XeO}_3(\text{s})$ 中含有 XeO_3 分子。 XeO_3 在水中稳定，但在固态时 XeO_3 会发生爆炸 (虽然该反应经常在动力学上很慢)。它在 OH^- 介质中形成 HXeO_4^- 离子: 此离子发生缓慢歧化，得到 XeO_6^{4-} :



Bonding in Noble Gas Compounds

As it was widely believed, prior to 1962, that the noble gases were chemically inert because of the stability, if not inviolability, of their electronic configurations, the discovery that compounds could in fact be prepared, immediately necessitated a description of the bonding involved. A variety of approaches has been suggested, none of which is universally applicable. The simplest molecular-orbital description is that of the 3-centre, 4-electron σ bond in XeF_2 , which involves only valence shell p orbitals and eschews the use of higher energy d orbitals. The orbitals involved are the collinear set comprising the $5p_x$ orbital of Xe, which contains 2 electrons, and the $2p_x$ orbitals from each of the F atoms, each containing 1 electron. The possible combinations of these orbitals are shown in Fig. A and yield 1 bonding, 1 nonbonding, and 1 antibonding orbital. A single bonding pair of electrons is responsible for binding all 3 atoms, and the occupation of the nonbonding orbital, situated largely on the F atoms, implies significant ionic character. The scheme should be compared with the 3-centre, 2-electron bonding proposed for boron hydrides.

A similar treatment, involving two 3-centre bonds accounts satisfactorily for the planar structure of XeF_4 but fails when applied to XeF_6 since three 3-centre bonds would produce a regular octahedron instead of the distorted structure actually found. An improvement is possible if involvement of the Xe 5d orbitals is invoked, since this produces a triplet level which would be subject to a Jahn-Teller distortion. However, the approach which as most consistently rationalized the stereochemistries of noble-gas compounds (as distinct from their bonding) is the electron-pair repulsion theory of Gillespie and Nyholm. This assumes that stereochemistry is determined by the repulsions between valence-shell electron-pairs, both nonbonding and bonding, and that the former exert the stronger effect. Thus, in XeF_2 the Xe is surrounded by 10 electrons (8 from Xe and 1 from each F) distributed in 5 pairs; 2 bonding and 3 nonbonding. The 5 pairs are directed to the corners of a trigonal bipyramid and, because of their greater mutual repulsions, the 3 nonbonding pairs are situated in the equatorial plane at 120° to each other, leaving the 2 bonding pairs perpendicular to the plane and so producing a linear F-Xe-F molecule.

In the same way XeF_4 , with 6 electron-pairs, is considered as pseudo-octahedral with its 2 nonbonding pairs trans to each other, leaving the 4 F atoms in a plane around the Xe. More distinctively, The 7 electron-pairs of XeF_6 suggest the possibility of a non-regular octahedral geometry and imply a distorted structure based on either a monocapped octahedral or a pentagonal pyramidal arrangement of electron-pairs, with the Xe-F bonds bending away from the projecting nonbonding pair.