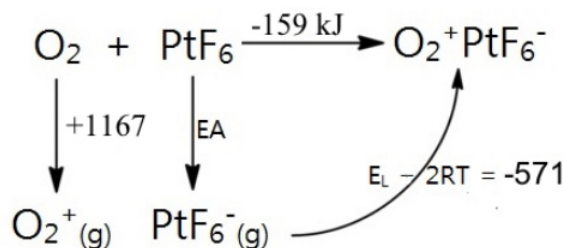


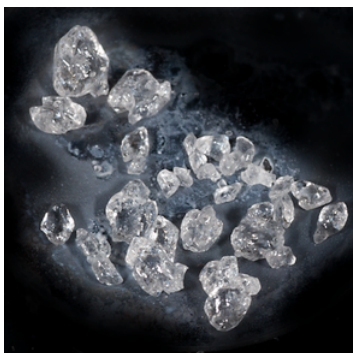
## 9.6: Discovery of Noble Gas Compounds

In 1962 at the University of British Columbia, Neil Bartlett was working with the powerful oxidizer  $\text{PtF}_6$  and, because of an accidental leak in his vacuum line, noticed the compound's reaction with  $\text{O}_2$  to generate a solid with formula " $\text{PtF}_6\text{O}_2$ ." The formula suggested Pt in the +10 oxidation state, which was clearly unreasonable because  $\text{PtF}_6$  was known to be a more powerful oxidizer than either molecular fluorine ( $\text{F}_2$ ) or molecular oxygen ( $\text{O}_2$ ). Bartlett noticed that the X-ray powder diffraction pattern of the compound was similar to that of  $\text{Cs}^+\text{AsF}_6^-$ , a salt with the CsCl structure in which octahedral  $\text{AsF}_6^-$  ions occupy the chloride ion sites. This led Bartlett to propose a formulation of  $\text{O}_2^+\text{PtF}_6^-$  for his new compound.<sup>[6]</sup> Magnetic susceptibility data subsequently confirmed the presence of the paramagnetic  $\text{O}_2^+$  cation, which (see Chapter 2) has a bond order of 2.5. This formulation implies that  $\text{PtF}_6$  was a strong enough oxidizing agent to oxidize molecular oxygen.

But just how strong an oxidizer is  $\text{PtF}_6$ ? Its electron affinity could be estimated by using a Born-Haber cycle, filling in the lattice energy of  $\text{O}_2^+\text{PtF}_6^-$  by means of Kapustinskii's formula:



The electron affinity (EA) for  $\text{PtF}_6$  can be calculated as  $\text{EA} = -159 - 1167 + 571 = -751 \text{ kJ/mol}$ . To put it in perspective, this is 417 kJ/mol more exothermic than the electron affinity of atomic fluorine (334 kJ).  $\text{PtF}_6$  was by far the strongest oxidizer that had ever been made!



Crystals of xenon difluoride ( $\text{XeF}_2$ ), which is made by photolysis of a gas mixture of Xe and  $\text{F}_2$ .  $\text{XeF}_2$  is used as a selective etchant for  $\text{SiO}_2$  in certain microelectronic fabrication processes. Prior to Neil Bartlett's discovery of the first xenon compound in 1962, it was believed that elements in group VIII (He, Ne, Ar, Kr, Xe) could not form chemical compounds. Since then chemists have discovered a rich family of noble gas compounds containing Xe, Kr, or Ar.

Bartlett recognized that Xe has ionization energy of +1170 kJ, which is very close to the ionization energy of  $\text{O}_2$ . Since  $\text{Xe}^+$  should be about the same size as  $\text{O}_2^+$ , the lattice energy should be about the same with  $\text{Xe}^+$  in the cation site of the  $\text{O}_2^+\text{PtF}_6^-$  structure. Since all of the other terms in the Born-Haber cycle for the reaction of Xe with  $\text{PtF}_6$  are the same, Bartlett concluded that  $\text{Xe}^+\text{PtF}_6^-$ , like  $\text{O}_2^+\text{PtF}_6^-$ , should be a stable compound. He purchased a lecture bottle of xenon gas and reacted the two compounds, producing an orange solid.<sup>[7]</sup> While the product initially formed in the reaction may in fact be  $\text{Xe}^+\text{PtF}_6^-$ , the  $\text{Xe}^+$  free radical is a powerful Lewis acid and reacts further with excess  $\text{PtF}_6$ . The ultimate product of the reaction is formulated  $[\text{XeF}^+][\text{Pt}_2\text{F}_{11}^-]$ , a salt which contains Xe in the +2 oxidation state and Pt in the +5 oxidation state. This was an important discovery because it shattered the dogmatic notion, which derived from the octet rule, that elements in group VIII could not form bonds with other elements. The name of this group was changed from the "inert gases" to the "noble gases." Subsequently, many compounds of Xe and a few of Kr and even Ar (which is much harder to oxidize) were synthesized and characterized.

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