

# The noble gases and their relevance to 21st century chemistry teaching

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On 23 May, 2006, the American Chemical Society, in conjunction with the Chemical Institute of Canada, designated the site of the research of Neil Bartlett on the noble gases as an International Historic Chemical Landmark. The text of the plaque, on the campus of the University of British Columbia in Vancouver, reads in part:

*In this building in 1962 Neil Bartlett demonstrated the first reaction of a noble gas. The noble gas family of elements — helium, neon, argon, krypton, xenon, and radon — had previously been regarded as inert. By combining xenon with a platinum fluoride, Bartlett created the first noble gas compound. This reaction began the field of noble gas chemistry, which became fundamental to the scientific understanding of the chemical bond.*

How is the synthesis of noble gas compounds of relevance to contemporary chemistry teaching? I contend that there are four educational contexts to the discovery: the discovery process itself, bonding energetics, and two aspects of periodic patterns.

## The Discovery Process

The discovery process for the formation of noble gas compounds was lengthy and convoluted.<sup>1</sup> Here I will pick on three particular incidents. In 1924, the German chemist Andreas von Antropoff made the suggestion that, because the noble gases (except helium) have eight electrons in their valence level, they should be capable of forming up to eight covalent bonds.<sup>2</sup> This proposal makes chemical sense: for example, phosphorus (5 electrons) forms PF<sub>5</sub>; sulfur (6 electrons) forms SF<sub>6</sub>, and iodine (7 electrons) forms IF<sub>7</sub>. Nine years later, Linus Pauling suggested that KrF<sub>6</sub> and XeF<sub>6</sub> should be preparable. Shortly afterwards, the American chemists Don Yost and Albert Kaye endeavoured to synthesize a compound by attempting to initiate a reaction between xenon and fluorine but they believed that they had been unsuccessful. Their apparent failure reinforced the view that the octet rule reigned supreme and that the Group 18 elements truly were inert gases.

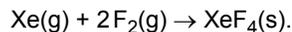
Bartlett started not from the premise of covalent bonding but from principles of ion formation. During his research, he had found that platinum(VI) fluoride was such a strong oxidizing agent, it would remove an electron from dioxygen to form [O<sub>2</sub><sup>+</sup>][PtF<sub>6</sub><sup>-</sup>]. He realized that the first ionization energy of atomic xenon was very close to that of the dioxygen molecule. Mixing xenon with platinum(VI) fluoride resulted in the formation of an orange-yellow solid which he believed to be [Xe<sup>+</sup>][PtF<sub>6</sub><sup>-</sup>]. In fact, it is now thought to have been a mixture of [XeF<sup>+</sup>][PtF<sub>6</sub><sup>-</sup>] and [XeF<sup>+</sup>][Pt<sub>2</sub>F<sub>11</sub><sup>-</sup>].<sup>3</sup> Nevertheless, this first documented reaction of xenon opened the floodgates of noble gas chemistry, including the synthesis of the XeF<sub>6</sub> that Pauling had predicted.

There are three major teaching points:

- the history of chemistry (and all other sciences) is 'messy' and cannot be reduced to a single heroic figure
- dogma (the inertness of the noble gases) is as unwise in science as it is in philosophies, politics, and religions, and
- until an experiment is actually performed, one cannot be sure of the product.

## Bonding Energetics

Despite the synthesis of xenon fluorides and oxides, there is much less simple chemistry for xenon than, for example, its neighbour, iodine. Or to phrase it as a question, why is it easy to make xenon fluorides, yet impossible to make simple xenon chlorides? An explanation can be found by looking at the energetics of formation of the xenon fluorides from the constituent elements. In this case, we will use xenon tetrafluoride as the example:



As the reaction involves a decrease in entropy (three moles of gas to none), to be spontaneous, the reaction must be significantly exothermic.

The Figure below shows a theoretical energy cycle for the formation of the compound. The first imaginary step is to break two moles of F–F covalent bonds and the second to form four moles of Xe–F bonds. We can see that the overall process is

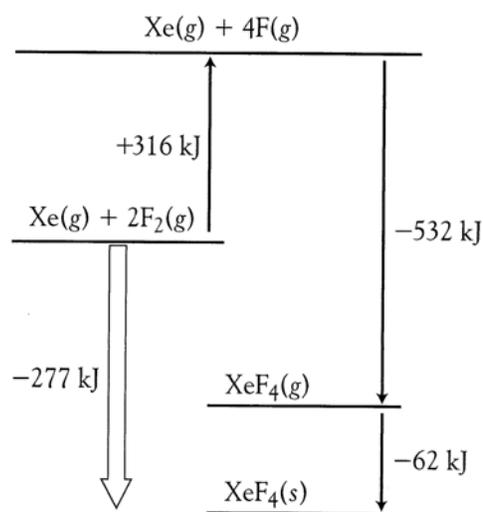


Figure. Enthalpy cycle for the formation of xenon tetrafluoride from its constituent elements.<sup>4</sup> (Rounding errors account for the 1kJ difference between the two sides.)

significantly exothermic ( $-277 \text{ kJ mol}^{-1}$ ) — including the small ‘bonus’ of the enthalpy of sublimation when the solid forms. It is the appreciable exothermicity that overrides the negative entropy factor and makes the reaction feasible.

Energy cycles are a very useful way of identifying the ‘why?’ in chemical reactions. In this case, the weakness of the F–F bond ( $158 \text{ kJ mol}^{-1}$  compared with  $240 \text{ kJ mol}^{-1}$  for the Cl–Cl bond) is a significant factor. (Note that there are significant variations in values of heteronuclear bond energies in the literature.) Thus, even though the Xe–F bond is quite weak ( $133 \text{ kJ mol}^{-1}$  compared with  $272 \text{ kJ mol}^{-1}$  for the I–F bond), the formation of four Xe–F bonds for the breaking of only two F–F bonds provides a significant net decrease in energy.

Although  $\text{XeF}_4$  is stable, the analogous xenon tetrachloride does not exist as an isolable compound at room temperature. By comparing bond energies with the fluorine analog we can see why. The Cl–Cl bond ( $240 \text{ kJ mol}^{-1}$ ) is significantly stronger than the F–F bond ( $158 \text{ kJ mol}^{-1}$ ). Conversely, using a ratio of the I–Cl and I–F bond energies ( $211$  and  $272 \text{ kJ mol}^{-1}$ , respectively), a theoretical Xe–Cl bond energy can be estimated to be about  $103 \text{ kJ mol}^{-1}$  as follows.

$$\frac{\text{BE}_{\text{Xe-Cl}}}{\text{BE}_{\text{Xe-F}}} \cong \frac{\text{BE}_{\text{I-Cl}}}{\text{BE}_{\text{I-F}}}$$

$$\therefore \text{BE}_{\text{Xe-Cl}} \cong \frac{\text{BE}_{\text{I-Cl}}}{\text{BE}_{\text{I-F}}} \times \text{BE}_{\text{Xe-F}} = \frac{211 \text{ kJ mol}^{-1}}{272 \text{ kJ mol}^{-1}} \times 133 \text{ kJ mol}^{-1}$$

$$= 103 \text{ kJ mol}^{-1}$$

Constructing a similar energy cycle to produce gaseous  $\text{XeCl}_4$  gives a net energy change of about  $+68 \text{ kJ mol}^{-1}$ . With entropy also opposing the compound’s formation, xenon tetrachloride cannot be energetically stable — and this is true of the other xenon halides as well.

*The formation of xenon fluorides provide excellent examples of the role of energetics (and bond energies in particular) in the feasibility of formation of covalently-bonded chemical compounds.*

### Periodic patterns — Isoelectronic series

One of the most fascinating aspects of periodicity is the formation of isoelectronic series of compounds. These can be defined as:

*Species (atoms, molecules, ions) are isoelectronic with each other if they have the same total number of electrons and of valence electrons.*

Isoelectronic pairs can be found among several iodine and xenon species. As the iodine atom has one less electron than the xenon atom, the iodine compound must be one unit more negative than its isoelectronic xenon analog. Some of these known pairs are:

IF and  $\text{XeF}^+$   
 $\text{IF}_2^-$  and  $\text{XeF}_2$   
 $\text{IF}_4^-$  and  $\text{XeF}_4$   
 $\text{IF}_5$  and  $\text{XeF}_5^+$   
 $\text{IF}_6^-$  and  $\text{XeF}_6$   
 $\text{IO}_2\text{F}_2^-$  and  $\text{XeO}_2\text{F}_2$

In addition, the pentafluoroxenon cation completes the four-member isoelectronic series:  $\text{SbF}_5^{2-}$ ,  $\text{TeF}_5^-$ ,  $\text{IF}_5$ ,  $\text{XeF}_5^+$ .

*The formulas of many xenon compounds reinforce the patterns of isoelectronic behaviour in the periodic table.*

### Periodic patterns — the relationship between the (n) and the (n+10) groups

Mendeléeev considered that there was a repetition of properties with each eighth element throughout the periodic table. To a certain extent, this is true. Using the modern numbering system, beyond the second period, we do find relationships between some elements in Group (n) and the corresponding elements in Group (n+10).<sup>5</sup> As an example, there are strong similarities between the chemistry of magnesium (Group 2) and zinc (Group 12).

In terms of formula, one of the most amazing links is between the metal osmium (Group 8) and the non-metal xenon (Group 18). It is in the +8 oxidation state where the similarity is most apparent. For example, osmium forms a pale yellow, strongly-oxidizing oxide,  $\text{OsO}_4$ , while xenon forms a pale yellow explosive oxide,  $\text{XeO}_4$ . There are parallels in the formulas of the oxyfluorides, too:  $\text{OsO}_2\text{F}_4$  and  $\text{XeO}_2\text{F}_4$  together with  $\text{OsO}_3\text{F}_2$  and  $\text{XeO}_3\text{F}_2$ . The highest fluorides for both elements are in the +6 oxidation state:  $\text{OsF}_6$  and  $\text{XeF}_6$ , and they both form corresponding fluoro-anions:  $\text{OsF}_7^-$  and  $\text{XeF}_7^-$ .

*The similarity in chemical formulas and properties between a heavy metal of Group 8 and a gas of Group 18 is a prime example of the (n) and (n+10) relationship in the periodic table.*

It may have been 44 years since the definitive synthesis of the first noble gas compound, but xenon compounds can still play a valuable role in our teaching of chemistry.

### References

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5. Reference 4, pages 194-197. ■