**Hypervalence**

The term ***hypervalent*** (or ***hypervalence***) was introduced in Section 4.1 of Chapter 4 (p 55) and referred to later in Chapter 6, Section 6.1 in relation to discussions about bonding in p-block element chemistry, particularly for those compounds which might be considered to have more than 8 valence electrons around the central element, i.e., those species which are sometimes said to violate the octet rule. Hypervalence was also defined in the Glossary. As noted briefly in Chapter 4 and again in Chapter 6, the concept of hypervalence and whether compounds with more (apparently) than 8 valence electrons actually violate the octet rule or not has been a matter of some contention in terms of how the electronic structure is best represented. This addendum provides a little more detail on hypervalence and cognate topics from a historical perspective (albeit without any pretence to being either comprehensive or fully referenced) and ends with some thoughts on the usefulness of the term, its value in a teaching context and some general comments about simple models.

A brief but excellent summary of the origin and history of the term hypervalent has been provided by Jensen1,2 which starts with the introduction of the term itself by Musher in 19693 who proposed a description of the bonding for those compounds of Groups 15, 16, 17 and 18 in which the valence4 of the element concerned exceeds 3, 2, 1 and 0 respectively. Thus, for example, trivalent PF3 was considered as a compound containing ‘normal’ covalent P–F bonds whereas pentavalent PF5 was proposed to contain so-called ‘hypervalent’ bonds associated with the linear F–P–F unit and was therefore described as a compound featuring hypervalence.5 Innocuous as this may seem, it was to lead to decades of debate which had, in fact, already started almost half a century earlier.

One of the key points of contention has been whether or not hypervalent compounds violate the octet rule, this rule having originated with Lewis and with Langmuir in the 1910’s. As Jensen describes, the discussion (although example compounds would not be referred to as hypervalent until after 1969) had begun in earnest in the 1920’s with Lewis favouring a description where all bonds are 2-centre, 2-electron (2c,2e) bonds whereas Langmuir argued for the primacy of the octet rule. If we remain with PF5 as an example, an insistence on all bonds being 2c,2e bonds would require octet expansion (i.e., 10 valence electrons for structure **A** with five P–F bonds), whereas an alternative (partial) ionic description for the bonding, as shown in **B**, would allow for retention of the octet around phosphorus (any one of the fluorines could carry the negative charge and the structure of PF5 would involve a ‘resonance’ between the five possibilities).



If we examine first structures of type **B**, these were later considered by Pauling in the 1940’s and further discussed by Coulson in the 1960’s in terms of the valence bond theory of electronic structure. It is fair to say, however, that representations of this nature involving resonance between ionic or partly ionic forms have become much less popular in recent decades although they have some merit in drawing attention to the polar nature of the bonds concerned (F is more electronegative than P).

For the fully covalent description implicit in structure **A**, the nature of the orbitals involved is all-important and derives more from a molecular orbital treatment of the electronic structure. It should be noted that Musher’s original bonding model involved only valence s and p orbitals such that compounds like PF5 were not considered to violate the octet rule. Musher’s model bore some resemblance to one proposed by Sugden in the 1920’s and 1930’s in which the axial P–F bonds were represented as 2-centre, 1-electron (2c,1e) bonds thereby retaining an octet overall (three equatorial 2c,2e bonds and two axial 2c,1e bonds). This was later developed in the 1940’s and 1950’s by, amongst others, Rundle and by Pimentel into the 3-centre, 4-electron (3c,4e) model described in detail for the I3– anion in Chapter 6 (p 111). Thus, in PF5, the three equatorial P–F bonds would be 2c,2e bonds formed using sp2 hybrids on the phosphorus whilst the linear, axial F–P–F unit would comprise a 3c,4e arrangement involving the remaining phosphorus p orbital in which the bonding orbital is delocalised over all three atoms but, crucially, the non-bonding orbital is localised only of the two fluorines with no contribution from the phosphorus. A total of 8 electrons are therefore associated with the phosphorus centre: three 2c,2e equatorial P–F bond pairs and the bonding 3c,4e pair for the F–P–F unit. To a first approximation, therefore, the octet rule is not violated.

An alternative model was proposed, however, notably by Pauling in the 1940’s, which would retain 2c,2e bonds to all fluorines in PF5. Thus, although the primary valence orbitals for phosphorus are the 3s and the three 3p orbitals, the vacant 3d orbitals are potentially available for bonding. Thus, it was proposed that a set of five dsp3 hybrids could be formed which allow for each P–F bond to be a 2c,2e bond and PF5 would therefore have 10 valence electrons: 5 from the phosphorus and 1 from each of the five fluorines.6 Likewise, a molecule such as SF6 would have six 2c,2e bonds and involve d2sp3 hybridisation at the sulfur centre. We can argue that this model reflects a prejudice for retaining the 2c,2e bonds favoured by Lewis, but the proposal hinges critically on the energetic availability (and to some extent, the radial extension) of 3d orbitals in these examples.7 Since at least the 1980’s with Kutzelnigg and certainly from the early 1990’s with authors such as Magnusson, Reed and Schleyer, d orbitals have been shown by means of quantitative electronic structure calculations to be energetically unavailable (i.e., too high in energy8) and on this basis, these and many other authors now argue that any bonding model involving d orbital hybrids such as dsp3 and d2sp3 should be abandoned. A useful recent summary is provided by Schwerdtfeger and Frenking.9

No discussion of the topic of this addendum can ignore the work of Gillespie who, as noted in Chapter 6, Section 6.3, has proposed a duodecet rule to account for the stability of species such as SF6. Gillespie’s argument for an octet rule and a duodecet rule are set out in detail on p 113-114 which we will not reprise here except to note that it is largely on this basis that Gillespie was inclined to reject the need for the term hypervalence. Much of Gillespie’s thinking on this matter is addressed in *Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities*10 which also covers much of the early history of the octet rule developed by Lewis. Furthermore, one cannot leave any mention of Gillespie’s contributions without reference to VSEPR Theory for which he was one of the key originators and its most vocal champion. As noted in Chapter 7, although VSEPR counts ten electrons around the phosphorus atom in PF5 and deduces the structure on that basis (derived from 5 pairs), no account need be given in terms of dsp3 hybridisation although this can, if one wishes, be assumed after the fact.

A look at the texts listed in the Bibliography and a number of other texts on inorganic chemistry reveals that if hypervalence is mentioned at all, its coverage is often cursory. The most recent editions of Housecroft and Sharpe and of Weller, Overton, Rourke and Armstrong (see Bibliography) do, however, address many of the points highlighted here but one of the most thorough treatments can be found in Keeler and Wothers.11

In conclusion, it can be argued that the term hypervalence and descriptions of molecules as hypervalent can and perhaps should now be reconsidered as argued in more detail in Chapter 4, Section 4.1 on p 55. If we accept that d orbital involvement is negligible and that the 3c,4e bonding model is a reasonable approximation for certain linear X–E–X arrangements, then any discussion of whether or not compounds such as PF5 or SF6 violate the octet rule becomes largely redundant and much of the requirement for a term such as hypervalence is unnecessary (although not, perhaps, in terms of the argument first made by Musher which equates hypervalence with the presence of what would now be described as 3c,4e bonds3).

Furthermore, as noted in the marginal note on p 55, it makes little sense to consider pentavalent phosphorus as hypervalent simply because pentavalent is greater than trivalent nor indeed to condone the use of the term hypovalent which is occasionally encountered for formally trivalent, six-electron species such as BF3. Moreover, according to the definition of valence (p 54), the classification of species such as [SiF5]– or [SiF6]2– as hypervalent lacks any logical basis since the silicon is tetravalent in each case just as it is in SiF4. Likewise, a description of hypothetical molecules such as [CH6]2+ or of isolable complexes such as [C(AuL)6]2+ (L = PPh3) as containing hypervalent carbon should be rejected (like silicon, carbon is never more than tetravalent). As some of the authors noted here have suggested, if the use of the prefix ‘hyper’ is to be retained, the term hypercoordinate has more merit than hypervalent.

As a final example of the ambiguities associated with hypervalence we can again consider representations of POCl3 as noted in Chapter 4, Section 4.1. Thus, whilst simple electron counting procedures would ascribe 10 electrons to the phosphorus centre in **E** (including VSEPR), only 8 are associated with the phosphorus atom in **C** and **D**. To class **E** as hypervalent but not **C** and **D** (both of which are better representations of the electronic structure) can only lead to confusion.



A further point to consider, however, is that if we adopt the 3c,4e bonding model and maintain that compounds such as PF5 are not classed as hypervalent since there are only 8 rather than 10 electrons around the phosphorus centre, why then are analogous compounds of the 2p elements so rarely encountered, e.g., NF5? One answer is that the 2p elements are simply too small to support coordination numbers of five or six in simple molecular species.12 Another factor is that the electronegativity of the 2p elements is sufficiently high to destabilise the non-bonding orbital localised solely on the X atoms in the linear X–E–X unit which is favoured for a less electronegative E and an electronegative X (e.g., F). This latter point would also account for why compounds such as PH5 are not stable.

Bearing in mind the discussion presented in Chapter 8 about simple models, we should recognise that all of the discussion in this addendum is based on simple models. More detailed, quantitative molecular orbital calculations and insights derived from alternative approaches to understanding electronic structure such as Spin Coupled Generalised Valence Bond Theory can and do shed further light on these and many other topics but detailed considerations resulting from these more advanced models are beyond the scope of this text.

***References***

1. See, Jensen, W. B., *J. Chem. Ed*., 2006, **83**, 1751-1752 and refs. therein.

2. For another short article which defines and describes hypervalence in the context of valence more generally, see, Smith, D. W., *J. Chem. Ed*., 2005, **82**, 1202-1204.

3. Musher, J. L., *Angew. Chem. Int. Ed*., 1969, **8**, 54-68.

4. We will use valence as defined in Chapter 4, Section 4.1 throughout this discussion.

5. In terms of the trigonal bipyramidal structure of PF5, this would involve the two axial P–F bonds being considered hypervalent with those to the three equatorial fluorines treated as ‘normal’ covalent bonds.

6. Note that a set of five dsp3 hybrids are not equivalent and comprise a sp2 set and a dp set as described in Section 6.3 on p 110 and which forms the basis for Bent’s rule which is also referred to in Chapter 7, Section 7.2 on p 122.

7. This is discussed in detail for SF6 in Chapter 8 in Section 8.2.

8. Accurate calculations do employ d orbitals as polarisation functions to more accurately determine the precise electronic and molecular structure, but this is ***not*** the same as d orbital occupancy.

9. Zhao, L., Pan, S., Holzmann, N., Schwerdtfeger, P., Frenking, G., *Chem. Rev*., 2019, **119**, 8781.

10. Gillespie, R. J., Popelier, P. L. A. (2001). *Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities*, Oxford University Press.

11. Keeler, J., Wothers, P. (2008). *Chemical Structure and Reactivity: An Integrated Approach*, Oxford University Press.

12. Higher coordination numbers are encountered for first row atoms albeit in interstitial environments such as observed for carbon in [C(AuL)6]2+ (L = PPh3).

The arguments concerning hypervalence discussed in this addendum are covered in much more detail in the following publication: *Hypervalence: A Useful Concept or One That Should Be Gracefully Retired?* N. C. Norman and P. G. Pringle, *Chemistry*, 2022, **4**, 1226-1249.