CH-110 Advanced General Chemistry I

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Beyond the Octet Rule

Topic 2C

Topic 2C.1 Radicals and biradicals
Topic 2C.2 Expanded valence shells
Topic 2C.3 Incomplete octets

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- Octet rule is a good starting point, there are exceptions that go beyond the octet.

WHAT DO YOU NEED TO KNOW ALREADY?

- Lewis structures
- Concept of resonance
- Assign formal charges in Lewis structure

2C Beyond the octet rule

Three types of exceptions to the octet rule

1. Molecules with an odd number of electrons
2. Certain elements are able to accommodate more than eight electrons in valence shell
3. Atoms in compounds may have incomplete octets

Radicals and Biradicals

Topic 2C.1

2C.1 Radicals and biradicals

1. Molecules with an odd number of electrons

2C.1 Radicals and biradicals

Self-test 2C.1B

Write the Lewis structure of nitrogen dioxide, NO_2.

2C.1: Radicals and biradicals

Summary

A radical is a species with an unpaired electron; a biradical has two unpaired electrons on either the same or different atoms.

Expanded Valence Shells

Topic 2C.2

2C.2: Expanded valence shells

Hypervalent compounds

A compound consisting of molecules that contain an atom with more than eight electrons is called **hypervalent**.

Variable covalence: when an element is able to form compounds with different numbers of attached atoms, e.g. PCl_3 vs. PCl_5.

What determines hypervalency?

- **Size of atom**: P is large enough to fit as many as six Cl atoms around it (PCl_5 known), N is too small (NCl_5 unknown)

2C.2: Expanded valence shells

Where are the extra electrons found?

2C.2: Expanded valence shells

Where are the extra electrons found?

Which explanation is better?

This depends on the molecule. To decide, one has to run detailed calculations as will be described in Topics 2F and 2G.

Important distinction: The first explanation makes use of d-orbitals, the second does not.

In this topic, the choice of model is **unresolved**, but we can still draw Lewis structures.

2C.2: Expanded valence shells

Example 2C.1: Writing a Lewis structure with an expanded valence shell

(a) Write the Lewis structure of sulfur tetrafluoride on the basis that the sulfur atom can expand its valence shell and give the number of electrons in that shell.

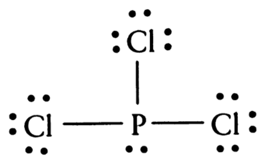
(b) Propose an ionic-covalent resonance structure for SF_4 in which the octet rule is obeyed for all atoms.

2C.2: Expanded valence shells

Variable valence of phosphorous

- Phosphorous has variable valence, e.g. forms toxic, colorless liquid phosphorous trichloride with a limited supply of chlorine:

$$P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(l)$$

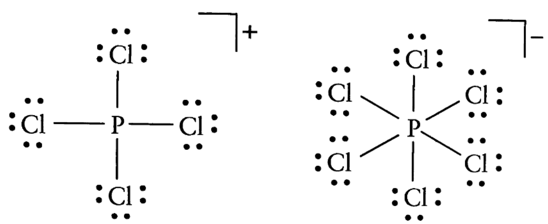


Phosphorus trichloride, PCl_3

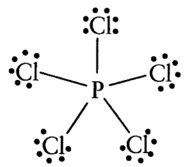
- PCl_3 obeys the octet rule
- When PCl_3 reacts with additional chlorine:

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

- At RT, PCl_5 is an ionic solid made of PCl_4^+ and PCl_6^-
- At 160 °C: a gas composed of PCl_5



9 Phosphorus pentachloride, $PCl_5(s)$

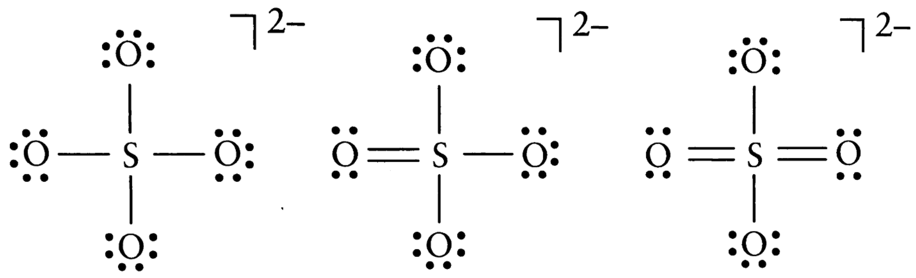


10 Phosphorus pentachloride, PCl_5

2C.2: Expanded valence shells

Example 2C.2: Selecting the dominant resonance structure for a molecule

Identify the dominant resonance structure of the sulfate ion (SO_4^{2-}) from the three structures shown (**11a**-**11c**) by calculating the formal charges on the atoms in each structure.



11a **11b** **11c**

2C.2: Expanded valence shells

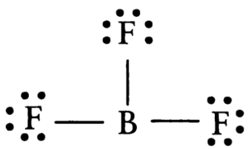
Summary

Apparent expansion of the valence shell can take place in elements of Period 3 and later. These elements can exhibit variable covalence and be hypervalent. Formal charge helps to identify the dominant resonance structure.

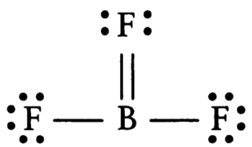
Incomplete Octets

Topic 2C.3

Boron may have incomplete octets



14 Boron trifluoride, BF_3

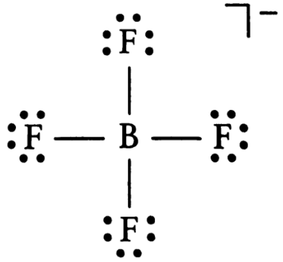


15 Boron trifluoride, BF_3

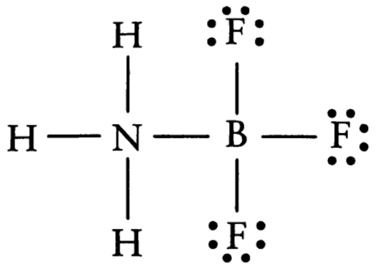
- Boron trifluoride only has six valence electrons at the boron atom (structure **14**)
- Structure **15** does not exist due to F’s high ionization energy: It does not like to share its electrons.
- Experimental evidence: B–F bond length is a resonance hybrid between **14** and **15**, with single bonds making the major contribution

2C.3: Incomplete octets

Coordinate covalent bonds



16 Tetrafluoroborate, BF_4^-



17

- A special way for boron (and similar atoms) to complete their octets: an additional atom or ion with a lone pair of electrons might form a bond providing *both* electrons.

A bond in which both electrons come from one of the atoms is called a **coordinate covalent bond**.

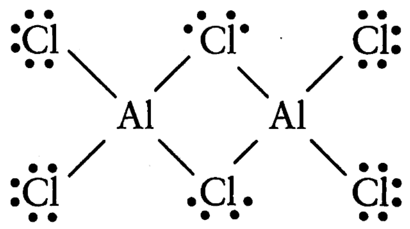
Examples:

BF_4^- forms when BF_3 is passed over metal fluoride (**16**)

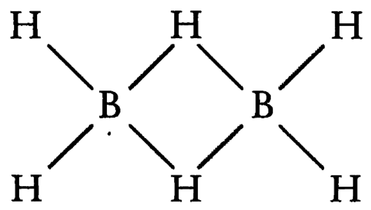
Or: $BF_3(g) + NH_3(g) \rightarrow NH_3BF_3(s)$ (**17**)

2C.3: Incomplete octets

Aluminum can also have unusual Lewis structures



18 Aluminum chloride, Al_2Cl_6



19 Diborane, B_2H_6

- **Formation of dimers** is another way to complete octets using coordinate covalent bonds.
- Linked **pairs of molecules**
- Examples: aluminum chloride (**18**)
- Dimer does exist for aluminum trichloride but not for boron trichloride (Al atom bigger)
- BH_3 exists as diborane (B_2H_6) (**19**)

2C.3: Incomplete octets

Summary

Compounds of boron and aluminum may have unusual Lewis structures in which boron and aluminum have incomplete octets or atoms that act as bridges.

The skills you have mastered are the ability to

- ❑ Draw the Lewis structures of molecules and ions with either expanded or incomplete valence shells.
- ❑ Use formal charge calculations to evaluate alternative Lewis structures.

Summary: You have learned that molecules with an unpaired electron and therefore having incomplete octets are called radicals. These compounds are normally very reactive. When drawing Lewis structures for molecules that contain Period 3 and later elements, you have seen that there are two possible explanations, one of which is to allow for the expansion of the valence shell by using d-orbitals and the other in which octets are preserved and there is ionic-covalent resonance.