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

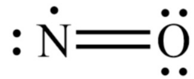
Radicals and Biradicals

Topic 2C.1

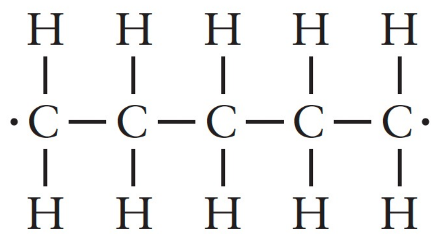
2C.1 Radicals and biradicals

1. Molecules with an odd number of electrons

- Species with at least one unpaired electron: **radicals**

E.g. methyl radical, $\cdot CH_3$ or nitric oxid, NO: 

- Radicals are highly reactive, cannot be stored, fleeting in nature
- Involved in ozone formation and decomposition
- **Biradical**: molecule with at least two unpaired electrons, usually on different atoms.
- Oxygen is a **biradical**: [He]$2s^2 2p_x^2 2p_y^1 2p_z^1$



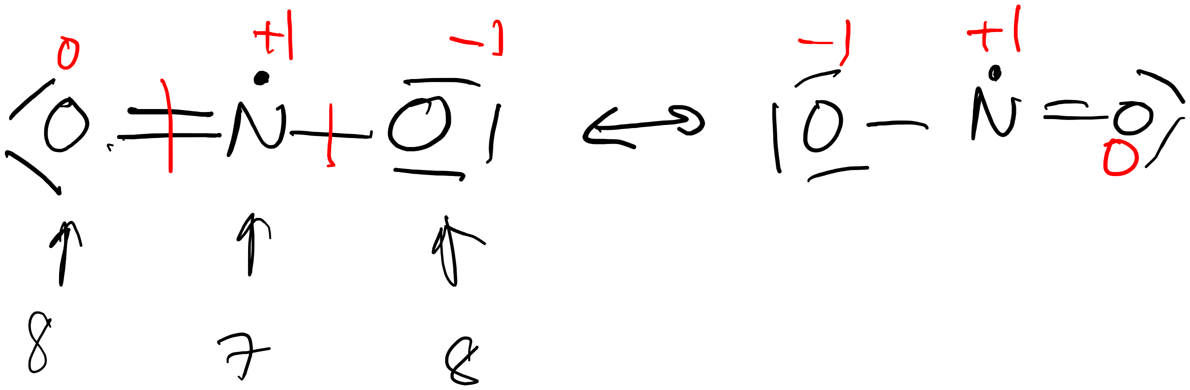
2C.1 Radicals and biradicals

Self-test 2C.1B

Write the Lewis structure of nitrogen dioxide, NO_2.

$5 + 2 \cdot 6 = 17\, e^{-}$

$8\, ep + 1\, e^{-}$



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? → elements in third period and above

- **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)

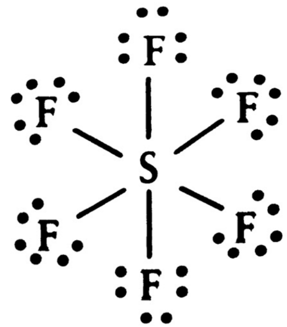
2C.2: Expanded valence shells

Where are the extra electrons found?

Two explanations:

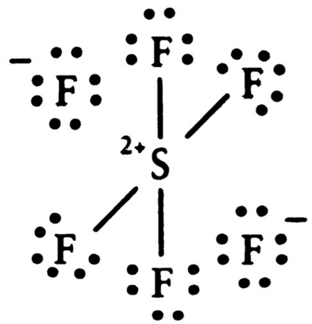
1. Occupation of d-orbitals: Valence shell expands by using d-orbitals as well as the s- and p-orbitals. Hypervalence is characteristic of Period 3 and beyond.

E.g. sulfur with [Ne]$3s^2 3p^4$ configuration (SF_6) has empty 3d-orbitals.



Sulfur hexafluoride, SF_6

2. Ionic-covalent resonance: This explanation preserves the octet rule. It treats structures as **resonance hybrid of ionic structures**, e.g. SF_6 is composed of $(SF_4)^{2+}$ and $(F^-)_2$. The cation has an octet, as do all the fluorine atoms and fluoride ions.



Sulfur hexafluoride, SF_6

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.

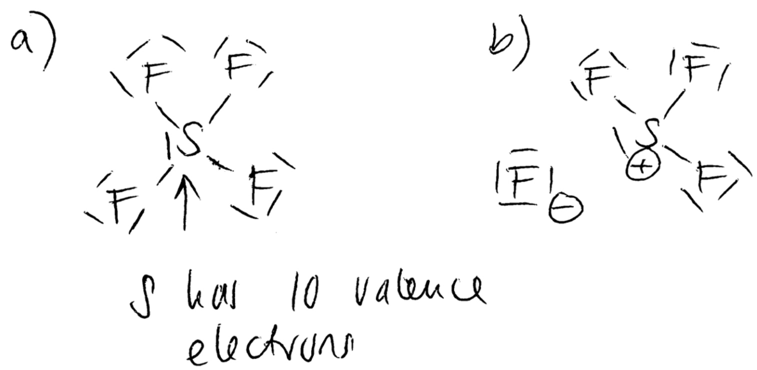
In this topic, the choice of model is **unresolved**, but we can still draw Lewis structures.

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

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

Solution from the book:

00 Topic 2C Beyond the Octet Rule

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

Sulfur tetrafluoride, SF_4, is used in the pharmaceutical industry to synthesize fluorocarbons, some of which are used as anesthetics. (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.

Anticipate Sulfur, in Group 16, has six valence electrons; if each fluorine atom provides one electron for the bond it forms, you should expect there to be $4+6=10$ electrons around the S atom.

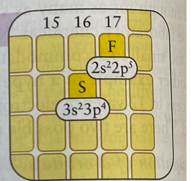
Plan (a) Elements in Period 3 and later periods can expand their valence shells to accept additional electrons. After assigning all the valence electrons to bonds and lone pairs to give each atom an octet, assign any remaining electrons to the central atom as lone pairs. (b) 10 electrons around the S atom would exceed the octet rule. Because fluorine can form fluoride anions, forming at least one structure of the form $SF_3^+F^-$ would transfer an electron pair away from the S atom.

Solve

Count the number of valence electrons.

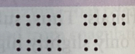
6 from sulfur (·S̤̈·)

7 from each fluorine atom (:F̤̈·)



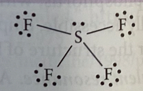
Find the number of electron pairs.

There are $6+(4\times7)=34$ electrons, or 17 electron pairs.



(a) Construct the Lewis structure.

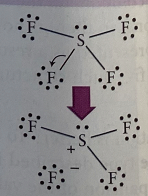
Give each F atom 3 lone pairs and 1 bonding pair shared with the central S atom; place the 2 extra electrons on the S atom. The S atom has 10 valence electrons.



(b) Construct an ionic–covalent Lewis structure.

The S atom has 10 valence electrons in the Lewis structure in (a). The S atom must lose 1 electron pair to have an octet.

Move 1 electron pair from an S—F bond to form $(SF_3)^+(F^-)$.



Evaluate (a) As expected, sulfur has 10 electrons in its expanded valence shell. According to the conventional model, the S atom needs to use one 3d-orbital in addition to its four s- and p-orbitals to accommodate those 10 electrons. (b) All atoms in the ionic–covalent Lewis structure have complete octets, and an expanded valence shell is not needed.

Self-test 2C.2A (a) Write the Lewis structure for xenon tetrafluoride, XeF_4, and give the number of electrons in the expanded valence shell. (b) Propose an ionic–covalent resonance structure for XeF_4 in which the octet rule is obeyed for all atoms.

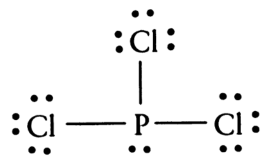
[*Answer:* (a) See (**7a**); 12 electrons. (b) See (**7b**).]

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:

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

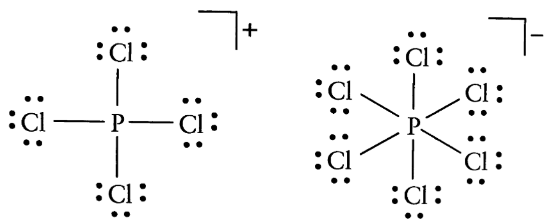


Phosphorus trichloride, PCl_3

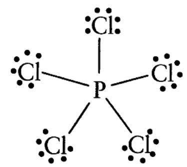
- PCl_3 obeys the octet rule
- When PCl_3 reacts with additional chlorine:

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

- 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, $PCl_5(s)$

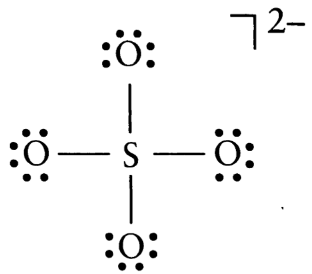


10 Phosphorus pentachloride, PCl_5

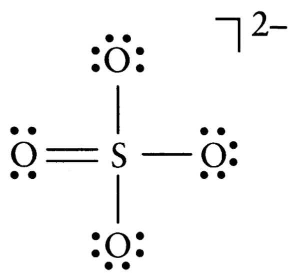
2C.2: Expanded valence shells

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

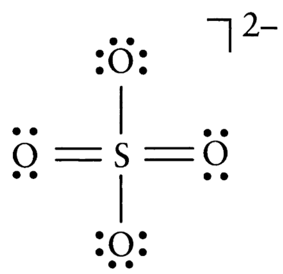
Identify the dominant resonance structure of the sulfate ion (SO_4^{2-}) from the three structures shown (**11a**-**11c**) by calculating the formal charges on the atoms in each structure.



11a



11b



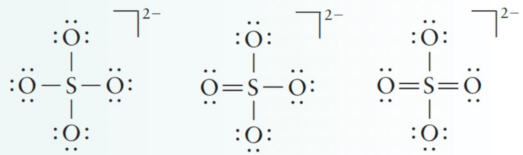
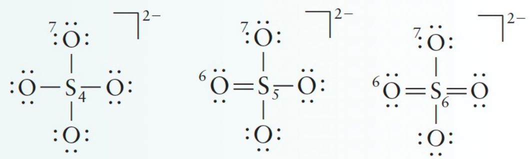
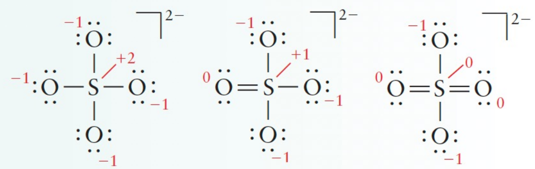
11c

2C.2: Expanded valence shells

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

Solution:

SOLVE Draw up the following table, in accord with Toolbox 2.2.

	26a	26b	26c
Step 1 Count the valence electrons (V).	O: 6 S: 6 Total: 30 electrons plus two electrons from the charge of −2, for a total of 16 pairs of electrons.		
Step 2 Draw the Lewis structure.			
Step 3 Assign electron ownership, $(L + \frac{1}{2}B)$.			
Step 4 Find the formal charge, $V - (L + \frac{1}{2}B)$.			

Evaluate The individual formal charges are closest to zero in structure (**26c**); so the structure with two double bonds is likely to make the biggest contribution to the resonance hybrid, even though the valence shell on the S atom has expanded to hold 12 electrons. Note this pattern for future reference. Also note that the formal charges of the atoms add up to the overall charge of the ion in each case.

2C.2: Expanded valence shells

Summary

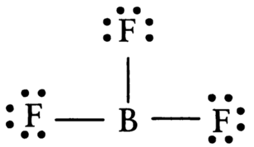
Apparent expansion of the valence shell can take place in elements of Period 3 and later. These elements can exhibit variable covalence and be hypervalent. Formal charge helps to identify the dominant resonance structure.

Incomplete Octets

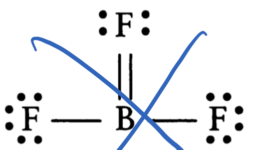
Topic 2C.3

2C.3: Incomplete octets

Boron may have incomplete octets



14 Boron trifluoride, BF_3

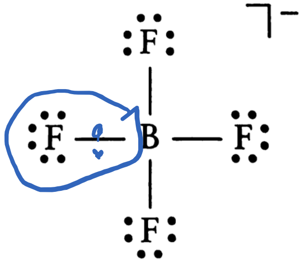


15 Boron trifluoride, BF_3

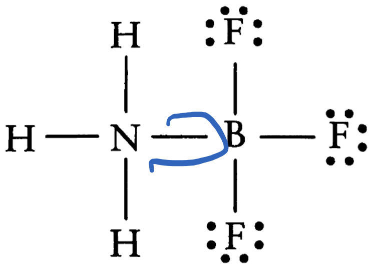
- Boron trifluoride only has six valence electrons at the boron atom (structure **14**)
- Structure **15** does not exist due to F's high ionization energy: It does not like to share its electrons.
- Experimental evidence: B–F bond length is a resonance hybrid between **14** and **15**, with single bonds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

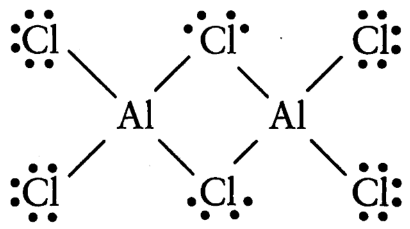
A bond in which both electrons come from one of the atoms is called a **coordinate covalent bond**.

Examples:

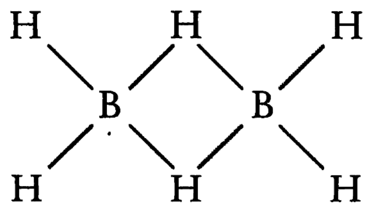
BF_4^- forms when BF_3 is passed over metal fluoride (**16**)

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

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.

2C Exercises from the book

Exercise 2C.2

Which of the following species are radicals? → uneven number $e^{\ominus}$

(a) NO_3 $5 + 3 \cdot 6 = 23$ ✓

(b) ICl_2^{+} $7 + 2 \cdot 7 - 1 = 20$ ✗

(c) CH_2O $4 + 2 + 6 = 12$ ✗

(d) HOCO $1 + 6 + 4 + 6 = 17$ ✓

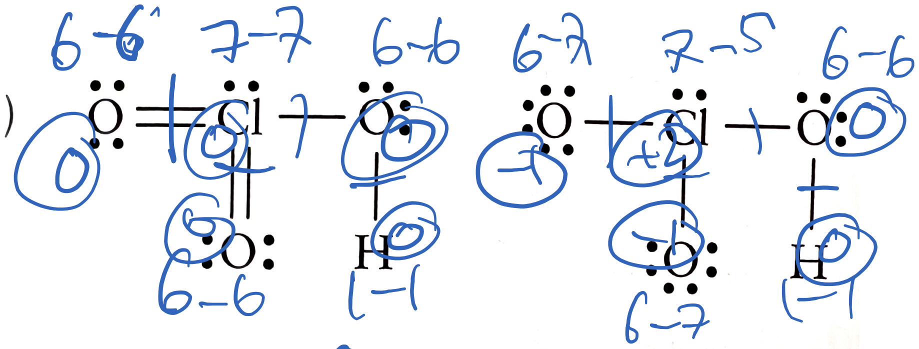
2C Exercises from the book

Exercise 2C.21

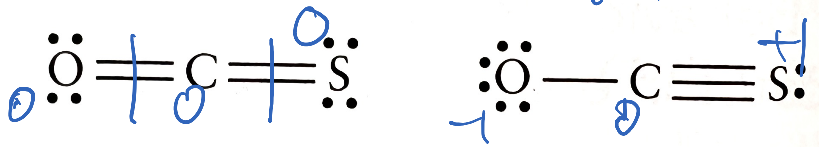
formal charge = $V - \left(L + \frac{1}{2}B\right)$

Calculate the formal charge on each atom in the following molecules. Identify the structure of lower energy in each pair.

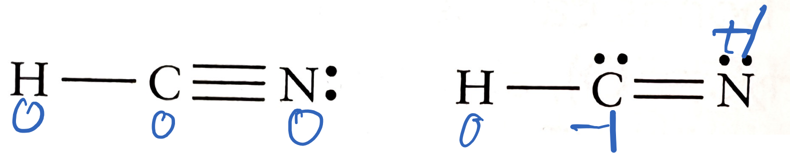
(a)



(b)



(c)



2C Exercises from the book

Exercise 2C.3

Draw the Lewis structure, including principal contributions to the resonance structure (where appropriate, allow for the possibility of octet expansion, including double bonds in different positions), for

(a) Periodate ion, IO_4^-

(b) Hydrogen phosphate ion, HPO_4^{2-}

(c) Chloric acid, $HClO_3$

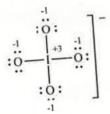
(d) Arsenate ion, AsO_4^{3-}

2C Exercises from the book

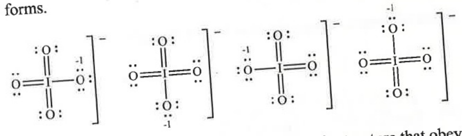
Exercise 2C.3

Solution from book:

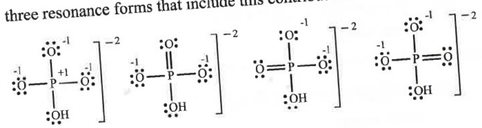
2C.3 (a) The periodate ion has one Lewis structure that obeys the octet rule:



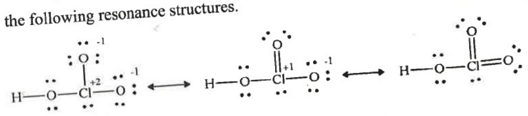
The formal charge of at I can be reduced to from +3 to 0 by including three double-bond contributions, thereby giving rise to four resonance forms.



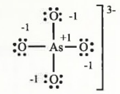
(b) The hydrogen phosphate ion has one Lewis structure that obeys the octet rule (the first structure shown below). The inclusion of one double bond to oxygen lowers the formal charge at P from +1 to 0. There are three resonance forms that include this contribution.



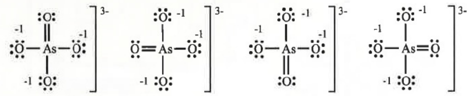
(c) There is one Lewis structure that obeys the octet rule shown below at the left. The formal charge at chlorine can be reduced to +1 by including one double bond contribution. The formal charge can be reduced to 0 if there are two double bond contributions. These contributions give rise to the following resonance structures.



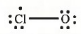
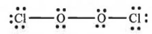
(d) The arsenate ion has one Lewis structure that obeys the octet rule.

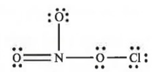


Just as in part (a), including one double bond to oxygen lowers the formal charge at As from +1 to 0. There are four resonance forms that include this contribution.



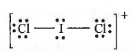
2C.5 The Lewis structures are

(a)  (b) 

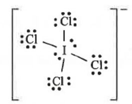
(c) 

Radicals are species with an unpaired electron, therefore only (a) is a radical.

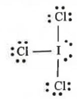
2C.7

(a) 

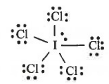
I has 2 bonding pairs and 2 lone pairs

(b) 

I has 4 bonding pairs and 2 lone pairs

(c) 

I has 3 bonding pairs and 2 lone pairs

(d) 

I has 5 bonding pairs and 1 lone pair