CH-110 Advanced General Chemistry I

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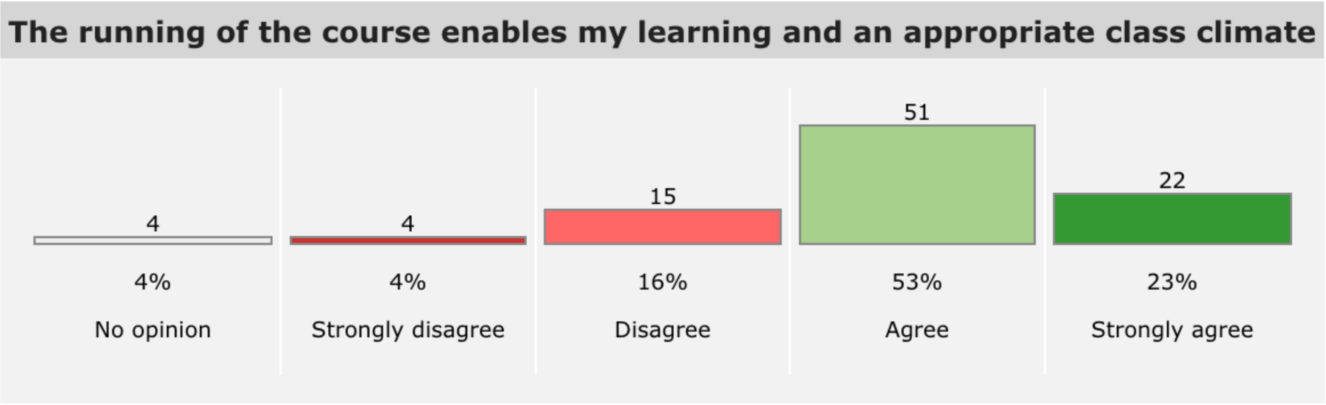
Housekeeping notes

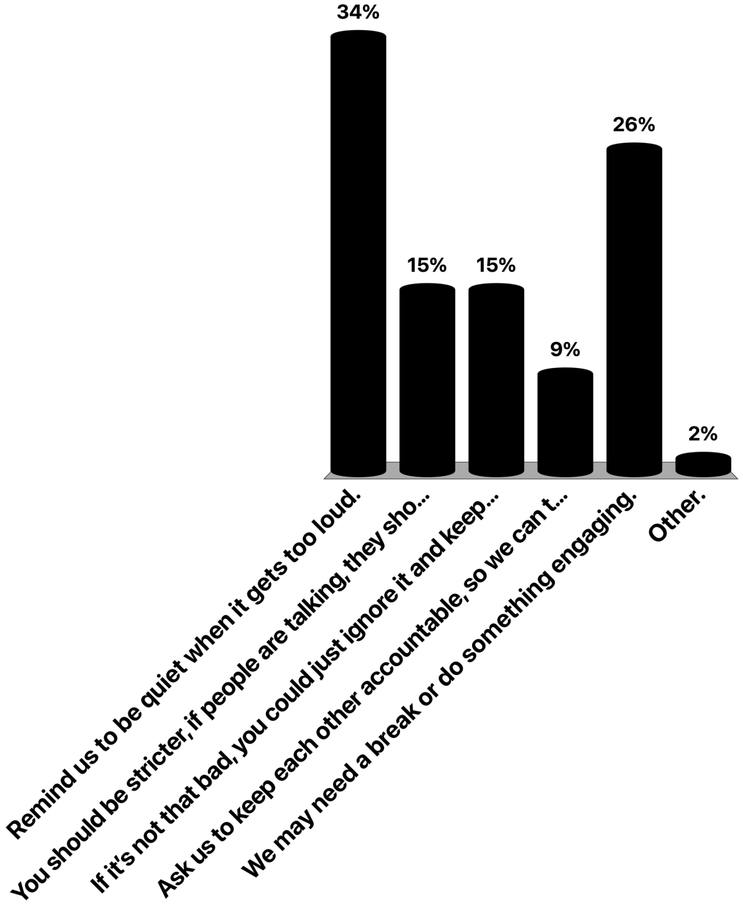
Indicative feedback:

- Too many slides, not clear what is important.
- No French translation for week 3 (now available).
- Too much noise in the classroom.



How would you prefer I react if there is too much noise in the classroom?

A. Remind us to be quiet when it gets too loud.
B. You should be stricter, if people are talking, they should leave.
C. If it’s not that bad, you could just ignore it and keep going.
D. Ask us to keep each other accountable, so we can tell others to be quiet.
E. We may need a break or do something engaging.
F. Other.



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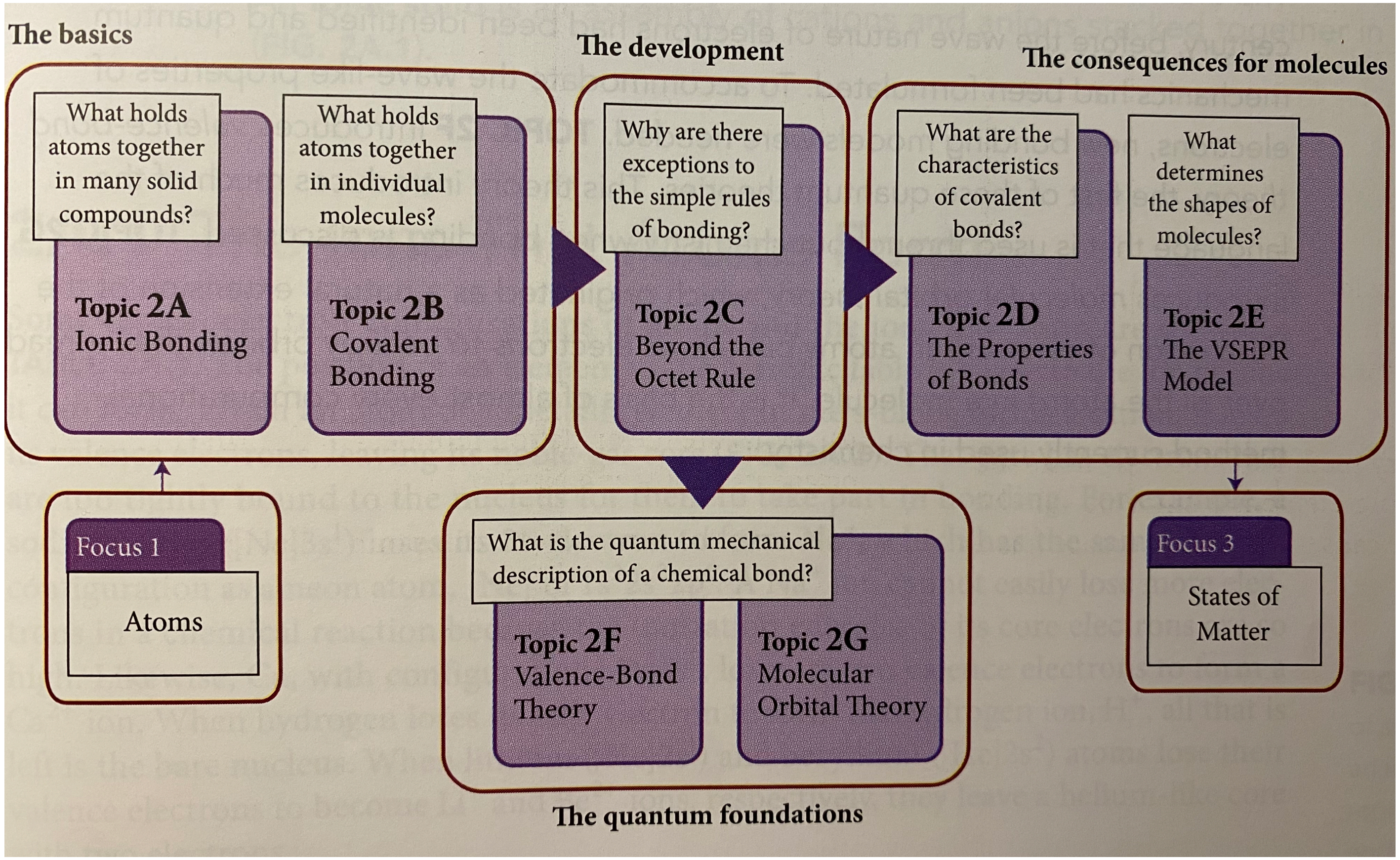
Bonds Between Atoms

Focus 2

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



The basics

What holds atoms together in many solid compounds?

Topic 2A Ionic Bonding

What holds atoms together in individual molecules?

Topic 2B Covalent Bonding

The development

Why are there exceptions to the simple rules of bonding?

Topic 2C Beyond the Octet Rule

The consequences for molecules

What are the characteristics of covalent bonds?

Topic 2D The Properties of Bonds

What determines the shapes of molecules?

Topic 2E The VSEPR Model

Focus 1

Atoms

What is the quantum mechanical description of a chemical bond?

Topic 2F Valence-Bond Theory

Topic 2G Molecular Orbital Theory

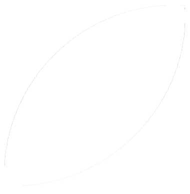
The quantum foundations

Focus 3

States of Matter

Covalent Bonding

Topic 2B



Last week: Topic 2B.1 Lewis Structures
Topic 2B.2 Resonance
Topic 2B.3 Formal Charge

WHY DO YOU NEED TO KNOW THIS MATERIAL?

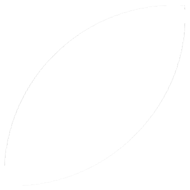
- Understanding the nature of covalent bonding is essential for interpreting structures, properties and reactions of molecules.

WHAT DO YOU NEED TO KNOW ALREADY?

- Electron configurations of many-electron atoms (Topic 1E)
- Lewis symbols (Topic 2A)
- Nomenclature for different types of compounds (Fundamentals D and C)
- Concept of oxidation number (Fundamentals K)
- Concept of electronegativity (Topic 1F)

Resonance

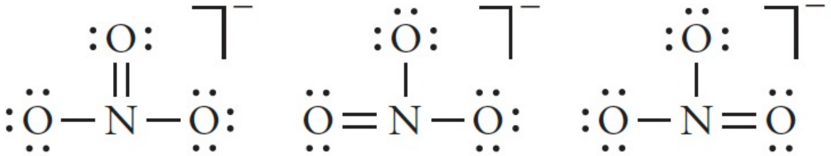
Topic 2B.2



2B.2: Resonance

Resonance and bond order

- Some molecules are not represented adequately by a single Lewis structure.
- Nitrate, NO_3^-, has three valid Lewis structures of equal energy:

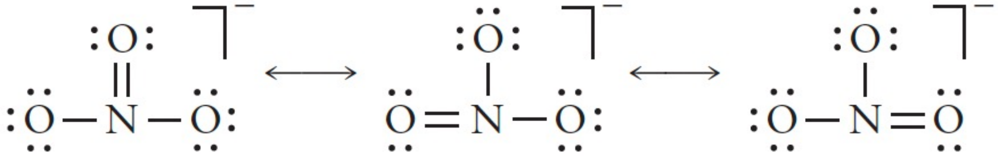


- Double bonds are shorter than single bonds, they hold atoms together more tightly.
- Observed bond length is the same for all three bonds: 124 pm
- Typical N–O single bond: 140 pm, typical N=O double bond: 120 pm
- **Bond order** is between 1 and 2 for nitrate NO bond

2B.2: Resonance

Resonance structures

- All three bonds are identical in NO_3^-
- Better model is to **blend all three Lewis structures**, each bond has intermediate properties between a single and a double bond



- **Blending of structures is called resonance depicted by double-headed arrows**
- The real structure is a **resonance hybrid**, the molecule does not flicker between structures, but is in a constant in-between state (analogy: mule, not horse, not donkey)

2B.2: Resonance

Delocalization

- Electrons that are shown in different positions in a set of resonance structures are said to be **delocalized**.
- Delocalization means that a **shared electron pair is distributed over several pairs of atoms** and cannot be identified with just one pair of atoms.
- The three resonance structures of nitrate do not exist as actual molecules, they are simply a way of showing that the **electrons are spread across the molecule**.
- Delocalization **lowers the energy** of a molecule.

2B.2: Resonance

Rules to write appropriate resonance structures

- In each contributing structure, **the nuclei of the atoms are in the same positions**; only the locations of lone pairs and bonding pairs are different.
- Equivalent structures (structures that differ only in the positions of multiple bonds and lone pairs) **contribute equally to the resonance**.
- **Low-energy structures contribute more** to the resonance mixture than high-energy structures. (You will see how to judge relative energies in the next section.)

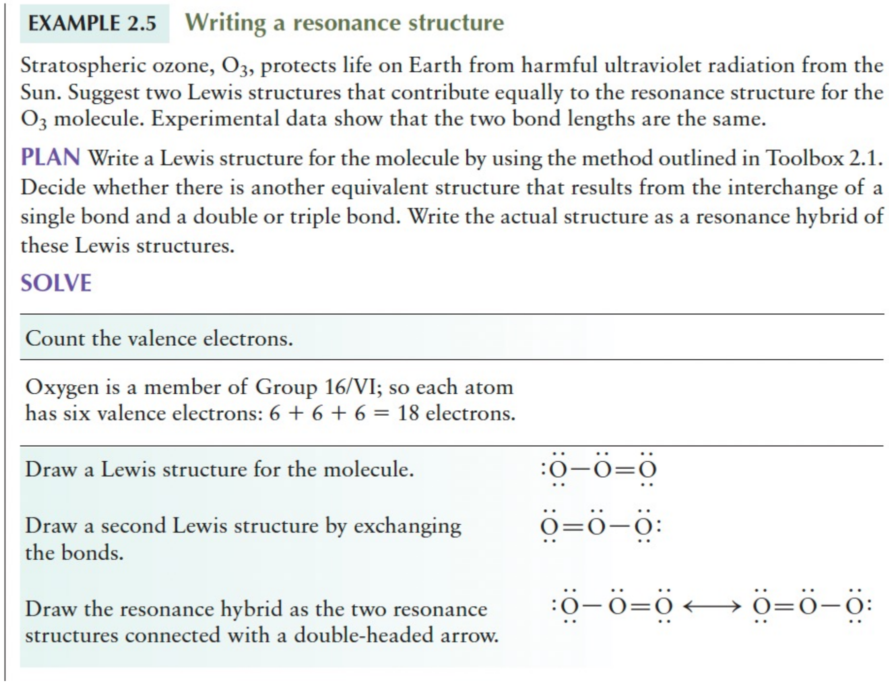
Note: resonance does NOT occur between structures with atoms in different arrangements. For example, no resonance occurs between hypothetical structures NNO and NON.

2B.2: Resonance

Example 2B.3: Writing a resonance structure (blackboard)

Suggest two Lewis structures that contribute equally to the resonance structure for the O_3 molecule. Experimental data show that the two bond lengths are the same.

Solution:



EXAMPLE 2.5 **Writing a resonance structure**

Stratospheric ozone, O_3, protects life on Earth from harmful ultraviolet radiation from the Sun. Suggest two Lewis structures that contribute equally to the resonance structure for the O_3 molecule. Experimental data show that the two bond lengths are the same.

PLAN Write a Lewis structure for the molecule by using the method outlined in Toolbox 2.1. Decide whether there is another equivalent structure that results from the interchange of a single bond and a double or triple bond. Write the actual structure as a resonance hybrid of these Lewis structures.

SOLVE

Count the valence electrons.

Oxygen is a member of Group 16/VI; so each atom has six valence electrons: 6 + 6 + 6 = 18 electrons.

Draw a Lewis structure for the molecule. $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-\overset{\cdot\cdot}{O}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$

Draw a second Lewis structure by exchanging the bonds. $\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\overset{\cdot\cdot}{O}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$

Draw the resonance hybrid as the two resonance structures connected with a double-headed arrow. $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-\overset{\cdot\cdot}{O}=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \longleftrightarrow \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=\overset{\cdot\cdot}{O}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$

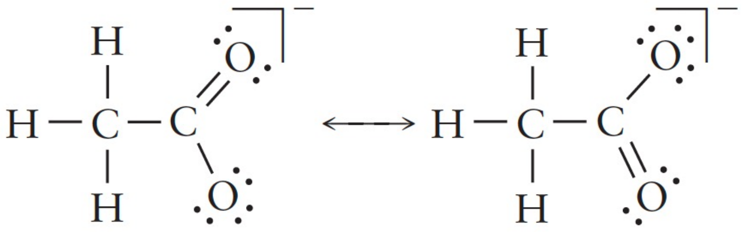
2B.2: Resonance

Example 2B.3: Writing a resonance structure (blackboard)

Write the Lewis structures contributing to the resonance hybrid for the (a) acetate ion, $CH_3CO_2^-$ and (b) nitrite ion, NO_2^-.

Solution:

a)

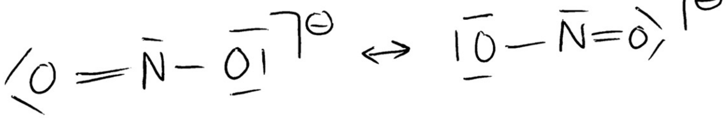


10 Acetate ion, $CH_3CO_2^-$

b)

$NO_2^{\ominus}$: Valence $e^{\ominus}$ $5 + 2\times 6 + 1 = 18 e^{\ominus}$

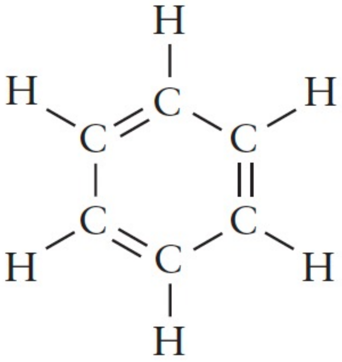
9 electron pairs



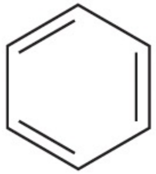
2B.2: Resonance

Benzene, C_6H_6

- Benzene is also a resonance hybrid
- Planar hexagonal ring of six C with each an H attached
- One Lewis structure shown (**11**): **Kekulé structure**
- Equivalent line or stick form shown in (**12**)



11 Kekulé structure



12 Kekulé structure, stick form

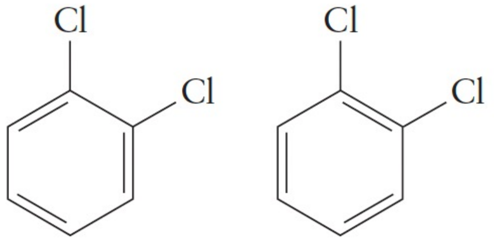
2B.2: Resonance

Benzene's properties do not align with Kekulé structure

One Kekulé structure does not fit all the experimental evidence:

1. **Reactivity**: benzene does not undergo reactions typical of compounds with double bonds
2. **Bond lengths**: All carbon-carbon bonds in benzene are the same length
3. **Structural evidence**: only one version of 1,2-dichlorobenzene (in which the chlorine atoms are attached to two adjacent carbon atoms) exists.

If the Kekulé structure were correct, there would be two distinct versions of 1,2-dichlorobenzene:

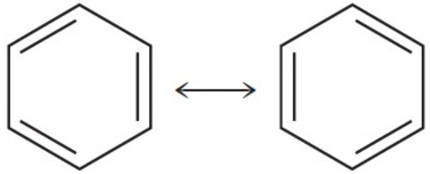


However, only one known to exist!

2B.2: Resonance

Concept of resonance resolves contradictions

- **Two Kekulé structures with exactly the same energy**: they only differ in the position of double bonds (**14**)
- Electrons shared in C=C double bonds are **delocalized over the entire molecule**
- Bond lengths intermediate between single and double bond and identical (circle in **15**)
- Resonance stabilizes a molecule → benzene less reactive than expected



14 Benzene resonance structure

15 Benzene, C_6H_6

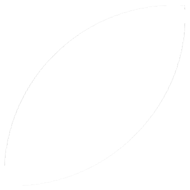
2B.2: Resonance

Summary

Resonance is a blending of structures with the same arrangement of atoms but different arrangements of electrons. Resonance results in electron delocalization; it spreads multiple-bond character over a molecule and results in a lower energy.

Formal Charge

Topic 2B.3



2B.3: Formal charge

Nonequivalent Lewis structures

Nonequivalent Lewis structures are Lewis structures that **do not correspond to the same energy**.

- They do NOT in general make the same contribution to a resonance structure.

How do you decide which resonance structures has the lowest energy?

- Compare the **number of valence electrons distributed around each atom** in a structure with the number of **valence electrons on the free atom.** The smaller the differences are, the lower is its energy and the greater is its contribution to a resonance hybrid.

2B.3: Formal charge

Formal charge as a measure of electron redistribution

- **Formal charge:** the charge an atom would have if the bonding were perfectly covalent (each atom has exactly a half-share in each pair of bonding electrons).

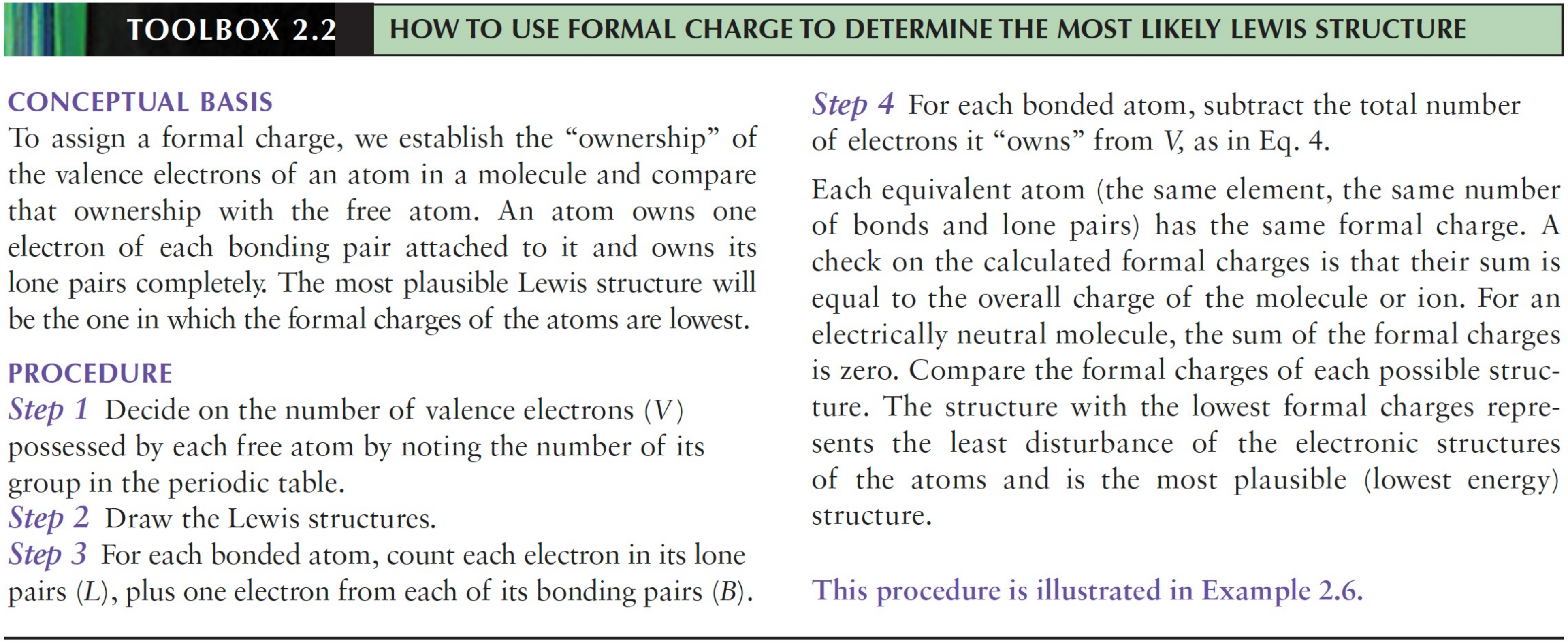
How many electrons does an atom "own" in a molecule?

- It "owns" all its lone pairs and half of each shared bonding pair.
- The formal charge is calculated as the difference between this number and the number of valence electrons in the free atom:

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

V is the number of valence electrons, L is the number of electrons present on the bonded atom as lone pairs, and B is the number of bonding electrons on the atom.

2B.3: Formal charge



TOOLBOX 2.2 **HOW TO USE FORMAL CHARGE TO DETERMINE THE MOST LIKELY LEWIS STRUCTURE**

CONCEPTUAL BASIS

To assign a formal charge, we establish the "ownership" of the valence electrons of an atom in a molecule and compare that ownership with the free atom. An atom owns one electron of each bonding pair attached to it and owns its lone pairs completely. The most plausible Lewis structure will be the one in which the formal charges of the atoms are lowest.

PROCEDURE

Step 1 Decide on the number of valence electrons (V) possessed by each free atom by noting the number of its group in the periodic table.

Step 2 Draw the Lewis structures.

Step 3 For each bonded atom, count each electron in its lone pairs (L), plus one electron from each of its bonding pairs (B).

Step 4 For each bonded atom, subtract the total number of electrons it "owns" from V, as in Eq. 4.

Each equivalent atom (the same element, the same number of bonds and lone pairs) has the same formal charge. A check on the calculated formal charges is that their sum is equal to the overall charge of the molecule or ion. For an electrically neutral molecule, the sum of the formal charges is zero. Compare the formal charges of each possible structure. The structure with the lowest formal charges represents the least disturbance of the electronic structures of the atoms and is the most plausible (lowest energy) structure.

This procedure is illustrated in Example 2.6.

2B.3: Formal charge

Example 2B.4: Selecting the most likely arrangement of atoms (blackboard)

Write three Lewis structures with different atomic arrangements for the thiocyanate ion (SCN^-) and select the most likely structure by identifying the structure with formal charges closest to zero. For simplicity, consider only structures with double bonds between neighbouring atoms.

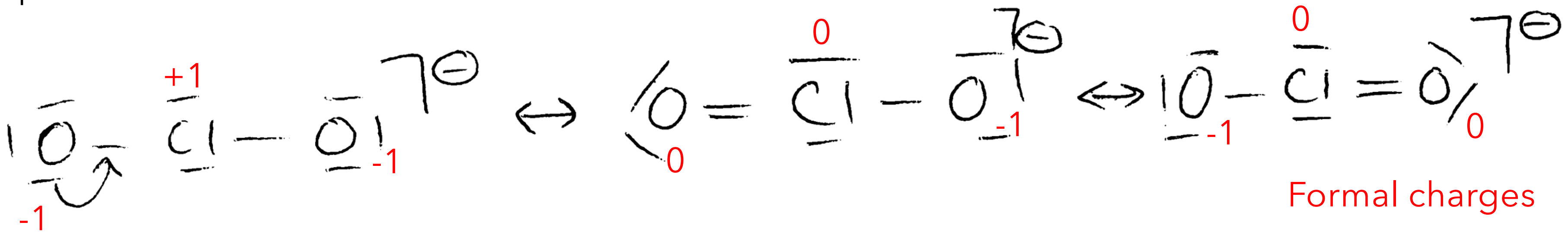
Reminder: Electronegativity TREND: F > O > N/Cl > Br > I > S > C/Se > H >…

Important addition: The electronegativity of N and Cl is very similar. Which one is higher or lower depends on the periodic table you use, for example, for the one in the book, the electronegativity of Cl > N, but for the one in the classroom, N > Cl.

2B.1: Lewis structures

Student question

The Lewis structure of chlorite ion could also have a double bond, why is the structure shown in class the preferred structure?



The first satisfies the octet rule. The 2nd and 3rd structure contain hypervalent chlorine. Which one is closest to the truth? Analysis of formal charges suggests 2nd and 3rd. Additionally, look at bond lengths:

Cl–O (single bond): 172 pm

Cl=O (double bond): 140 pm

C–O in ClO_2^-: 156 pm → Chlorite has a bond order between 1 and 2.

Formal charge to predict atom arrangement in molecules

- If the atom has **more electrons in the molecule** than when it is a free, neutral atom, then the atom has a **negative formal charge**, like a monatomic anion.
- Of the assignment of electrons **leaves the atom with fewer electrons** than when it is free, then the atom has a **positive formal charge**, as if it were a monatomic cation.

Formal charge can be used to predict the most favorable arrangement of atoms in a molecule and most likely Lewis structure for that arrangement:

- A Lewis structure in which the **formal charge of the individual atoms are closest to zero** typically represents the lowest-energy arrangement of the atoms and electrons.
- The structure of lowest energy is typically the one with a **positive formal charge on the least-electronegative atoms**.

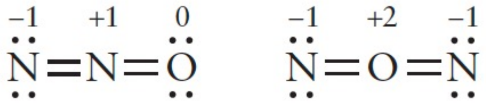
2B.3: Formal charge

Formal charge to predict atom arrangement in molecules

- A **low formal charge** (as close to zero as possible) indicates that an atom has undergone only a small redistribution of electrons relative to the free atom.
- For carbon dioxide, the formal charge predicts that the structure OCO is more likely than COO.
- Similarly, it predicts that NNO is more likely than NON for N_2O.

$$\overset{0}{O}=\overset{0}{C}=\overset{0}{O} \qquad \overset{0}{O}=\overset{+2}{O}=\overset{-2}{C}$$

17



$$\overset{-1}{N}\equiv\overset{+1}{N}=\overset{0}{O} \qquad \overset{-1}{N}=\overset{+2}{O}=\overset{-1}{N}$$

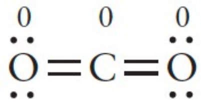
18

2B.3: Formal charge

Formal charge vs. oxidation number

Formal charge and oxidation number both provide information about the number of electrons around an atom in a compound, but are distinct in origin and significance:

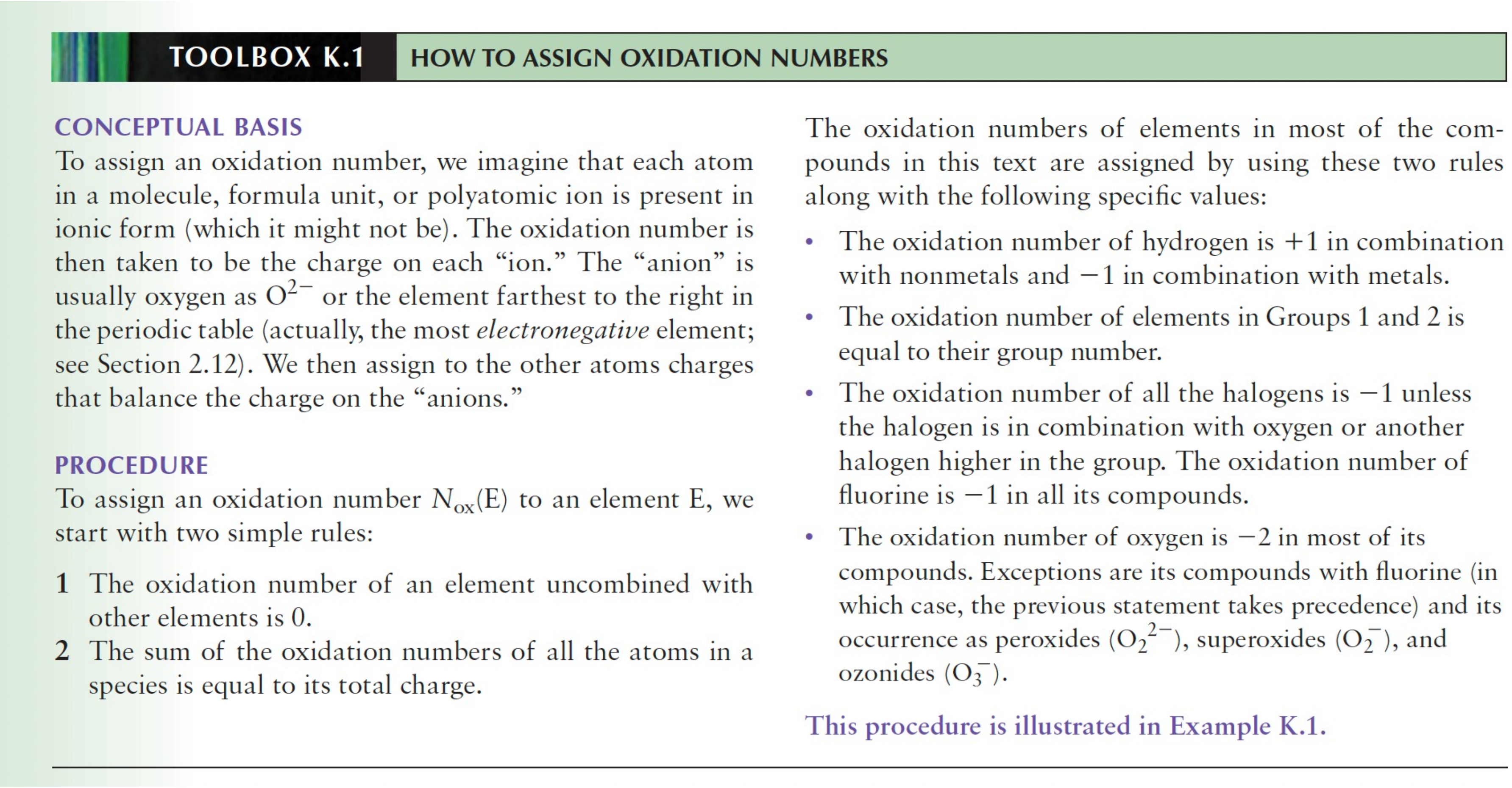
- Formal charge **exaggerates the covalent character** of bonds by assuming that the electrons are shared equally.
- Oxidation number **exaggerates the ionic character of bonds**. It represents the atoms as ions, and ***all* the electrons in a bond are assigned to the more electronegative atom** (the atom with the greater attraction for electrons).
- For CO_2: formal charge is zero. Oxidation number of carbon is +IV.



- Formal charges **depend on the particular Lewis structure** drawn, oxidation numbers **do not**.
- Formal charges are used to assess **relative energies of Lewis structures**, oxidation numbers are used when assessing the **oxidizing and reducing properties** of molecules.

2B.3: Formal charge

Reminder: How to assign oxidation numbers



TOOLBOX K.1 **HOW TO ASSIGN OXIDATION NUMBERS**

CONCEPTUAL BASIS

To assign an oxidation number, we imagine that each atom in a molecule, formula unit, or polyatomic ion is present in ionic form (which it might not be). The oxidation number is then taken to be the charge on each "ion." The "anion" is usually oxygen as O^{2-} or the element farthest to the right in the periodic table (actually, the most *electronegative* element; see Section 2.12). We then assign to the other atoms charges that balance the charge on the "anions."

PROCEDURE

To assign an oxidation number $N_{ox}(E)$ to an element E, we start with two simple rules:

1. The oxidation number of an element uncombined with other elements is 0.
2. The sum of the oxidation numbers of all the atoms in a species is equal to its total charge.

The oxidation numbers of elements in most of the compounds in this text are assigned by using these two rules along with the following specific values:

- The oxidation number of hydrogen is +1 in combination with nonmetals and −1 in combination with metals.
- The oxidation number of elements in Groups 1 and 2 is equal to their group number.
- The oxidation number of all the halogens is −1 unless the halogen is in combination with oxygen or another halogen higher in the group. The oxidation number of fluorine is −1 in all its compounds.
- The oxidation number of oxygen is −2 in most of its compounds. Exceptions are its compounds with fluorine (in which case, the previous statement takes precedence) and its occurrence as peroxides (O_2^{2-}), superoxides (O_2^-), and ozonides (O_3^-).

This procedure is illustrated in Example K.1.

2B.3: Formal charge

Summary

The formal charge gives an indication of the extent to which atoms have gained or lost electrons in the process of covalent bond formation; atom arrangements and Lewis structures with the lowest formal charges are likely to have the lowest energy.

The skills you have mastered are the ability to

☐ Draw the Lewis structures of molecules.

☐ Write the resonance structures for a molecule.

☐ Use formal charge calculations to select the most likely atom arrangement.

Summary: You have learned that a covalent bond consists of a shared electron pair and that atoms typically acquire a complete octet (or duplet for hydrogen) of electrons. The patterns of electron-pair sharing in covalent compounds are represented by drawing Lewis structures. You have seen that in some cases, it is necessary to represent a molecule as a resonance hybrid that spreads multiple-bond character over the entire molecule. You have seen that the lowest-energy Lewis structure can often be identified by calculating the formal charges of the atoms.

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

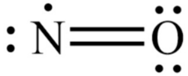
Topic 2C.1

2C.1 Radicals and biradicals

1. Molecules with an odd number of electrons

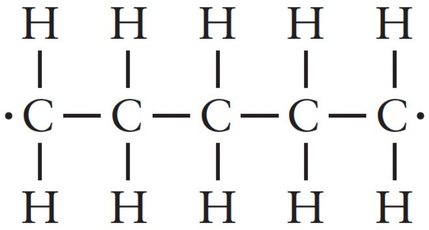
- Species with at least one unpaired electron: **radicals**

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



$:\dot{\mathrm{N}}=\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$

- Radicals are highly reactive, cannot be stored, fleeting in nature
- Involved in ozone formation and decomposition
- Antioxidants prevent damage by radicals
- **Biradical**: molecule with at least two unpaired electrons, usually on different atoms.
- Oxygen is a **biradical**: $[He]2s^2 2p_x^2 2p_y^1 2p_z^1$
- See: https://www.youtube.com/watch?v=Lt4P6ctf06Q



2C.1 Radicals and biradicals

Self-test 2C.1B (blackboard)

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)

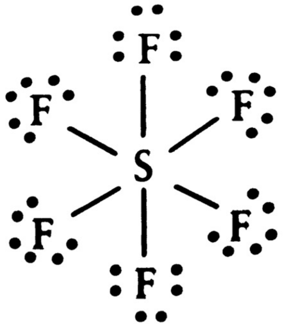
2C.2: Expanded valence shells

Where are the extra electrons found?

Two explanations:

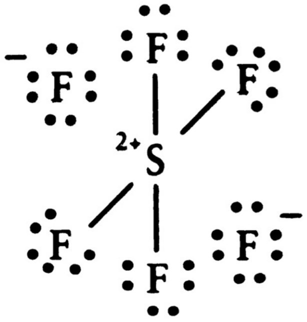
1. Occupation of d-orbitals: Valence shell expands by using d-orbitals as well as the s- and p-orbitals. Hypervalence is characteristic of Period 3 and beyond.

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.

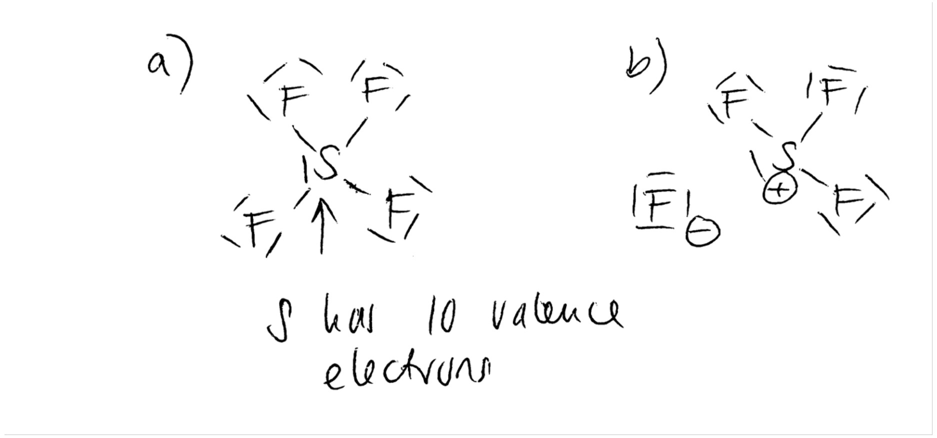
In this topic, the choice of model is **unresolved**, but we can still draw Lewis structures.

2C.2: Expanded valence shells

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

(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.

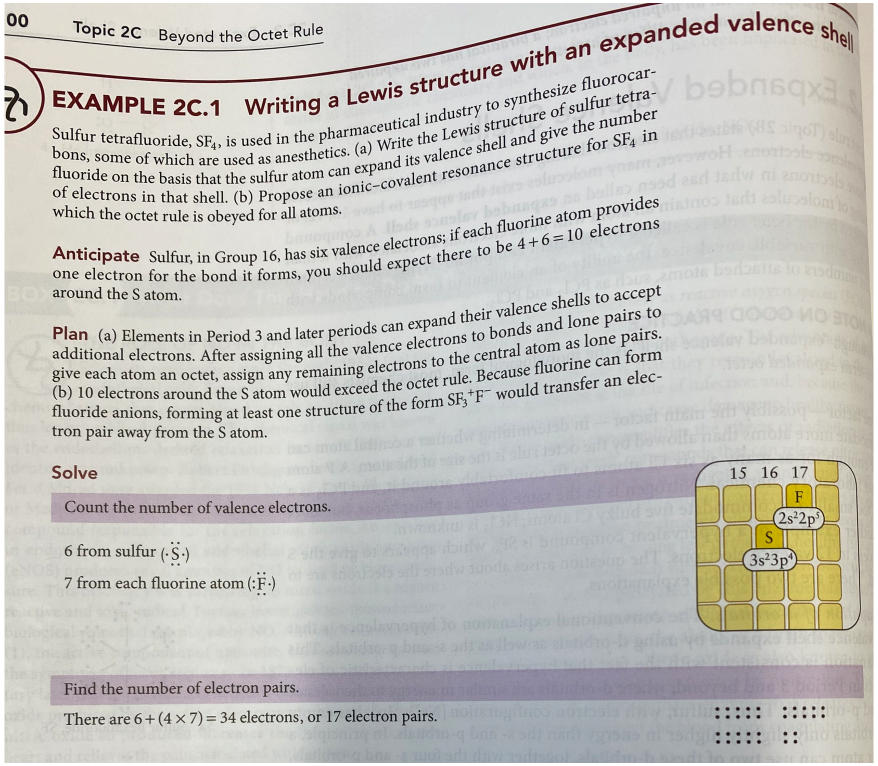
(b) Propose an ionic-covalent resonance structure for SF_4 in which the octet rule is obeyed for all atoms.



2C.2: Expanded valence shells

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

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

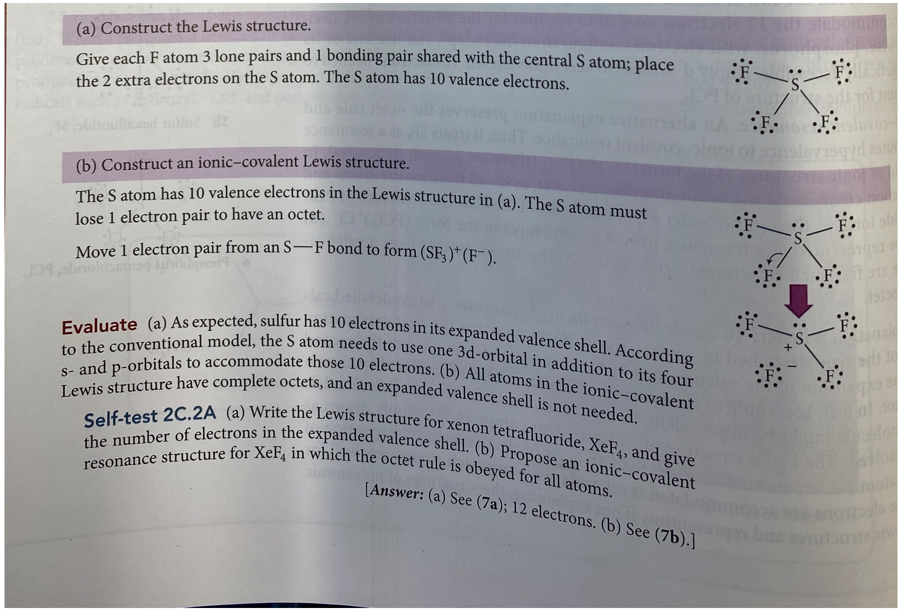
Count the number of valence electrons.

6 from sulfur ($\cdot\ddot{\underset{\cdot\cdot}{S}}\cdot$)

7 from each fluorine atom ($:\ddot{\underset{\cdot\cdot}{F}}\cdot$)

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.

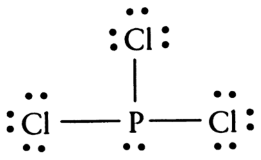
[***Answer:*** (a) See (**7a**); 12 electrons. (b) See (**7b**).]

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:

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

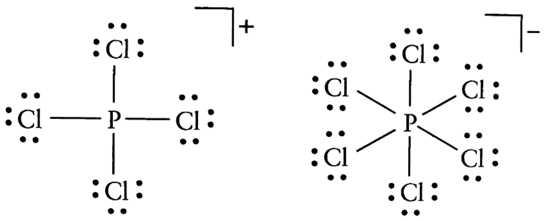


Phosphorus trichloride, PCl_3

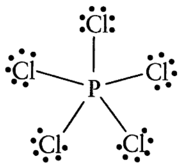
- PCl_3 obeys the octet rule
- When PCl_3 reacts with additional chlorine:

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

- 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, $PCl_5(s)$

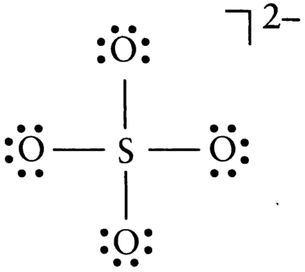


10 Phosphorus pentachloride, PCl_5

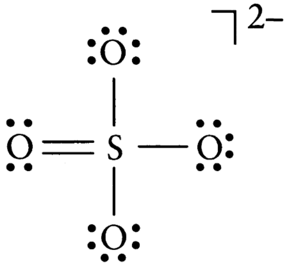
2C.2: Expanded valence shells

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

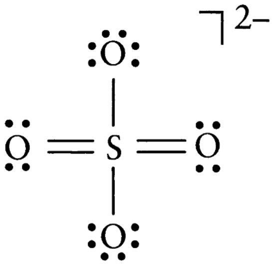
Identify the dominant resonance structure of the sulfate ion (SO_4^{2-}) from the three structures shown (**11a**-**11c**) by calculating the formal charges on the atoms in each structure.



11a



11b

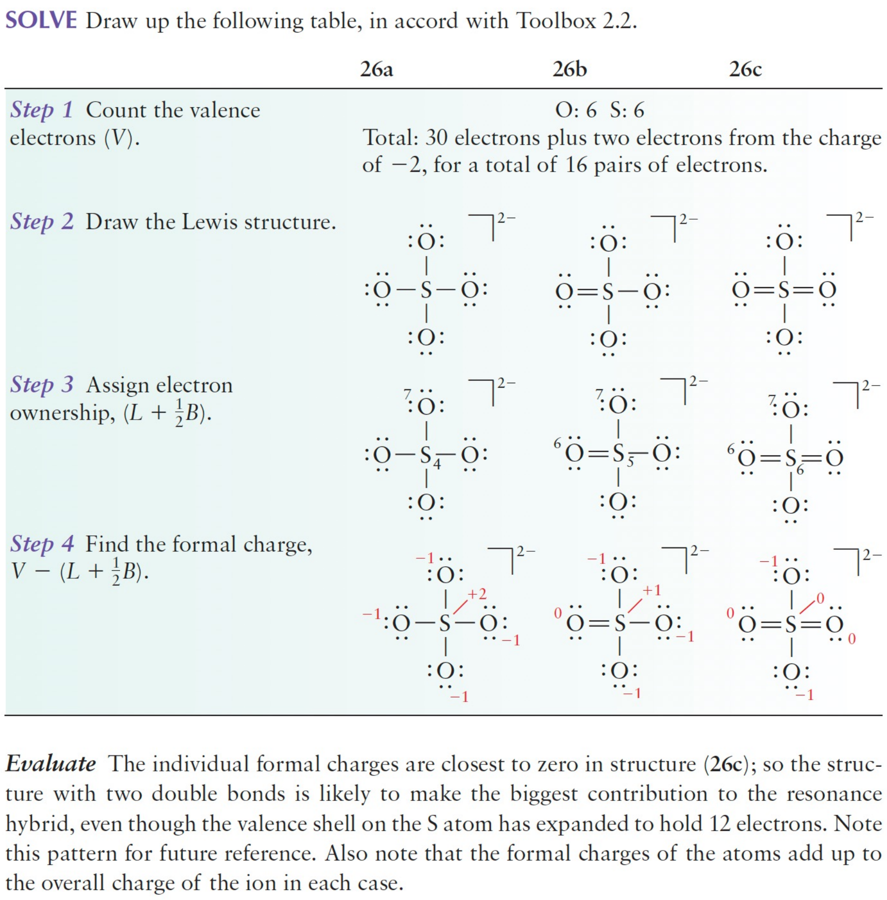


11c

2C.2: Expanded valence shells

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

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

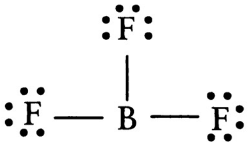
Apparent expansion of the valence shell can take place in elements of Period 3 and later. These elements can exhibit variable covalence and be hypervalent. Formal charge helps to identify the dominant resonance structure.

Incomplete Octets

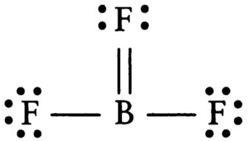
Topic 2C.3

2C.3: Incomplete octets

Boron may have incomplete octets



14 **Boron trifluoride, BF_3**

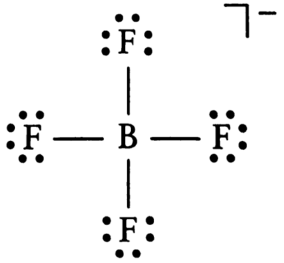


15 **Boron trifluoride, BF_3**

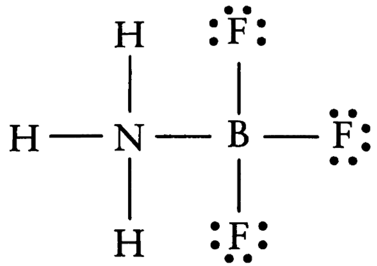
- Boron trifluoride only has six valence electrons at the boron atom (structure **14**)
- Structure **15** does not exist due to F's high ionization energy: It does not like to share its electrons.
- Experimental evidence: B–F bond length is a resonance hybrid between **14** and **15**, with single bonds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

2C.3: Incomplete octets

Coordinate covalent bonds



16 Tetrafluoroborate, BF_4^-



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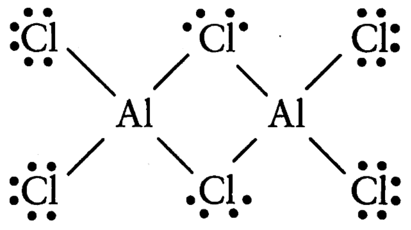
- A special way for boron (and similar atoms) to complete their octets: an additional atom or ion with a lone pair of electrons might form a bond providing *both* electrons.
- A bond in which both electrons come from one of the atoms is called a **coordinate covalent bond**.

Examples:

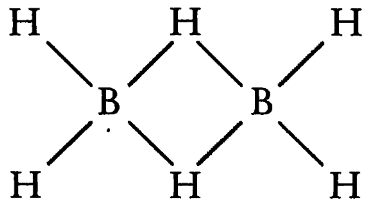
BF_4^- forms when BF_3 is passed over metal fluoride (**16**)

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)
- Also exists for 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.