CH-110 Advanced General Chemistry I

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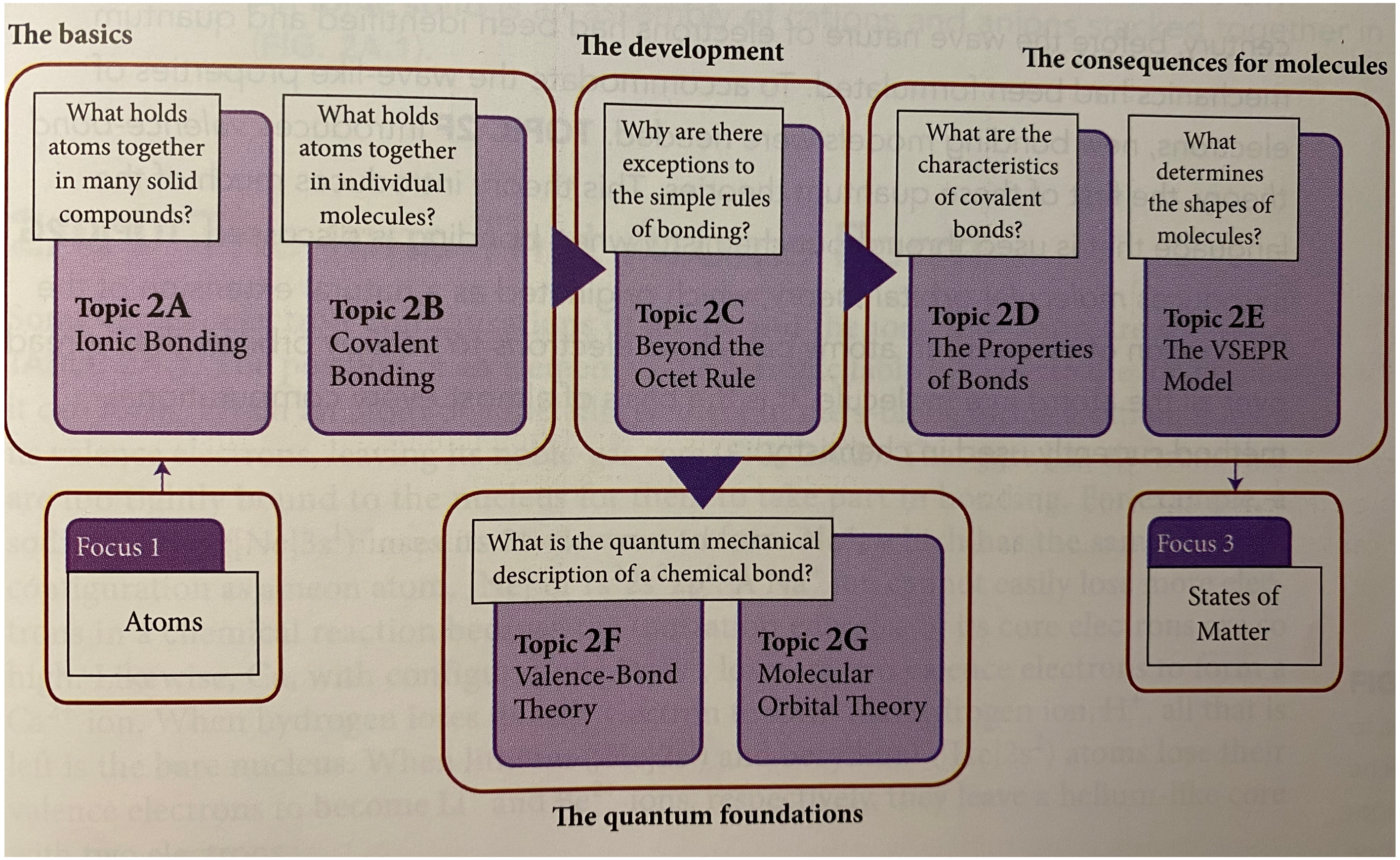
Bonds Between Atoms

Focus 2

Overview Chapter 2 (Focus 2: Bonds Between Atoms)



Covalent Bonding

Topic 2B

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)

Lewis Structures

Topic 2B.1

2B.1: Lewis structures

The nature of covalent bonds

- How do nonmetals make bonds? With ionization energies that are too high to form ions?
- Why is there a particular **valence of an element** (a preferred number of bonds it wants to form)?
- In 1916, G. N. Lewis published an explanation:

He proposed that a covalent bond is a pair of electrons shared between two atoms.

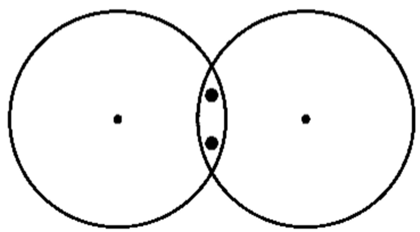


Figure 2B.1

2B.1: Lewis structures

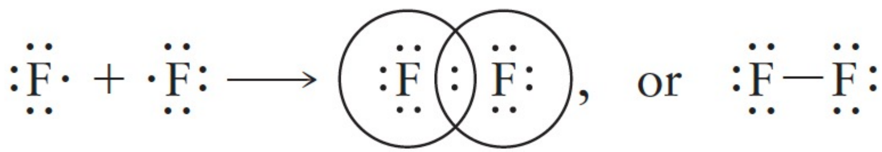
Octet rule

- When atoms form **ions**: they **gain or lose** electrons to reach the same number of electrons as the nearest noble gas.
- When atoms form **covalent** bonds: they **share** electrons to reach the same number of electrons as the nearest noble gas.

2B.1: Lewis structures

The Lewis structure of hydrogen and fluorine

- Lewis symbol for hydrogen: H·
- Two hydrogen atoms share two electrons between two nuclei
- Lewis structure: a shared pair of electrons is represented by a line (–)
- Lewis structure of hydrogen gas, H_2 is H–H
- The two electrons interact with both nuclei, each atom achieves a full duplet
- Fluorine atom has seven valence electrons:



- The circles drawn around each F atom show how each F atom gets an octet by sharing one electron.

Multiple bonds and bond order

- A single shared pair of electrons between two atoms → **single bond**
- Two electron pairs shared between two atoms → **double bond**
- Three electron pairs shared between two atoms → **triple bond**
- **Bond order**: describes the number of shared electron pairs (or bonds) between atoms.

Molecule	Bond order
H_2	1
F_2	1
O_2	2
N_2	3

2B.1: Lewis structures

Valence electrons

Definition: Electrons in the outermost shell (highest principal quantum number n).

- **For main-group elements**: only the outer s and p electrons count.

  E.g. iodide, I^-, with electronic configuration $[Kr]4d^{10}5s^{2}5p^{6}$ has eight valence electrons, the 4d-electrons don't count.

- **For transition metals**: both s and d electrons beyond the noble-gas core are valence electrons.

  E.g. manganese, Mn, with electronic configuration $[Ar]3d^{5}4s^{2}$ has seven valence electrons.

2B.1: Lewis structures

Lone pairs

- A lone pair is a pair of valence electrons **not involved in bonding.**

- In F_2, each atom has three lone pairs that strongly repel each other, making F_2 highly reactive.
- In contrast, N_2 has a strong triple bond and is very unreactive (often used as inert gas in chemical synthesis).

2B.1: Lewis structures

Self-test

Write the Lewis structures for HBr, O_2, and N_2 and state how many lone pairs each atom possesses.

2B.1: Lewis structures

Lewis structures for polyatomic molecules: methane CH_4

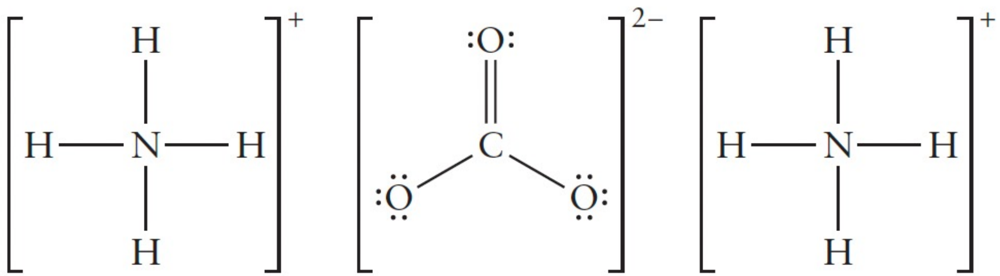
2B.1: Lewis structures

Some patterns to remember

2B.1: Lewis structures

Polyatomic ions

- Same procedure for polyatomic ions, e.g. NH_4^+ or CO_3^{2-}.
- Only difference: electrons are added or subtracted to account for charge.
- Oxoanions, e.g. CO_3^{2-}: first atom is central atom
- For cation and anion pairs: treat charges separately, they don't share electrons.
- Ammonium carbonate $(NH_4)_2CO_3$:



2B.1: Lewis structures

TOOLBOX 2.1 **HOW TO WRITE THE LEWIS STRUCTURE OF A POLYATOMIC SPECIES**

CONCEPTUAL BASIS

We look for ways of using all the valence electrons to complete the octets (or duplets).

PROCEDURE

Step 1 Count the number of valence electrons on each atom; for ions adjust the number of electrons to account for the charge. Divide the total number of valence electrons in the molecule by 2 to obtain the number of electron pairs.

Step 2 Write down the most likely arrangements of atoms by using common patterns and the clues indicated in the text.

Step 3 Place one electron pair between each pair of bonded atoms.

Step 4 Complete the octet (or duplet, in the case of H) of each atom by placing any remaining electron pairs around the atoms. If there are not enough electron pairs, form multiple bonds.

Step 5 Represent each bonded electron pair by a line.

To check on the validity of a Lewis structure, verify that each atom has an octet or a duplet. As we shall see in Section 2.10, a common exception to this rule arises when the central atom is an atom of an element in Period 3 or higher. Such an atom can accommodate more than eight electrons in its valence shell. Consequently, the most stable Lewis structure may be one in which the central atom has more than eight electrons.

This procedure is illustrated in Examples 2.3 and 2.4.

2B.1: Lewis structures

Example 2B.1: Writing the Lewis structure of a molecule or an ion

Write the Lewis structures of (a) water, H_2O; (b) methanal, H_2CO; and (c) the chlorite ion, ClO_2^-.

2B.1: Lewis structures

Example 2B.2: Writing Lewis structures for molecules with more than one central atom

Write the Lewis structures for acetic acid, CH_3COOH, the carboxylic acid in vinegar that forms when the ethanol in wine is oxidized. In the –COOH group, both O atoms are attached to the same C atom, and one of them is bonded to the final H atom. The two C atoms are bonded to each other

2B.1: Lewis structures

Summary

In the Lewis structure of a polyatomic species, all the valence electrons are used to complete the octets (or duplets) of the atoms present by forming single or multiple bonds; some electrons may be left as lone pairs.

Resonance

Topic 2B.2

2B.2: Resonance

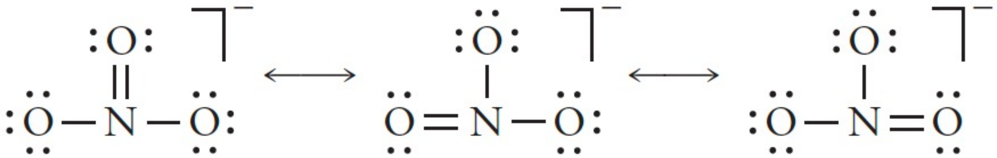
Resonance and bond order

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

2B.2: Resonance

Resonance structures

- 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 <u>resonance</u> depicted by double-headed arrows**

2B.2: Resonance

Delocalization

- Delocalized electrons are **shared over several atoms** rather than between just two.
- The resonance structures of nitrate do not represent real, separate molecules but show that the **electrons are spread across the molecule**.
- Delocalization **stabilizes** the molecule and lowers its energy.

2B.2: Resonance

Rules for resonance structures

- Atoms stay in the same positions; only electrons move.
- Equivalent structures contribute equally.
- Lower-energy structures contribute more. (You will see how to judge relative energies in the next section.)
- Resonance does **not** occur if atom positions differ.

2B.2: Resonance

Example 2B.3: Writing a resonance structure

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.

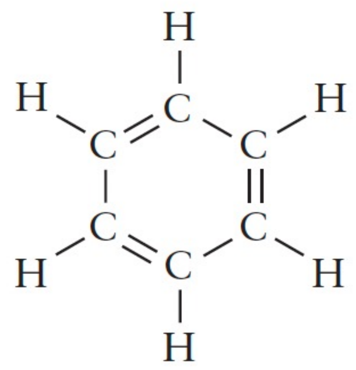
Example 2B.3: Writing a resonance structure

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

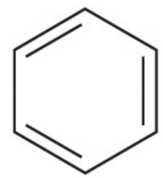
2B.2: Resonance

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



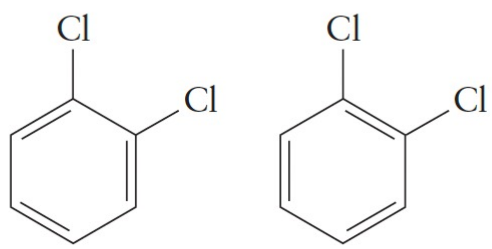
12 Kekulé structure, stick form

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) can be characterized.

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

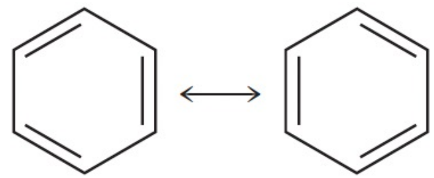


However, only one known to exist!

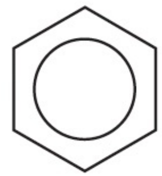
2B.2: Resonance

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

- Have different energies and contribute unequally.
- The most stable (lowest-energy) form has formal charges closest to zero

2B.3: Formal charge

Formal charge

Formal charge: The charge an atom would have if bonds were purely covalent.

Each atom “owns” all its lone-pair electrons and half of its bonding electrons.

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

V is the number of valence electrons

L is the number of electrons present on the bonded atom as lone pairs

B is the number of bonding electrons on the atom.

Lower formal charges → more stable structure.

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

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.3: Formal charge

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

2B.1: Lewis structures

Follow-up chlorite ion

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

2B.3: Formal charge

Formal charge and electronegativity

- More electrons than neutral → negative charge
- Fewer electrons than neutral → positive charge.
- The most stable Lewis structure has **formal charges closest to zero**, with any positive charge on the least electronegative atom.
- If charges are unavoidable, **positive charges** belong 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:

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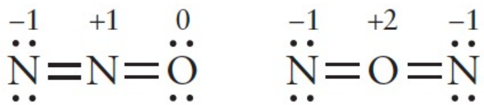

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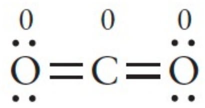
2B.3: Formal charge

Formal charge vs. oxidation number

- **Formal charge** assumes **equal sharing** → emphasizes **covalency**.
- Oxidation number assigns electrons to the more electronegative atom → emphasizes ionicity.
- Example: CO_2 → formal charge = 0, oxidation number of C = +4. 

- Formal charge depends on the **Lewis structure**; oxidation number does not.
- Formal charge helps compare structures; oxidation number tracks redox behavior.

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.