CH-110 Advanced General Chemistry I

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Ionic Bonding

Topic 2A

Last Tuesday: Topic 2A.1 The ions that atoms form
Last Tuesday: Topic 2A.2 Lewis symbols
Last Tuesday: Topic 2A.3 The energetics of ionic bond formation
Last Tuesday (to be continued): Topic 2A.4 Interactions between ions

WHY DO YOU NEED TO KNOW THIS MATERIAL?

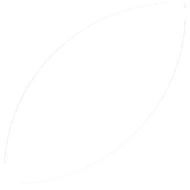
- One of the principal kinds of bonding in compounds.

WHAT DO YOU NEED TO KNOW ALREADY?

- Electron configurations of many-electron atoms (Topic 1E)
- Potential energy, nature of Coulomb interaction between charges (Fundamentals A)
- Ionic radius, ionization energy, and electron affinity (Topic 1F)

Interactions Between Ions

Topic 2A.4



2A.4 Interactions between ions

Last Tuesday: Coulomb potential energy of two individual ions

$$E_{p,12} = \frac{(z_1 e)\times(z_2 e)}{4\pi\varepsilon_0 r_{12}} = \frac{\mathrm{z_1 z_2 e^2}}{4\pi\varepsilon_0 r_{12}}$$

- $z_1 e$: charge of ion 1 with e, the fundamental charge
- $z_2 e$: charge of ion 2
- r_{12}: distance between the centers of the two ions
- ε_0: the electric constant
- **Note**: The charge number, z, is positive for cations and negative for anions, and the charge of an ion is ze, where e is the fundamental charge. Chemists, however, almost always refer to z itself as the charge and speak of a cahrge of +1, –1, and so on. In other words, chemists typically refer to charge as **multiples of the fundamental charge**.

2A.4 Interactions between ions

Last Tuesday: Potential energy in a 3D array of ions with different charges

- Every ion in an ionic solid is attracted to all the oppositely charged ions and repelled from all the other ions with like charges.

$$E_p = A \times \frac{N_A z_1 z_2 e^2}{4\pi\varepsilon_0 d}$$

- Note that $z_1 z_2$ is **negative**, as the ions have opposite charges.
- The factor A is a numerical coefficient called the **Madelung constant**, its value depends on how the ions are arranged about one another (see **Topic 3G**)
- The potential energy **is strongly negative** when the ions are highly charged (large values of z) and when the separation between them is small (small values of d)

2A.4 Interactions between ions

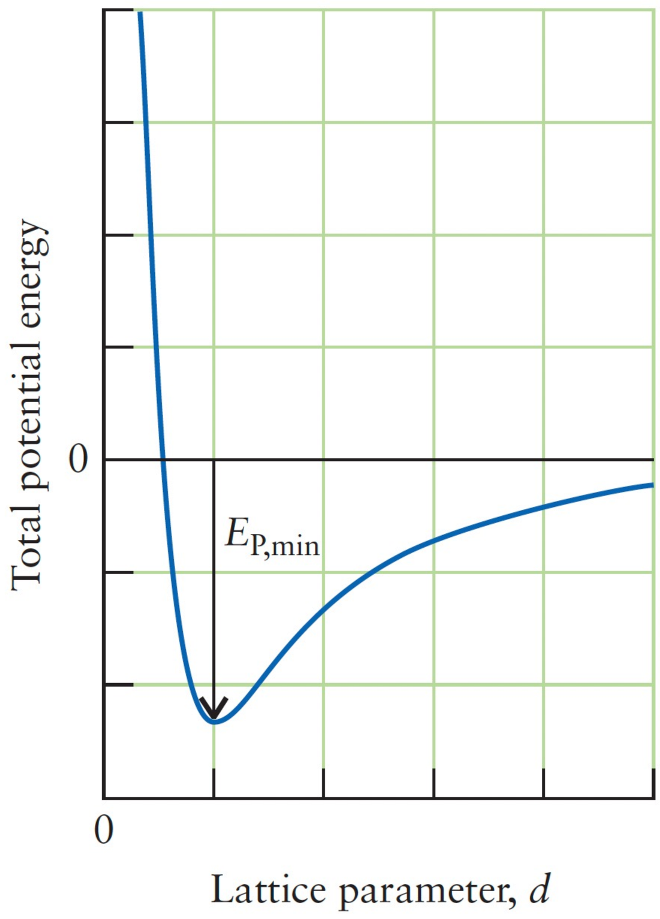
Potential energy of interaction

- Potential energy becomes **more negative** as separation (d) **decreases**
- As soon as the ions come into contact: **repulsive effects** between neighbors become important: energy quickly rises again.
- Repulsive contribution to the potential energy rises rapidly with decreasing separation:

$$E_p^* \propto e^{-\frac{d}{d^*}} \text{ with } d^* \text{ a constant (usually 34.5 pm)}$$

- The total energy is the sum of E_p and E_p^* and passes through a minimum as the ions approach each other, then rises sharply again when they are very lcose (**Fig. 2A.10**).

Figure 2A.10



2A.3: The energetics of ionic bond formation

Summary

Ionic solids typically have high melting points and are brittle. The lattice energy of an ionic solid is large when the ions are small and highly charged.

The skills you have mastered are the ability to

- ☐ Write the electron configuration for an ion.
- ☐ Account for the formation of ions in terms of ionization energy, electron affinity, and the electrostatic interactions between them.
- ☐ Predict the chemical formula of an ionic compound and draw its formula unit by using Lews symbols
- ☐ Account for the origin and magnitude of the lattice energy.

Summary: You have learned that in ionic bonding, electrons are transferred from one atom to another and that the patterns of ionic bond formation can be represented by formula units based on Lewis symbols. You have seen that the greater the charge and the smaller the ion, the greater the energy lowering when an ionic solid forms from widely separated atoms.

Student questions

Is there any easy way to remember the order of orbitals in the building-up principle?

1. Look at the periodic table
2. Follow this trick:

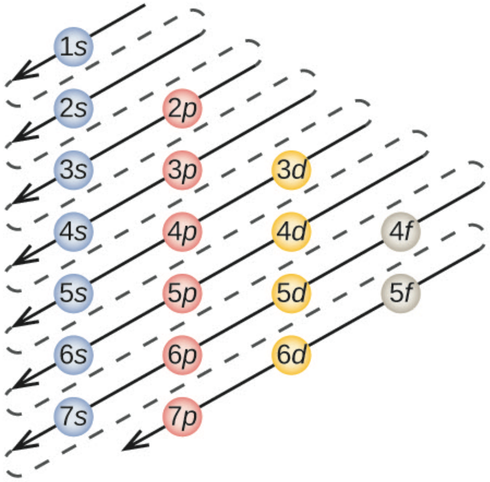


Figure source: https://wisc.pb.unizin.org/minimisgenchem/chapter/electron-configurations-orbital-box-notation-m7q7/

Student questions

Here's another image to show you the relative energies of **empty** orbitals.

Be aware that energies change after orbitals are filled. E.g. the *n*d-orbitals will be lower compared to their (*n*+1)s-orbitals after filling.

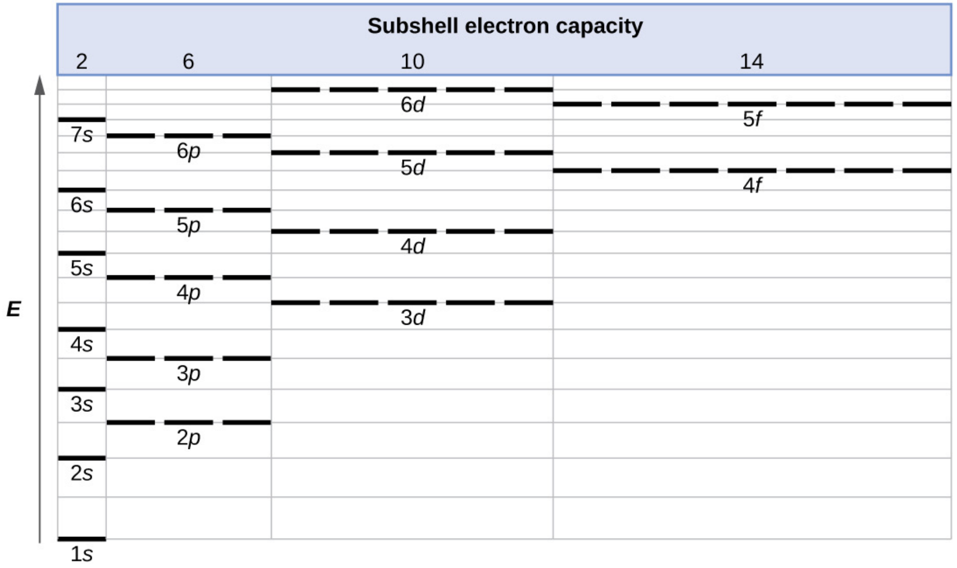


Figure source: https://wisc.pb.unizin.org/minimisgenchem/chapter/electron-configurations-orbital-box-notation-m7q7/

Student questions

What is the definition of “valence electrons”? For example, what are the valence electrons for iodide? Do we include the filled 4d-orbitals in the valence shell?

Definition in our textbook “the electrons in the outermost shell”.

A more refined definition:

For the **main group elements**, the valence electrons are defined as those electrons residing in the electronic shell of **highest principal quantum number *n***.

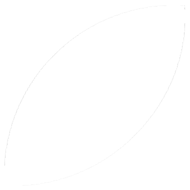
- Iodide, I^-, with electronic configuration $[Kr]4d^{10}5s^25p^6$ has eight valence electrons, the 4d-electrons don’t count.

For the **transition metals**, a valence electron is defined as an electron that resides **outside a noble-gas core**. In the transition metal block, the d-orbitals are very close in energy to the s-orbitals and thus, both are important for the reactivity of these metals and are both considered valence electrons.

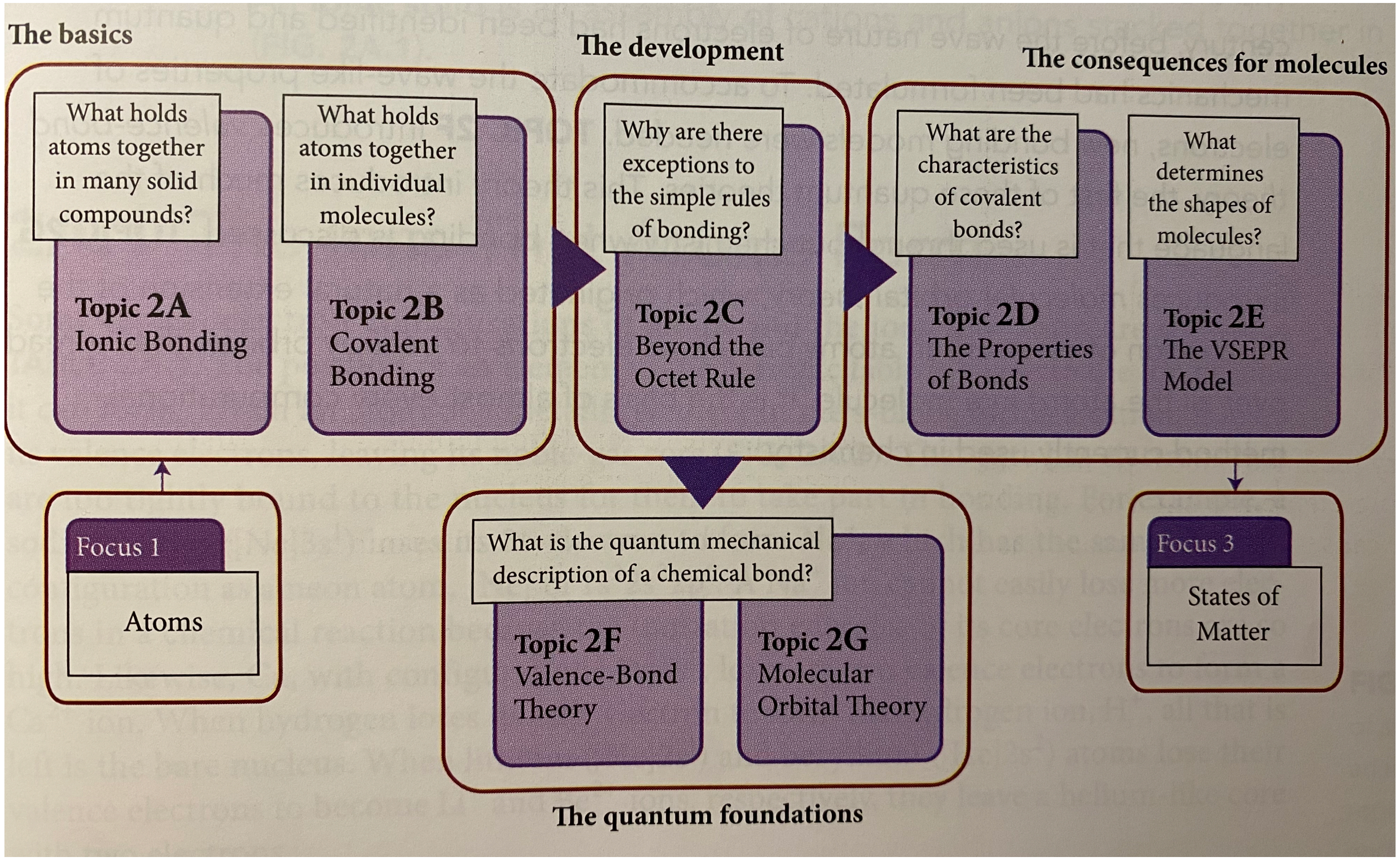
- For example, manganese, Mn, with electronic configuration $[Ar]4s^23d^5$ has seven valence electrons.

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

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.

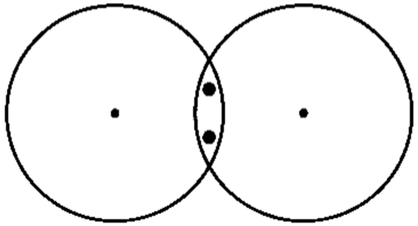


Figure 2B.1

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.

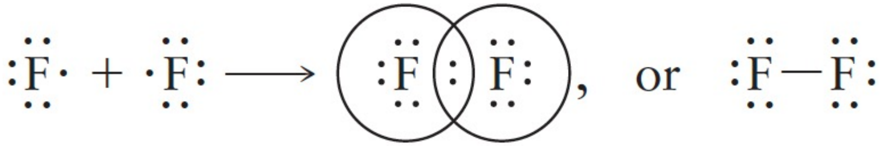
Octet rule:

In covalent bond formation, atoms go as far as possible toward completing their octets (or duplet in the case of hydrogen) by sharing electron pairs.

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.

2B.1: Lewis structures

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**: the number of bonds that link a specific pair of atoms

Molecule	Bond order
H_2	1
F_2	1
O_2	2
N_2	3

2B.1: Lewis structures

Lone pairs

- A fluorine has six lone pairs of electrons, three on each atom
- A lone pair is a pair of **valence electrons that is not involved in bonding**.
- The three lone pairs on one F atom repel the other three lone pairs on the second F atom. This repulsion is so strong that it almost overcomes the bonding effect of the shared electron pair → F_2 gas is highly reactive!
- Multiple bonds stronger than one single bond: N_2 gas is unreactive

2B.1: Lewis structures

Self-test

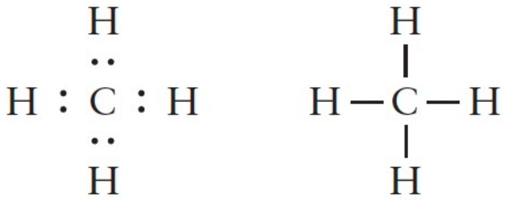
Write the Lewis structures for HBr, O_2, and N_2 and state how many lone pairs each atom possesses.

2B.1: Lewis structures

Lewis structures for polyatomic molecules: methane CH_4

1. Count the valence electrons available from all the atoms in the molecule. For methane, the Lewis symbols of the atoms are:

2. Arrange the dots representing the electrons so that the C atom has an octet, each H atom has a duplet, and the C and H atoms share electron pairs.
3. Draw the arrangement shown below; the Lewis structure of methane is then drawn as shown, where the four shared electron pairs are indicated by lines.



Carbon is **tetravalent**

Note: the Lewis structure does not show the geometrical shape of a molecule.

2B.1: Lewis structures

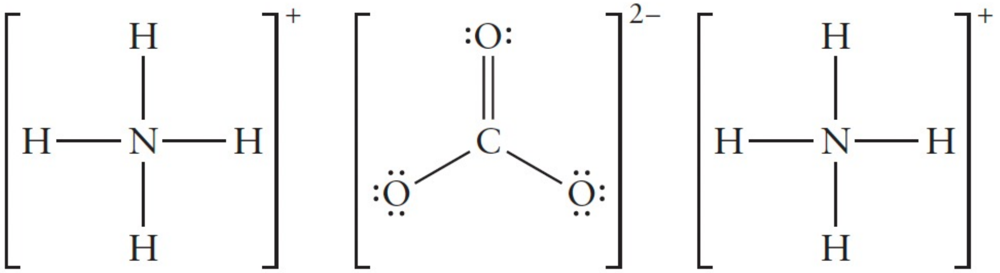
Some patterns to remember

- An H atom is always terminal (bonded to only one other atom)
- A central atom is bonded to at least two other atoms
- **To start:** choose as the central atom the element with the lowest ionization energy/the lowest electronegativity. Atoms with high ionization energies/high electronegativities are more reluctant to share electrons and more likely keep their electrons in lone pairs.
- **Rule of thumb:** arrange atoms symmetrically around the central atom, e.g. SO_2 is arranged as OSO not SOO. Or OF_2 is arranged as FOF and not OFF.
- Common exception is dinitrogen monoxide (N_2O) is arranged asymmetrically as NNO.
- Acids are also exceptions to this rule because the H atoms are written first and not the central atom.

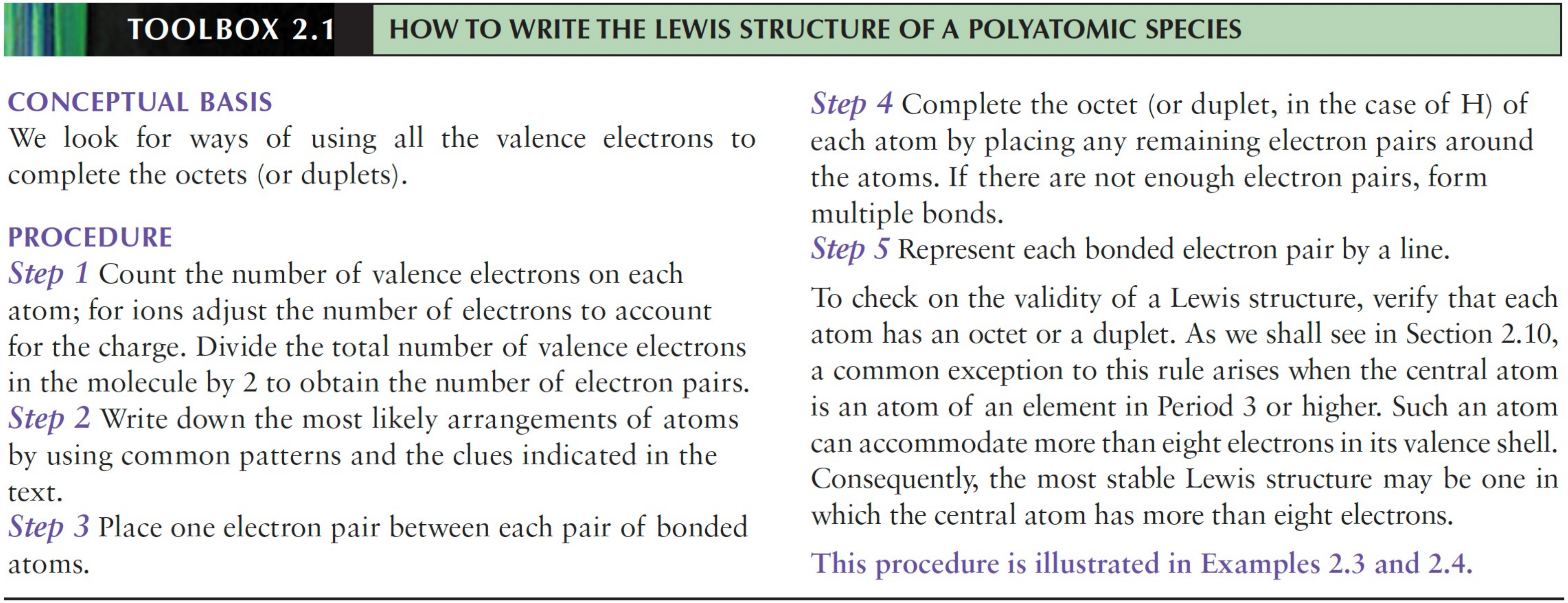
2B.1: Lewis structures

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 (blackboard)

2B.1: Lewis structures

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

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.

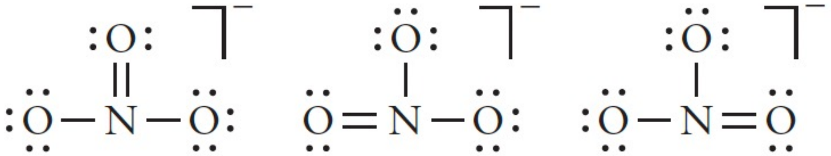
Resonance

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:

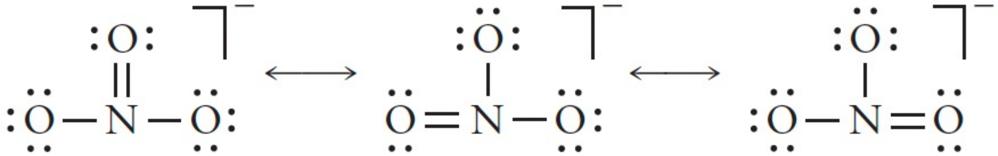


- Double bonds are shorter than single bonds, they hold atoms together more tightly.
- Observed bond length is the same for all three bonds: 124 pm
- Typical N–O single bond: 140 pm, typical N=O double bond: 120 pm
- **Bond order** is between 1 and 2 for nitrate NO bond

2B.2: Resonance

Resonance structures

- All three bonds are identical
- 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 (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.
- Blending of several structures enables the electrons to be distributed in a way that optimizes their contributions to the total energy.

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.

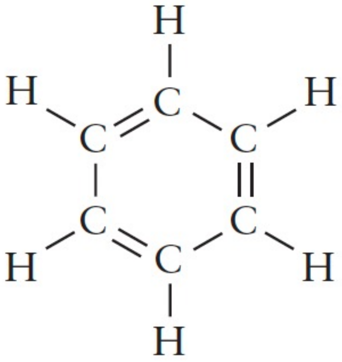
2B.2: Resonance

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

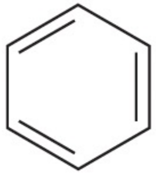
2B.2: Resonance

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

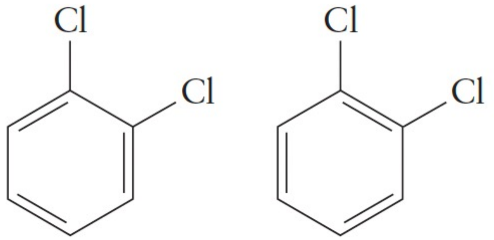
2B.2: Resonance

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:

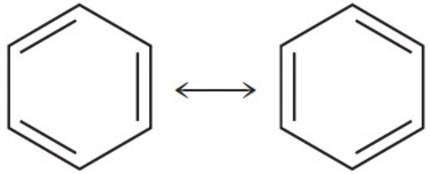


However, only one known to exist!

2B.2: Resonance

Concept of resonance resolves contradictions

- **Two Kekulé structures with exactly the same energy**: they only differ in 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

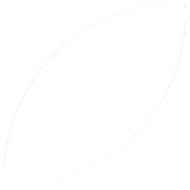
2B.2: Resonance

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 had 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

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.

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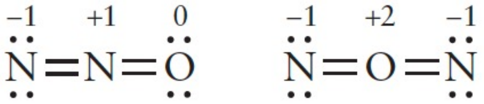

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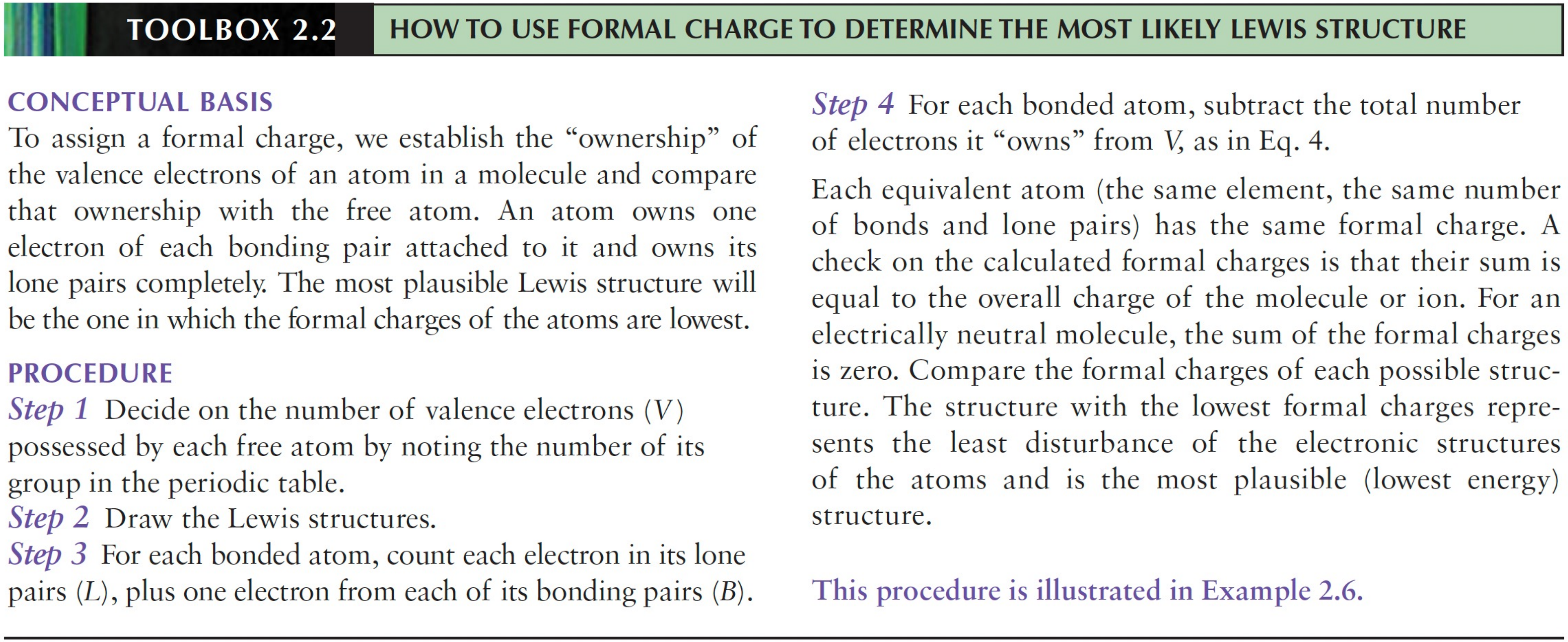
2B.3: Formal charge



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

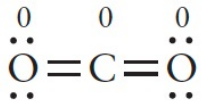
Example 2B.4: Selecting the most likely arrangement of atoms (blackboard)

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

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.