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

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

- $z_1 e$: 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

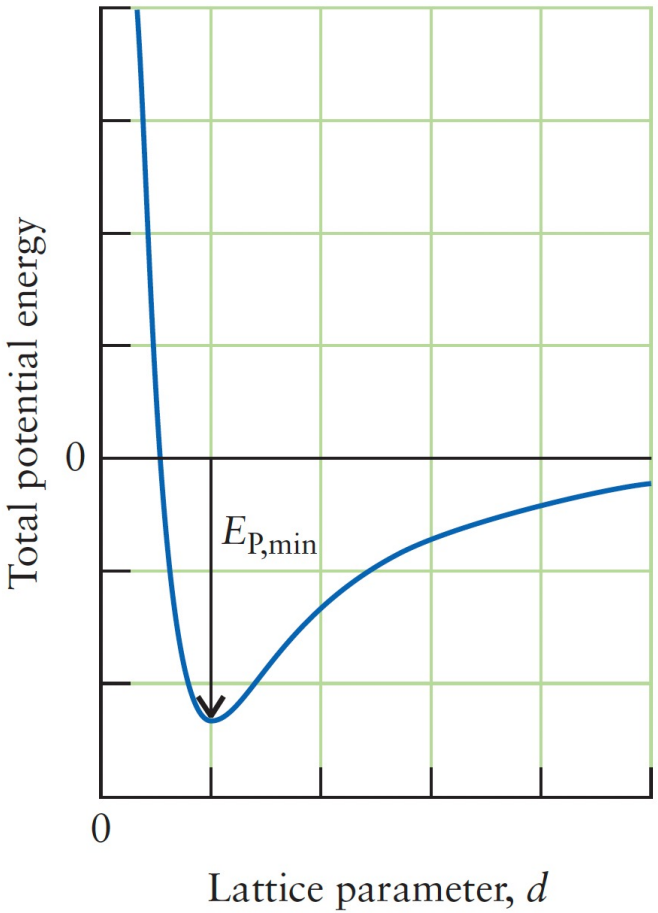
Potential energy of interaction

- 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:

$$E_p^* \propto e^{-\frac{d}{d^*}}$$ with d^* 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:

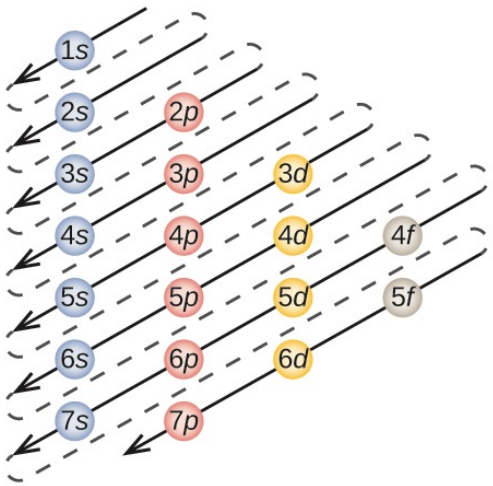


Figure source: https://wisc.pb.unizin.org/minimisgenchem/chapter/electron-configurations-orbital-box-notation-m7q7/

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.

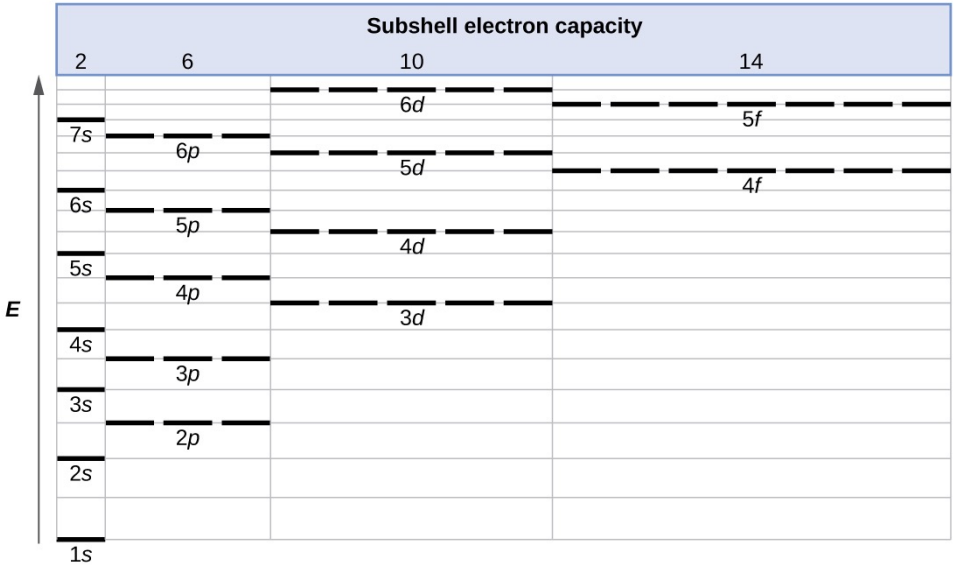


Figure source:
https://wisc.pb.unizin.org/minimisgenchem/chapter/electron-configurations-orbital-box-notation-m7q7/

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.

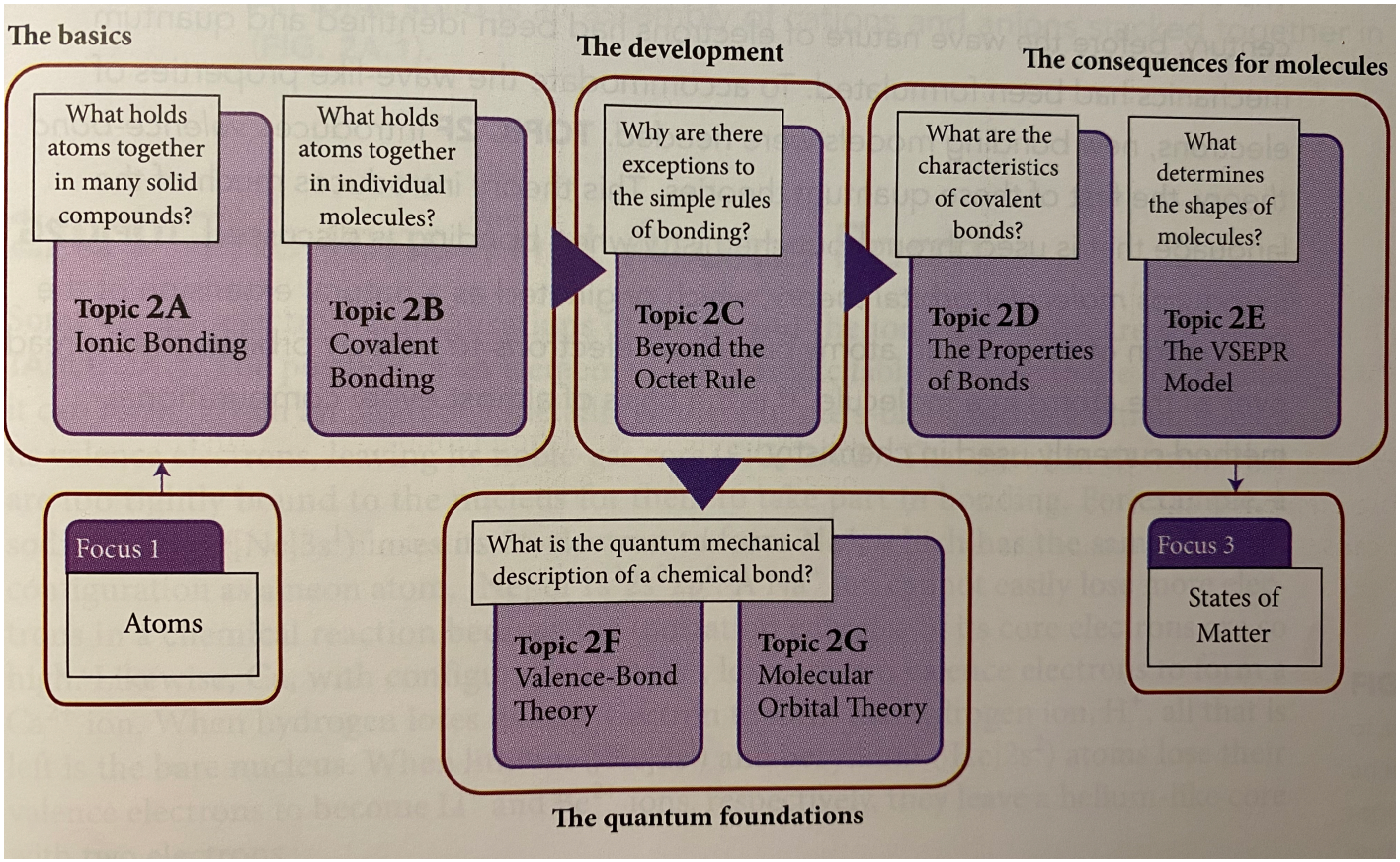
For the **transition metals**, a valence electron is defined as an electron that resides **outside a noble-gas core**. In the transition metal block, the d-orbitals are very close in energy to the s-orbitals and thus, both are important for the reactivity of these metals and are both considered valence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

- For example, manganese, Mn, with electronic configuration $[Ar]3d^54s^2$ has seven valence electrons.

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.

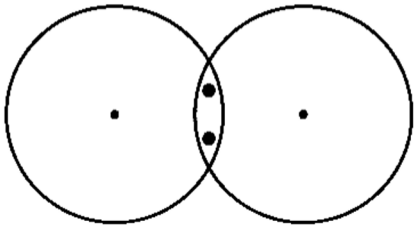


Figure 2B.1

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.

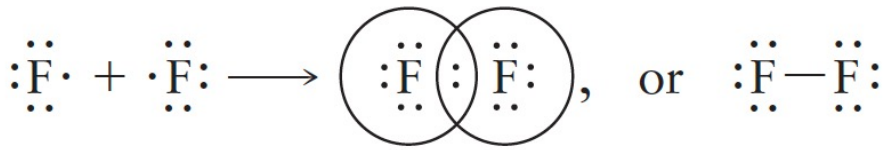
Octet rule:

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.

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

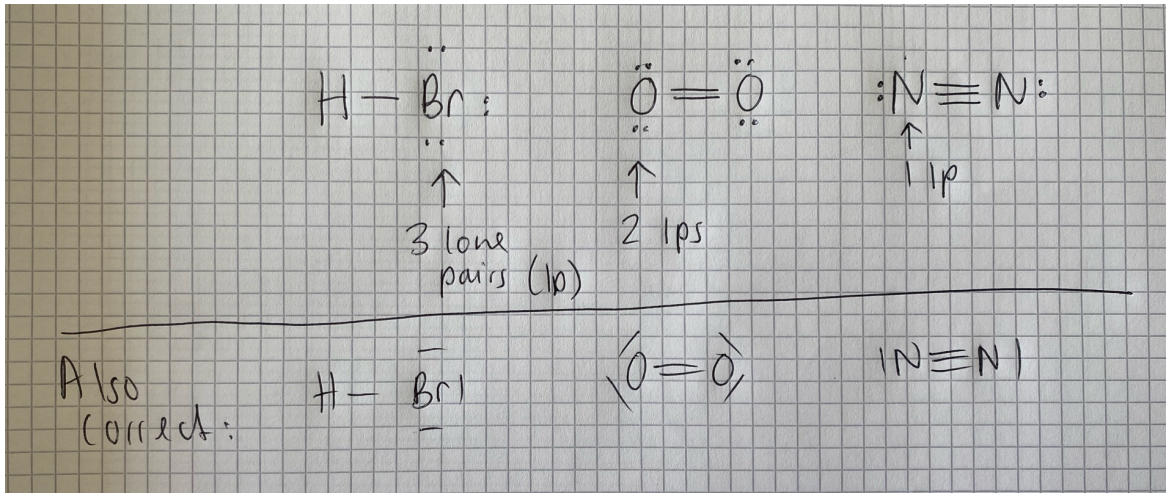
Lone pairs

- 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.

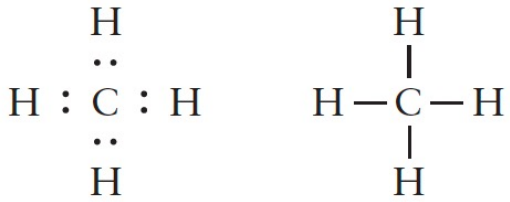


Lewis structures for polyatomic molecules: methane CH_4

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

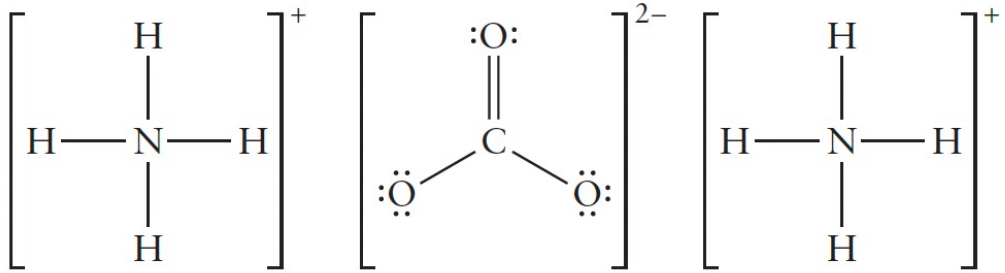
Some patterns to remember

- 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)

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

SOLVE

	(a) H_2O	(b) H_2CO	(c) ClO_2^-
Step 1 Count the valence electrons and adjust the number for charges on ions.	1 + 1 + 6 = 8	1 + 1 + 4 + 6 = 12	7 + 6 + 6 + 1 = 20
Count the electron pairs.	4	6	10
Step 2 Arrange the atoms.	H O H	H C O H	O Cl O
Step 3 Connect the atoms with bonding electron pairs.	H : O : H	H C : O H	O:Cl:O
Count electron pairs not yet located.	: :(2)	: : :(3)	: : : : : : : :(8)
Step 4 Complete the octets.	H : Ö : H	H C::Ö H	:Ö:Cl:Ö:$^-$
Step 5 Represent the bonds.	H−Ö−H	H | C=Ö | H	:Ö−Cl−Ö:$^-$

2B.1: Lewis structures

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

Write the Lewis structure 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.

Anticipate The formula of acetic acid suggests that the molecule consists of a CH_3— group and a —COOH group. We can anticipate that the CH_3— group, by analogy with methane, will consist of a C atom joined to three H atoms by single bonds.

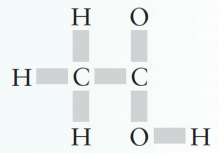
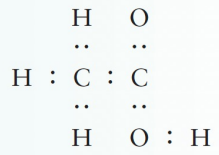
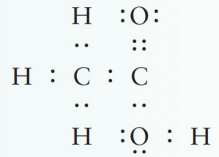
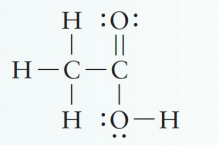
PLAN Apply the procedure in Toolbox 2.1.

SOLVE

	CH_3COOH
Step 1 Count the valence electrons to determine the number of electron pairs:	: : : : : : : : : : : :

$4 + (3 \times 1) + 4 + 6 + 6 + 1 = 24$, 12 pairs

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

Step 2 Arrange atoms (linked atoms are indicated by the rectangles).	
Step 3 Connect the atoms with bonding electron pairs.	
Count electron pairs not yet located.	: : : : : (5 pairs)
Step 4 Complete the octets.	
Step 5 Represent the bonds.	

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.

2B.1: Lewis structures

Student question

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

Answer: I will start the class with this example on Tuesday and explain!