

Chem 115 POGIL Worksheet - Week 10

More on Configurations and Periodic Trends

Why?

In addition to the valence configuration, the size of an atom or ion and the attraction between the nucleus and the outermost electrons play important roles in determining the chemistry of an element. Knowing the trends in atomic and ionic sizes, ionization energies, and electron affinities aids in understanding chemical behavior and prepares us to understand the nature of chemical bonds.

A chemical bond exists between any two atoms that are strongly attracted to one another in a compound or element. Ionic compounds are held together mainly by electrostatic forces of attraction between the oppositely charged ions, creating *ionic bonding*. Atoms in nonmetallic elements and molecular compounds are held together by sharing of electrons, creating *covalent bonding*. These two types of bonding represent extreme models, with most real bonds lying somewhere in between. One way of assessing the ionic or covalent character of a bond is the difference in *electronegativity* between the two bonded atoms. When a compound consists of molecules with covalent bonds, a Lewis model is often a simple way of describing its bonding.

Learning Objective

- Know periodic trends of atomic size, ionic size, ionization energy, and electron affinity
- Understand the reasons for metallic, nonmetallic, and metalloid character
- Understand why some acids dissolve in water to make acidic solution, while others dissolve in water to make basic solutions
- Understand the distinction between ionic and covalent bonding
- Understand the electronegativity scale and its use for assessing bond type
- Understand the concept of lattice energy as a measure of bonding strength in ionic compounds
- Understand the concept of covalent bonding in terms of the Lewis model

Success Criteria

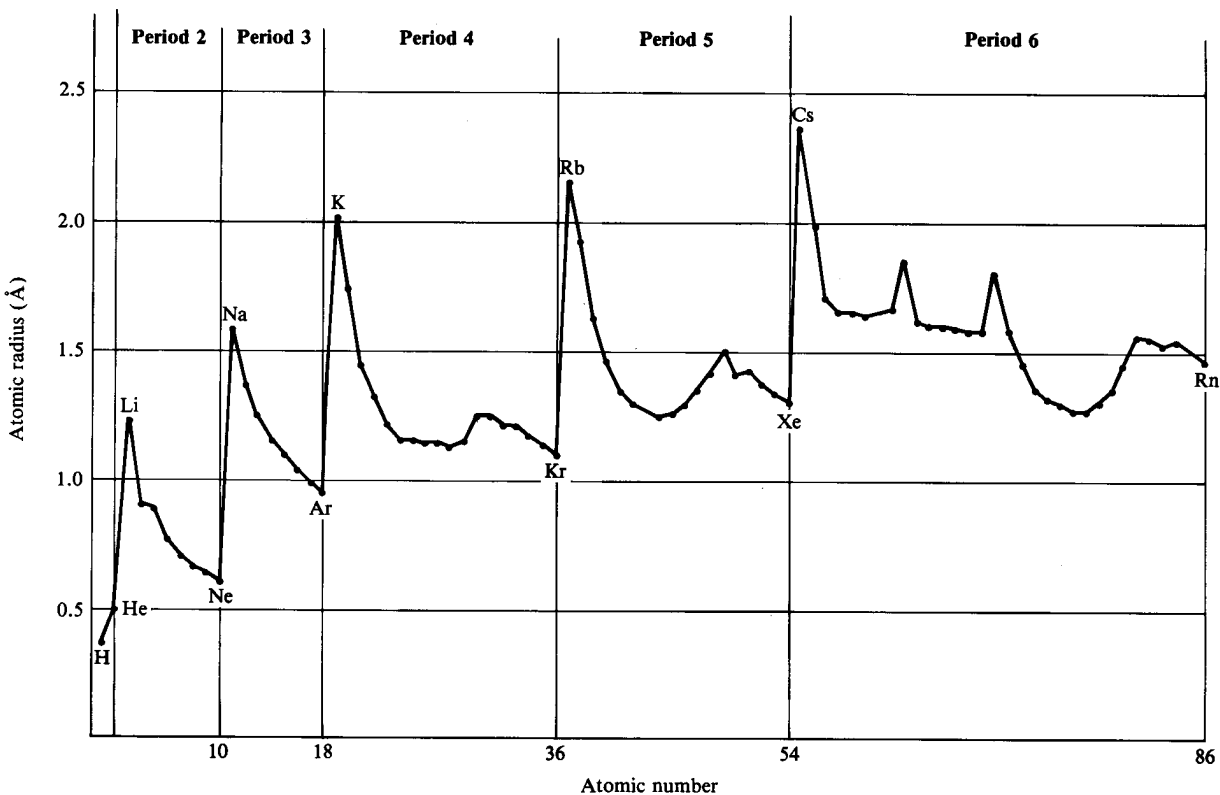
- Be able to predict size differences among atoms and ions
- Be able to predict differences in ionization energy and electron affinity among elements.
- Be able to predict relative reactivity of related elements
- Be able to predict the acid-base character of oxides
- Be able to describe the character of a bond on the basis of electronegativity differences
- Be able to predict relative lattice strengths among ionic compounds
- Be able to draw Lewis dot structures of simple molecular compounds
- Be able to assign formal charges in a Lewis structure and use these to assess relative reasonableness of the model
- Be able to write resonance forms where appropriate and be able to assess relative bond strength in molecules represented by resonance forms.

Prerequisite

- Have read Chapter 7 and sections 8.1-8.7.

Information (Trends in Sizes of Atoms)

Trends in sizes of atoms are the most important to understand, because other trends can often be rationalized on that basis. The following plot shows how atomic size varies through the periodic table.



Across the periodic table, sizes of atoms show the following trends, with many irregularities:

Size increases down a group. The outermost electrons are in successively more extensive orbitals as n increases.

Size decreases across a period. Electrons are added to the same shell and do not shield one another very effectively from the increasing nuclear charge. This causes all orbitals (including the outermost size-determining orbitals) to contract as Z increases.

Transition elements contract up to the middle of the series and then expand toward the end. Shielding becomes more effective after the d subshell is half filled. This makes the size-determining ns electrons move out further towards the end of each transition series.

Lanthanides contract slowly across the series. This results from inefficient shielding by $4f$ electrons below the size-determining $6s$ electrons. The result is called the *lanthanide contraction*. Because the lanthanide filling occurs between the second and third transition series, the second and third transition elements in each period have nearly the same size. For example, both Ru and Os have a radius of 130 pm.

Key Questions

1. Using only a periodic table, predict the order of increasing atomic radius for each of the following sets of elements:

Ca, Mg, Be

Al, Tl, Si

Ga, Br, Ge

Zn, Cd, Fe

Information (Sizes of Ions)

Ionic radii for cations and anions are estimates, because it is virtually impossible to determine experimentally where the electron density of a cation begins and an anion ends in any ion pair. Tabulated values of ionic radii represent values that most consistently predict the measured separations between typical cation-anions pairs in many binary ionic compounds. The trends in ion sizes are very regular, with virtually no exceptions.

Ionic radii of ions increase with negative charge and decrease with positive charge.

Compare radii (in picometers, pm) for the following isoelectronic species with the Ne configuration (ten electrons):

O^{2-}	F^{-}	Na^{+}	Mg^{2+}	Al^{3+}
140	133	97	66	51

Notice that for this series size increases with negative charge and decreases with positive charge. The same trends can be seen in differently charged ions of the same element. For example, compare the radii for Cu(I) and Cu(II) ions:

Cu^{+} 96 pm Cu^{2+} 69 pm

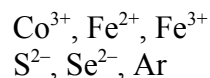
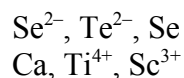
Ionic radii increase down a group for ions of the same charge.

In the chart below, note the trends in the sizes (radii in picometers, pm) of the following ions with the same charge.

Li ⁺ 60	Be ²⁺ 31		O ²⁻ 140	F ⁻ 136
Na ⁺ 95	Mg ²⁺ 65	Al ³⁺ 50	S ²⁻ 184	Cl ⁻ 181
K ⁺ 133	Ca ²⁺ 99	Ga ³⁺ 62	Se ²⁻ 198	Br ⁻ 195
Rb ⁺ 148	Sr ²⁺ 113	In ³⁺ 81	Te ²⁻ 221	I ⁻ 216
Cs ⁺ 169	Ba ²⁺ 135	Tl ³⁺ 95		

Key Questions

2. For each of the following sets of atoms and ions, arrange the members in order of increasing size.

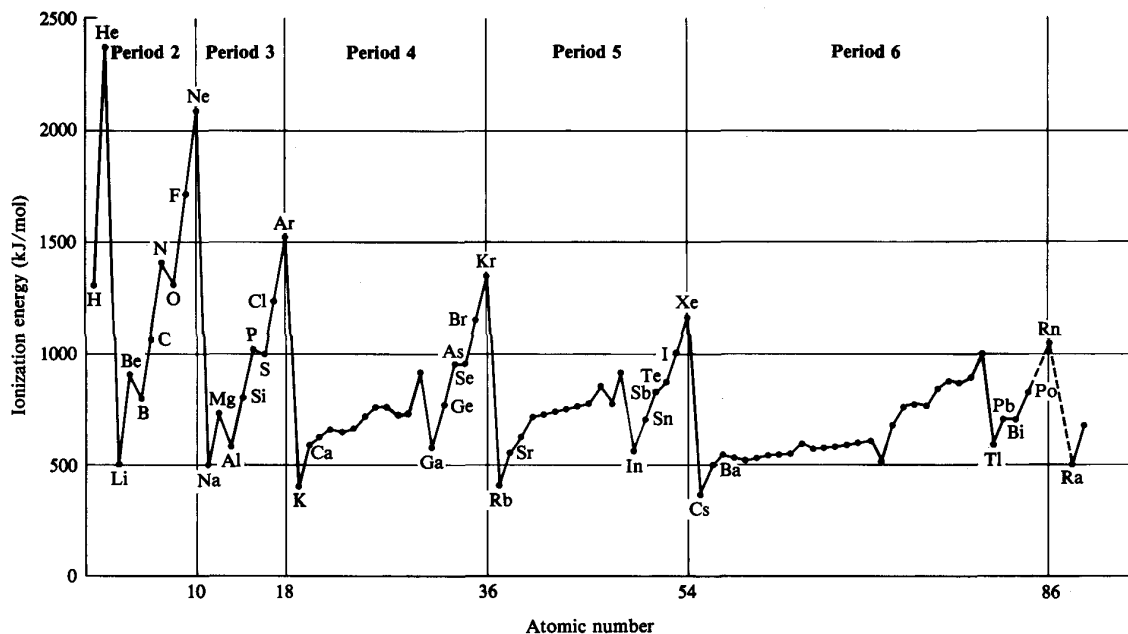


Information (Ionization Energy)

Ionization energy, I , is the energy required to remove an electron from a gaseous species. The *first ionization energy*, I_1 , refers to removing one electron from a neutral atom:

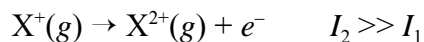


All ionization energies are positive, because it takes energy to remove an electron from the attraction of an atom's nucleus. The following plot shows the variation of first ionization energies across the periodic table.



Trends in first ionization energies can be understood on the basis of size of atoms. The valence electrons are closer to the nucleus to which they are attracted in a smaller atom; thus, more energy will be required to remove an electron by ionization. Consistent with size trends, first ionization energies generally increase across a period and decrease down a group.

Subsequent ionization energies (I_2, I_3, \dots), which remove successive electrons, require larger and larger amounts of energy, because the electron is being removed from a smaller species with an increasingly positive charge (a cation):



Key Questions

3. Based on position in the periodic table, which element of the following pairs has the higher first ionization energy?

O, Ne Ca, Sr K, Cr Br, Sb In, Sn

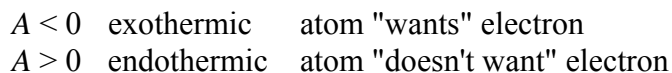
4. First ionization energies tend to increase across a period. But in period 2, Be has a higher first ionization energy than B, and N has a higher first ionization energy than O. Explain, [Hint: Look at the valence configurations, and recall that half-filled and fully filled subshells have extra stability.]

Information (Electron Affinity)

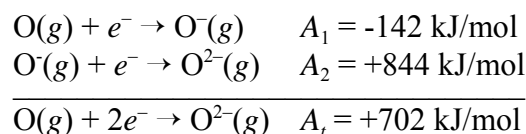
Electron affinity is defined by the general reaction



In general, the additional electron is added to a lowest-energy vacant orbital in the valence subshell, or in the next subshell if all valence subshells are already full. First electron affinities can be either exothermic or endothermic, depending on whether the atom "wants" the additional electron or not.



Although first electron affinities may be either positive or negative, *all second and succeeding electron affinities are positive (endothermic)*. This is the result of repulsions between the additional electron and the negative ion that was formed in the first electron affinity process. For example, consider the stepwise formation of $O^{2-}(g)$:



Electron affinity data are limited, owing to experimental difficulties, and values vary greatly, depending on the source of the data. The following table of electron affinity data gives typical values (kJ/mol).

1A	2A	3A	4A	5A	6A	7A
H -73						
Li -60	Be +100*	B -27	C -122	N +9*	O -141	F -328
Na -53	Mg +30*	Al -44	Si -134	P -72	S -200	Cl -348
K -48	Ca ?	Ga -30	Ge -120	As -77	Se -195	Br -325
Rb -47	Sr ?	In -30	Sn -121	Sb -101	Te -190	I -295
Cs -45	Ba ?	Tl -30	Pb -110	Bi -110	Po -183	At -270

*Estimated value

In general, the gross trends in first electron affinities are:

Electron affinities tend to become more negative across a period. This is the result of progressively smaller atomic sizes, placing the added electron closer to the nucleus.

Electron affinities tend to become less negative (or positive) down a group. The added electron is placed in an orbital that is progressively further away from the nucleus.

Nonmetals tend to have high (negative) electron affinities, and metals tend to have low (slightly negative or positive) electron affinities. This is consistent with the tendency of nonmetals to form anions, while metals resist forming negative ions.

Noble gases have positive electron affinities. The added electron is placed in a higher-energy orbital above a very stable closed-shell configuration. The combination of high nuclear charge shielding and disruption of a stable configuration mitigates anion formation.

Key Questions

5. On the basis of electronic configurations or any other appropriate considerations, explain the differences in the electron affinities of the following pairs of species.

Na, $A_1 < 0$; Mg, $A_1 > 0$

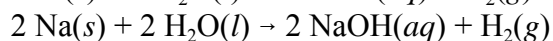
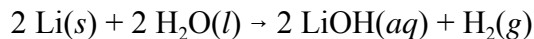
Br, $A_1 \ll 0$; Kr, $A_1 > 0$

N, $A_1 > 0$; O, $A_1 < 0$

O, $A_1 < 0$; O⁻, $A_2 > 0$

Information (Periodic Trends in Chemical Properties)

The chemical behavior of elements is a consequence of their electronic structure. Not surprisingly, similarities in the behavior of elements in the same group are a result of their having the same kind of valence configuration. The differences are often a matter of degree, reflecting changes in the attraction between the nucleus and valence electrons (i.e., effective nuclear charge). For example, both Li and Na react with water to form aqueous solutions of their ionic hydroxides and hydrogen gas:



The reaction with lithium is very gentle, but with sodium it usually results in an explosion of burning hydrogen in air. The difference is understandable by comparing the smaller size and higher ionization energy of lithium with the larger size and lower ionization energy of sodium. In short, the energy input is less in the case of sodium, and the reaction's exothermic energy output is greater.

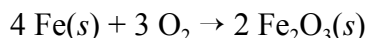
As we have seen, elements can be categorized as metals, nonmetals, and metalloids. Each category has a characteristic range of ionization energies and electron affinities.

Metals – low ionization energies, low electron affinities (negative or weakly positive)

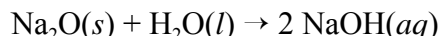
Nonmetals – high ionization energies, high electron affinities (negative)

Metalloids - intermediate ionization energies and electron affinities

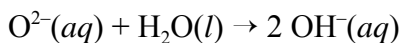
Owing to their relatively low ionization energies, metals tend to form cations, and when they combine with nonmetals they form ionic substances. For example, when metals combine with oxygen they form ionic oxides.



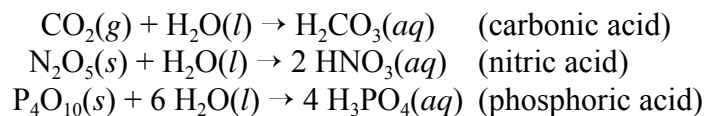
Metal oxides tend to dissolve in water to form hydroxide ion (OH^-). Therefore, *metal oxides are basic*.



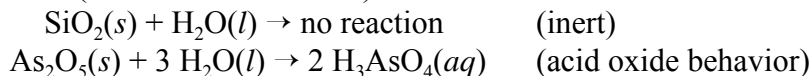
This is a result of the *hydrolysis* of the O^{2-} ion in water:



Nonmetals have ionization energies that are too high for stable cation formation, but their favorable electron affinities tend to result in anion formation. When combined with metal cations or complex cations, the resulting compounds are ionic. However, when nonmetals combine with each other, the compounds are molecular. In contrast to metals, the *oxides of nonmetals are acidic*. In molecular oxides, there are no oxide ions, and the oxygen is too tightly bound to be hydrolyzed into hydroxide ion in water. Instead, the nonmetal oxides tend to add both oxygen and hydrogen from water to make a molecular acid.

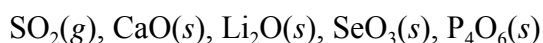


Properties of metalloids fall between metals and nonmetals. To behave as metals, metalloids such as Si, Ge, As would have to form very highly charged cations (Si^{4+} , Ge^{4+} , As^{5+}). Such small and highly charged cations would have a strongly attractive effect on the electrons around any anions with which they might combine. This would cause considerable sharing of electron density between the two. As we will see, sharing of electron density tends to be associated with molecule formation. Therefore, the oxides of metalloids are usually not ionic, and are generally not basic, as would be the case for true metals. They may have no acid-base character in water (essentially inert) or may be acidic (like molecular oxides).



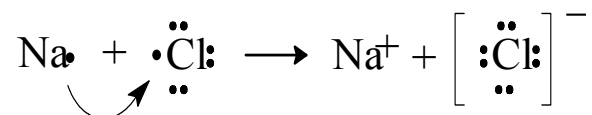
Key Questions

6. Calcium is generally less reactive than potassium but more reactive than magnesium. Explain.
7. For each of the following oxides, indicate whether it is ionic or molecular and whether it is acidic or basic. Then, write a balanced equation for the reaction expected between each oxide and water.



Information (Bond Type and Electronegativity)

An **ionic bond** is formed by electrostatic forces of attraction between ions. For example, NaCl is composed of Na^+ ions and Cl^- ions in a cubic array. At the atomic level, we can imagine the formation of these ions through a process in which an electron from an atom of Na is transferred to an atom of Cl.



In this representation, the dots around each species indicate the valence electrons. This method of representation is called an **electron-dot model** or **Lewis-dot model** (after G. N. Lewis who devised the scheme). The complete transfer of an electron and formation of discrete ions, which this process suggests, would lead to a **purely ionic bond**. In actuality, complete transfer never occurs in the formation of an ionic compound, and there is always some degree of sharing of electrons between the ion pair. Therefore, the purely ionic bond must be regarded as only a hypothetical extreme model, an approximation in real cases.

At the opposite extreme, a **covalent bond** is formed by sharing electrons between atoms. If the atoms are identical, a **homonuclear bond** will result in which the sharing of electron density is equal between the bonded atoms. This constitutes a **pure covalent bond**. All elements that exist in molecular form have pure covalent bonds between their atoms; e.g., H_2 , O_2 , N_2 , P_4 , S_8 . If the two atoms are different, a **heteronuclear bond** will result in which the sharing of electron density is unequal. The atom with the greater attraction for electrons will acquire a greater share of the total electron density, giving it more electron density than it had as an isolated atom. In the bond, this atom will have acquire a **partial negative charge**, indicated δ^- . The other atom will lose some of its electron density, giving it a **partial positive charge**, indicated δ^+ . The unequal sharing of electron density in heteronuclear covalent bonds gives them **polarity** and **partial ionic character**.

The attraction an atom has for electrons *in a chemical bond* is called its **electronegativity**. This is not a directly measurable quantity, and historically there have been several different approaches to estimating it. In the 1930s, Linus Pauling developed a scale of electronegativities that was widely adopted, and that has been modified and improved over the years. On the

zero indicates that it does not totally surrender an electron in forming FrF. This is consistent with the point previously made: *the ideal of a perfect ionic bond, for which $\delta\chi = 4.0$, does not exist.*

There is no precise cut-off point between polar covalent and ionic bonding. Nonetheless, if $\delta\chi \geq 1.7-1.8$, the bond is *probably* best regarded as ionic. Values of $\delta\chi$ that lie below but near this imprecise border may be regarded as polar covalent; i.e., covalent with an appreciable amount of ionic character. Values of $\delta\chi$ that lie above but near this border may be called ionic, but will have some degree of covalent character, becoming less as $\delta\chi$ increases. In light of the trends in electronegativity, the most ionic binary compounds can be expected to be formed by combinations of elements in the lower left portion of the periodic table with those in the upper right; i.e., metals and nonmetals. The most covalent bonds are expected among near-neighbor nonmetallic elements.

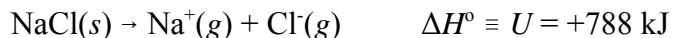
Difference in electronegativity, taken in isolation, can sometimes mislead about the nature of a bond. While $\delta\chi \geq 1.7-1.8$ may suggest ionic bonding, a compound whose bonds are in this range is probably *not ionic if it is a gas or a liquid*. Recall that simple ionic compounds are solids at room temperature. Cases like this involve very polar covalent bonds. Likewise, if a bond between two *different* elements has $\delta\chi = 0$, it is not purely covalent. Different elements have differing abilities to attract electrons in a chemical bond, but the electronegativity scale is simply too imprecise to indicate the difference. All heteronuclear bonds should be regarded as polar to some extent. If $\delta\chi = 0$, the bond is virtually pure covalent, but not exactly so. The only truly pure covalent bonds exist in molecules of elements; i.e., homonuclear bonds.

Key Questions

- Using the electronegativity values in the table above, calculate $\delta\chi$ for the pairs of elements forming bonds in each of the following species, and describe the type of bonding as either pure covalent, polar covalent, or ionic: H_2 , HCl , PbBr_2 , NaCl , NBr_3 .
- Calculate $\delta\chi$ for the bonds in HF and NCl_3 and describe them.

Information (Lattice Energy)

The measure of the stability of an ionic substance's crystal lattice is the **lattice energy**, defined as the enthalpy associated with completely separating one mole of solid ionic compound into its gaseous ions. For $\text{NaCl}(s)$ the lattice energy, U , is defined as



This is always an endothermic enthalpy, because breaking up the crystal lattice requires overcoming the attractions between the cations and anions. The higher the attraction between cations and anions, the higher will be the lattice energy. The lattice energy for an ionic compound is not directly measurable. However, the enthalpy of formation for an ionic compound can be measured, and along with data to calculate the enthalpies of formation of the

ions, the value of U can be calculated by applying the Law of Hess in a series of thermochemical equations called the **Born-Haber cycle**. (See your text for further details.)

Large values of lattice energy, implying a stable crystal lattice, are favored by (a) higher ionic charges, (b) smaller ions, and (c) shorter distances between ions. The following data illustrate these trends for the ionic compounds formed by the indicated pairs of ions.

		Selected Lattice Energies, U° (kJ/mol) (Born-Haber Cycle Data)				
		F ⁻	Cl ⁻	Br ⁻	I ⁻	O ²⁻
Li ⁺		1049.0	862.0	818.6	762.7	2830
Na ⁺		927.7	786.8	751.8	703	2650
K ⁺		825.9	716.8	688.6	646.9	2250
Rb ⁺		788.9	687.9	612	625	2170
Cs ⁺		758.5	668.2	635	602	2090
Mg ²⁺			2326			3795
Ca ²⁺						3414
Sr ²⁺			2127			3217

Key Questions

10. Explain the following trends in lattice energy.

- a. $\text{KF} < \text{CaO} < \text{ScN}$ b. $\text{NaCl} > \text{RbBr} > \text{CsBr}$ c. $\text{MgO} > \text{MgCl}_2$

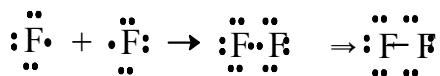
Information (Lewis Dot Diagrams)

The first model that attempted to describe covalent bonding in terms of sharing of electrons was developed by G. N. Lewis and Irving Langmuir in 1916. In this model a chemical bond is formed when one or more pairs of electrons are shared between two atoms in such a way that each achieves the equivalent of a noble gas configuration. The electrons are usually represented by dots (\cdot or $:$), with shared pairs (bonds) represented by a line for each pair ($-$, $=$, \equiv). For H_2 each H atom brings an electron to the bond, so through sharing the two nuclei have two electrons, equivalent to the configuration of He.



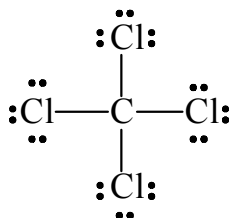
Each H has a net of 2 electrons through sharing.

For F_2 each F atom brings 7 electrons to the molecule, for a total of 14. Through sharing each achieves an octet of electrons.



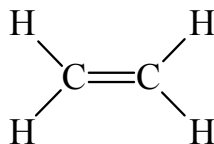
Each F has a net of 8 electrons through sharing.

Most elements, with the exception of hydrogen, achieve an octet through sharing. Hydrogen achieves a pair, like He. For example, in CCl_4 all atoms achieve an octet.

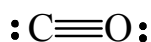


Each C-Cl bond is a **single bond**, defined as resulting from one electron pair shared between two atoms. The other electrons about each Cl are considered to be non-bonding electrons.

In some cases more than one bond can be formed between a pair of atoms. The carbon-carbon bond in C_2H_4 is a **double bond** in which two pairs of electrons are shared between the carbon atoms.



The carbon-oxygen bond in carbon monoxide is a triple bond, in which three pairs of electrons are shared between the carbon and oxygen atoms.



The **bond order** refers to the number of shared pairs forming bonds. Thus, the bond orders of a single, double, and triple bond are 1, 2, and 3, respectively. When two atoms can form bonds of varying bond order, the higher the bond order the stronger the bond will be. The measure of a bond's strength is its **dissociation energy**, D , which is the enthalpy required to break one mole of the bonds. Compare the following data for C-C bonds:

Compound	$d_{\text{C-C}}$	$D_{\text{C-C}}$
$\text{H}_3\text{C}-\text{CH}_3$	1.54 Å	368 kJ/mol
$\text{H}_2\text{C}=\text{CH}_2$	1.34 Å	435 kJ/mol
$\text{HC}\equiv\text{CH}$	1.20 Å	962 kJ/mol

Note that the bond lengths become shorter as bond order increases. In general, *as bond order increases between a pair of atoms bond strength increases and bond length decreases.*

The "octet rule" is sometimes violated with justifications. A few elements, particularly in groups 2 (Be) and 13 (B, Al) and some heavier elements in group 14 (Sn, Pb) occasionally form "**electron deficient**" compounds, in which the *central atom* has less than an octet. Examples of electron deficient compounds include BeH_2 in the gas phase and BF_3 . On the other hand, some elements *in the third and higher periods* occasionally form compounds in which the central atom has more than an octet. This is called **hypervalence**. Examples of hypervalent compounds include PF_5 , SF_6 , and XeF_4 . Only large central atoms from the third or higher periods are capable of forming hypervalent compounds, and only some of their compounds do so.

In order to construct Lewis models of bonding, you should follow the specific procedures detailed below, *in the order given*.

- ① Arrange the atoms of the compound or complex ion so as to show how they are linked together by chemical bonds. When in doubt, assume that the *least electronegative* atom is central (not an outer atom). Hydrogen is almost always an outer (pendant) atom.
- ② Count the valence electrons for each atom. For non-transition elements, the number of valence electrons is the same as the last digit of the group number (e.g., in group 16 there are 6 valence electrons). For a complex anion, add electrons equal to the negative charge. For a complex cation, subtract electrons equal to the positive charge. The total is the number of electrons to be used in generating the model.
- ③ Draw in single bonds (–) between all atoms that are linked together, keeping in mind that each bond represents the use of two electrons from the total established in step ②.
- ④ With the remaining electrons, first add pairs (:) to all of the outer atoms to make octets (except H), then add any leftover electrons to the central atom. The octet for each atom includes pairs used to make bonds in step ③.
- ⑤ Leave no electrons unpaired unless the total number of electrons is odd.
- ⑥ Count the number of electrons about the central atom to see if an octet has been made there. If not, try moving non-bonding pairs (:) from outer atoms to make double or triple bonds to the central atom. However, note that
 - (a) hydrogen and the halogens do not form multiple bonds, and
 - (b) elements in the third and higher periods usually do not form effective multiple bonds.
- ⑦ If there are too few electrons to give octets to all atoms (except hydrogen), the central atom *might* be electron deficient, particularly if it is Be, B, or Al. However,
 - (a) outer atoms are *never* electron deficient, and
 - (b) C, N, O, and F *always have an octet*, except in rare circumstances.
- ⑧ Sometimes central atoms from the *third and higher periods* have more than an octet (*hypervalence*), but only when necessary. However,
 - (a) outer atoms are *never hypervalent*, and
 - (b) C, N, O, and F are *never hypervalent*.

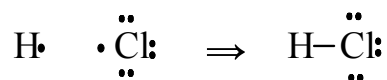
- ⑨ The representation of any anion or cation should be surrounded by square brackets ([]) with the charge indicated on the outside as a superscript.
- ⑩ Count up the number of electrons in the completed model to be sure it is the same as the total established in step ②.

Key Questions

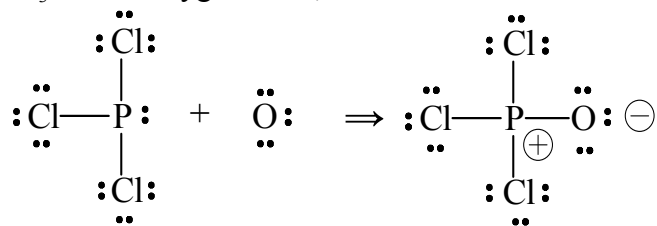
11. Following the steps given above, draw Lewis dot structures for the following molecular species: NF_3 , H_2O , NH_4^+ , SO_4^{2-} , H_2CO , C_2H_2 .
12. Following the steps above, draw Lewis dot structures for the following molecular species, which may be electron deficient or hypervalent: AlCl_3 , XeF_4 , XeF_2 , BeCl_2

Information (Formal Charge)

In terms of "electron bookkeeping" of Lewis models, some bonds are formed by each atom contributing electrons. The bond in HCl fits this model.



In other cases one atom seems to be donating a pair of electrons to the other. The P-O bond in Cl_3PO , formed from PCl_3 and an oxygen atom, illustrates.



We might imagine that as a result of this bond formation the oxygen has gained electron density and the phosphorous has lost electron density. One way of indicating this kind of change in the electron environments about bonded atoms is through the use of **formal charges** of the type marked on the model of Cl_3PO . Formal charges can be described as the charges atoms would have if all elements had the same electronegativity. For example, if both H and Cl had equal attraction for the electrons in HCl there would be no net change in their electron environments. In Cl_3PO , by contrast, equal sharing of the pair between P and O would mean a loss of an electron by P and a gain of an electron by O, resulting in the formal charges indicated. Of course all electronegativities are not equal, so formal charges should only be regarded as a formalism, as the name suggests. They do not accurately reflect the actual distribution of charge across a molecule. Nonetheless, formal charge assignments, if used with care, can be qualitatively useful in deciding which of several possible dot-models best represents the bonding in a molecule.

Formal charges are assigned to a Lewis dot model by a special set of bookkeeping rules for counting electrons:

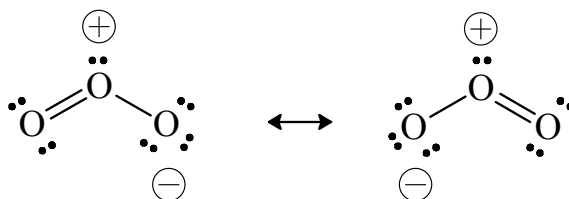
- ① Write the electron dot structure (Lewis dot model) for the compound or complex ion.
- ② Count electrons about each atom by the following method:
 non-bonded pair (:) = 2
 bonded pair (–) = 1
 [Note: *This is not the same as the method used to determine octets in constructing Lewis dot models.*]
- ③ Compare the number of electrons counted in this manner with the number of valence electrons the isolated neutral atom would have.
- ④ If the count is higher than for the neutral atom, assign a negative formal charge equal to the difference. Write the formal charge inside a circle next to the atom (e.g., \ominus).
- ⑤ If the count is lower than for the neutral atom, assign a positive formal charge equal to the difference. Write the formal charge inside a circle next to the atom (e.g., \oplus).
- ⑥ The algebraic sum of all positive and negative formal charges for a neutral molecule should be zero. For a complex ion, it should equal the net charge on the ion.

Key Questions

13. Show the formal charges on all atoms in the sulfate ion, SO_4^{2-} , whose Lewis dot structure you developed in Key Question 11.

Information (Resonance)

Sometimes when we write the Lewis structure for a molecule we find that it is only one of two or more possible representations. Consider the Lewis structure for ozone, O_3 . Either of the following two structures is equally likely.



These two equivalent representations are called **resonance forms** or **canonical forms**. Neither by itself is an adequate representation of the bonding in ozone. Indeed, neither represents the state of the molecule in its lowest-energy state (its *ground state*). The true state of the molecule is an average of these hypothetical extreme structures. The need to postulate multiple resonance forms is actually only a manifestation of the limited ability of Lewis models to represent the bonding for certain molecules, using only one model.

All experimental evidence suggests that both O-O bonds in ozone are equivalent and indistinguishable. This would not be the case if ozone consisted of one O-O single bond and one O=O double bond. The two equally likely resonance forms of ozone suggest that one of the two pairs used in forming a double bond in each structure really has equal probability over both bonds. In other words, a pair of electrons may be thought of as being **delocalized** over both bonds. This is in contrast to pairs that can be thought of as being **localized** in one bond between two atoms. If the true state of the molecule is an average of the resonance forms, then each O-O bond in ozone is really neither a true single bond, nor a true double bond. Rather, it must be something in between. If we associate one unit of bond order (B.O. = 1) with each shared pair, then the bond order for each O-O bond could be estimated to be $1\frac{1}{2}$, the result of three pairs shared over two equivalent bonds. Comparison of bond length and dissociation energy data for O-O bonds in a variety of compounds is consistent with this conclusion.

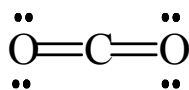
Molecule	O-O B.O.	Length (Å)	D (kJ/mol)
H ₂ O ₂	1	1.49	138
O ₃	$1\frac{1}{2}$	1.28	300
O ₂	2	1.21	496

In general, for one of equivalent bonds in a structure represented by a set of *equally contributing* resonance forms, the bond order can be estimated as the number of electrons shared among the equivalent bonds divided by the number of bonds:

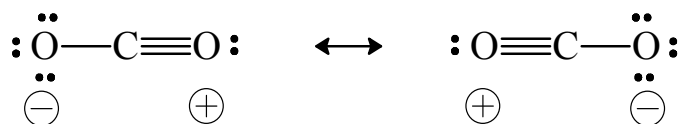
$$\text{B.O.} = \frac{x \text{ bond pairs}}{y \text{ equivalent bonds}}$$

For ozone, we have three pairs over two equivalent bonds; i.e., $\text{B.O.} = 3/2 = 1\frac{1}{2}$.

Sometimes a molecule that can be represented by a single Lewis dot model shows properties that suggest contributions from other resonance forms. Carbon dioxide is such a case. The Lewis model for CO₂ seems adequate:



But a typical C=O double bond is expected to be 1.22 Å, whereas the measured distance in CO₂ is 1.15 Å, a bit short. We can rationalize the shorter distance by assuming minor contributions from the following two canonical forms:



The formal charges suggest that these are less likely forms than the model that has no formal charge separation. Consequently, they are expected to be minor contributors to the description of the overall bonding in CO_2 . Nonetheless, their inclusion is consistent with observed shorter bond length. In a case such as this, where all canonical forms do not contribute equally, we cannot give a numerical value for the bond order. Nonetheless, we can rationalize differences in bond strength and length.

When discussing the bonding in a molecule that is a resonance hybrid, it is important to understand that the canonical forms are not real: no bond is flipping back and forth between being single, double, or triple. The goal in drawing resonance forms is to determine the collection of hypothetical extreme models whose average reasonably represents the electron distribution in the molecule. In keeping with this understanding, the following guidelines should be followed:

- ① Draw all resonance structures (canonical forms) with exactly the same geometry, the same atom-pair linkages, and the same orientation on the page.
- ② Do not move atoms from form to form. Only bonds to the same atoms change from form to form.
- ③ Where the "octet rule" is observed, all forms obey it.
- ④ The number of electron pairs must be the same across all forms.
- ⑤ Resonance forms that minimize formal charges, minimize formal charge separations, and avoid placing like formal charges on adjacent atoms are more reasonable and will be greater contributors to the overall description of the molecule.
- ⑥ **Remember: Resonance forms are not real states of the molecule.** The average of all the hypothetical resonance forms is *suggestive* of the actual electron distribution across the molecule.

Key Questions

14. The nitrate ion, NO_3^- , can be represented by a series of three equivalent resonance forms. Show the resonance forms of NO_3^- , including formal charges, and estimate the bond order of the N–O bonds in this ion.
15. FNO_2 can be represented by three non-equivalent resonance forms. Draw the three canonical forms of FNO_2 and assess their relative contributions to the resonance hybrid description of the molecule. What is the approximate N–O bond order?

Periodic Table of the Elements

1A 1																8A 18	
1 H 1.008	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3B 3	4B 4	5B 5	6B 6	7B 7	8 8	8B 9	10 10	1B 11	2B 12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc [98]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	89 Ac [227]	104 Rf [261]	105 Db [262]	106 Sg [263]	107 Bh [264]	108 Hs [265]	109 Mt [268]	110 Uun [269]	111 Uuu [272]	112 Uub [277]						

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]