

General chemistry

Chapter 6

Chemical bonding

I- Ionic Bond

Introduction

- Atoms combine to achieve a more stable electron configuration. Maximum stability results when an atom is isoelectronic with a noble gas.
- **OCTET RULE**
- A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

Lewis dot symbol

- When discussing the octet rule, we do not consider *d* or *f* electrons. Only the *s* and *p* electrons are involved in the octet rule (**valance electrons**), making it a useful rule for the *main group elements*, an octet in these atoms corresponds to an electron configurations ending with s^2p^6 .
- **Lewis dot symbol** consists of the symbol of an element and one dot for each valence electron in an atom of the element.
- Note that, except for helium, the number of valence electrons each atom has is the same as the group number of the element (for the main groups).

1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
• H							He :
• Li	• Be •	• B •	• C •	• N •	• O •	• F •	• Ne •
• Na	• Mg •	• Al •	• Si •	• P •	• S •	• Cl •	• Ar •
• K	• Ca •	• Ga •	• Ge •	• As •	• Se •	• Br •	• Kr •
• Rb	• Sr •	• In •	• Sn •	• Sb •	• Te •	• I •	• Xe •
• Cs	• Ba •	• Tl •	• Pb •	• Bi •	• Po •	• At •	• Rn •
• Fr	• Ra •						

Lewis dot symbols for the representative elements and the noble gases. The number of unpaired dots corresponds to the number of bonds an atom of the element can form in a compound.

The Ionic Bond

- An **ionic bond** is the electrostatic force that holds ions together in an ionic compound.
- Atoms of elements with low ionization energies tend to form cations, while those with high electron affinities tend to form anions.
- **Monatomic ions** contain only one atom as Na^+ and Cl^- . **Polyatomic ions** are ions containing more than one atom, such as OH^- and CN^- .
- As a rough rule, the elements most likely to form cations in ionic compounds are the alkali metals (Group 1A) and alkaline earth metals (Group 2A), and the elements most likely to form anions are the halogens and oxygen.

1A	2A													13A	14A	15A	16A	17A	8A
	2																		
Li ⁺															C ⁴⁺	N ³⁻	O ²⁻	F ⁻	
Na ⁺	Mg ²⁺	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B		Al ³⁺		P ³⁻	S ²⁻	Cl ⁻		
K ⁺	Ca ²⁺				Cr ²⁺ Cr ³⁺	Mn ²⁺ Mn ³⁺	Fe ²⁺ Fe ³⁺	Co ²⁺ Co ³⁺	Ni ²⁺ Ni ³⁺	Cu ⁺ Cu ²⁺	Zn ²⁺					Se ²⁻	Br ⁻		
Rb ⁺	Sr ²⁺									Ag ⁺	Cd ²⁺			Sn ²⁺ Sn ⁴⁺		Te ²⁻	I ⁻		
Cs ⁺	Ba ²⁺									Au ⁺ Au ³⁺	Hg ₂ ²⁺ Hg ²⁺			Pb ²⁺ Pb ⁴⁺					

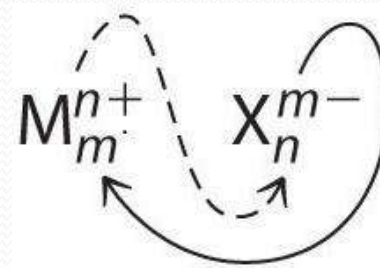
Figure 2.10

Common monatomic ions arranged according to their positions in the periodic table. Note that the Hg_2^{2+} ion contains two atoms.

Formula of Ionic Compounds

- The formulas of ionic compounds are usually the same as their empirical formulas.
- In order for ionic compounds to be electrically neutral, the sum of the charges on the cation and anion in each formula unit must be zero.
- Knowing the symbols and charges of the cations and anions is essential for formula of ionic compounds. For the monoatomic ions, you can figure out the charges from the position of the element in the periodic chart.
- If the charges are numerically equal, then no subscripts are necessary.
- If the charges on the cation and anion are numerically different, we apply the following rule to make the formula electrically neutral:

The subscript of the cation is numerically equal to the charge on the anion, and the subscript of the anion is numerically equal to the charge on the cation.

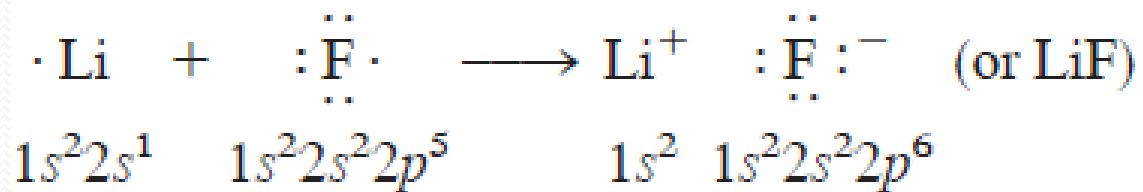


Formula of Ionic Compounds

- In the formation of LiF, the following reaction occur:

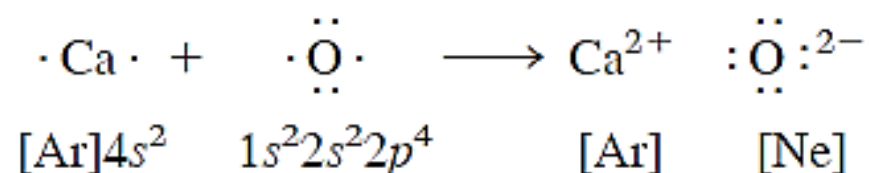


- Using Lewis dot symbols, we represent the formation of ionic bond between lithium and fluorine like this:

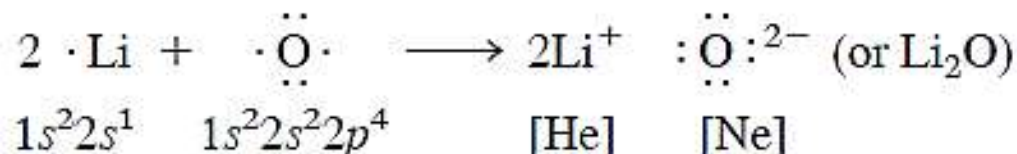


- We normally write the empirical formulas of ionic compounds without showing the charges. The + and - are shown here to emphasize the transfer of electrons. The compound itself is electrically neutral.

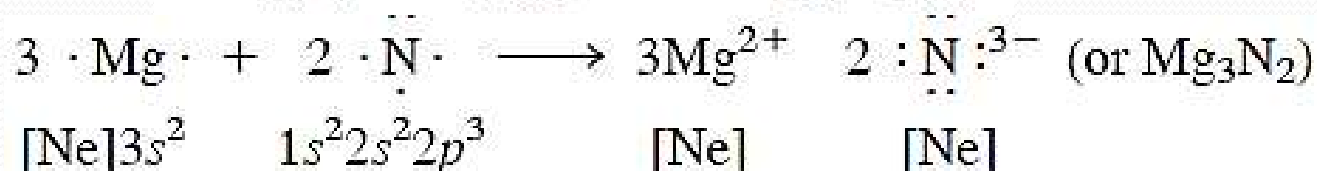
- Calcium burns in oxygen to form calcium oxide:



- Lithium burns in air to form lithium oxide (Li_2O):



- When magnesium reacts with nitrogen at elevated temperatures, magnesium nitride (Mg_3N_2), forms:

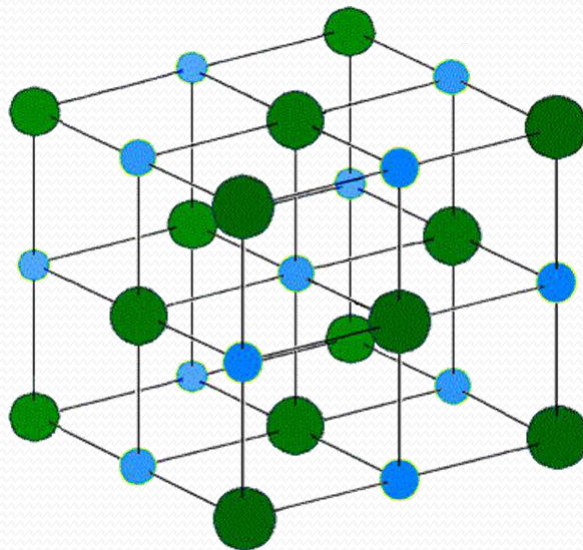


Notes

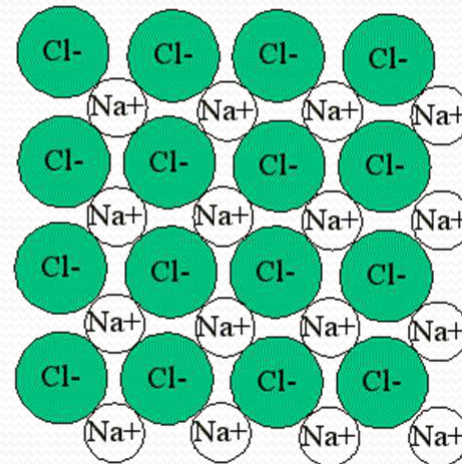
- Although beryllium and magnesium related to group 2A and are metals, most beryllium compounds and some magnesium compounds (MgH_2 , for example) are molecular rather than ionic in nature.
- Boron is a metalloid from group 3A, does not form binary ionic compounds. Other metallic elements in Group 3A form ionic and many molecular compounds.
- Take care that the following elements normally exist as diatomic molecules: hydrogen (H_2), nitrogen (N_2) and oxygen (O_2), as well as the Group 7A elements—fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

Lattice Energy of Ionic Compounds

- **Ionic bonding** is the attraction between positively- and negatively-charged ions. These oppositely charged ions attract each other to form ionic networks (or **lattices**).
- When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge.



Slice through a NaCl crystal



Lattice Energy of Ionic Compounds

- Thus, the overall stability of a solid ionic compound depends on the interactions of all these ions and not merely on the interaction of a single cation with a single anion.
- A quantitative measure of the stability of any ionic solid is its **lattice energy**, defined as the energy required to completely separate one mole of a solid ionic compound into gaseous ions.
- The larger the lattice energy, the more stable the solid and the more tightly held the ions, and so the solid has a higher melting point.

Lattice Energy of Ionic Compounds

- The lattice energy between two doubly charged species > that between a doubly charged ion and a singly charged ion > that between singly charged anions and cations.

Lattice Energies and Melting Points of Some Ionic Compounds

	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
NaCl	788	801
NaBr	736	750
MgCl ₂	2527	714
MgO	3890	2800
CaO	3414	2580

Naming ionic Compounds

- Metal cations take their names from the elements.

Na^+	sodium ion (or sodium cation)
K^+	potassium ion (or potassium cation)
Mg^{2+}	magnesium ion (or magnesium cation)
Al^{3+}	aluminum ion (or aluminum cation)

- The anion is named by taking the first part of the element name and adding “-ide.”

Group 5A	Group 6A	Group 7A
N Nitride (N^{3-})	O Oxide (O^{2-})	F Fluoride (F^-)
P Phosphide (P^{3-})	S Sulfide (S^{2-})	Cl Chloride (Cl^-)
	Se Selenide (Se^{2-})	Br Bromide (Br^-)
	Te Telluride (Te^{2-})	I Iodide (I^-)

Naming ionic Compounds

- Many ionic compounds are **binary compounds**, or compounds formed from just two elements. For binary ionic compounds the first element named is the metal cation, followed by the nonmetallic anion.
- Thus, NaCl is sodium chloride. Potassium bromide (KBr), zinc iodide (ZnI₂), and aluminum oxide (Al₂O₃).

Naming ionic Compounds

- other ionic substances are called **ternary compounds**, meaning compounds consisting of three elements.
- The “-ide” ending is also used for certain anion groups containing different elements, such as hydroxide (OH) and cyanide (CN).
- Thus, the compounds LiOH and KCN are named lithium hydroxide and potassium cyanide.

Some of the names and charges of common polyatomic cations and anions are listed in Table IV.

Table IV

Cations		Anions		
+1	+2	-1	-2	-3
NH_4^+ ammonium	VO^{2+} vanadyl	OH^- hydroxide		
H_3O^+ hydronium		CN^- cyanide	CrO_4^{2-} chromate	
NO^+ nitrosyl		MnO_4^- permanganate	$\text{Cr}_2\text{O}_7^{2-}$ dichromate	
		NO_2^- nitrite	SO_3^{2-} sulfite	AsO_3^{3-} arsenite
		NO_3^- nitrate	SO_4^{2-} sulfate	AsO_4^{3-} arsenate
		ClO^- hypochlorite		
		ClO_2^- chlorite		
		ClO_3^- chlorate		
		ClO_4^- perchlorate		
		HCO_3^- bicarbonate or hydrogen carbonate	CO_3^{2-} carbonate	
		H_2PO_4^- dihydrogen phosphate	HPO_4^{2-} hydrogen phosphate	PO_4^{3-} phosphate
		CH_3COO^- acetate	$\text{C}_2\text{O}_4^{2-}$ oxalate	

Naming ionic Compounds

- Certain metals, especially the *transition metals*, can form more than one type of cation.
- Example: Iron can form two cations: Fe^{+2} and Fe^{+3} . For designating different cations of the *same* element use Roman numerals. The Roman numeral I is used for one positive charge, II for two positive charges, and so on. This is called the *Stock system*.
- In this system, the Fe^{+2} and Fe^{+3} ions are called iron (II) and iron (III), and the compounds FeCl_2 and FeCl_3 are called iron (II) chloride and iron (III) chloride, respectively.
- The old style system has different suffixes in their names. For example, Fe^{2+} is called the ferrous ion, and Fe^{3+} is called the ferric ion; Cu^+ is the cuprous ion, and Cu^{2+} is the cupric ion. Notice that the ion with the lesser charge ends with -ous and the one with greater charges ends with -ic. In

Examples

KI	potassium ion + iodide ion = potassium iodide
CoCl ₂	cobalt(II) ion + two chloride ions = cobalt(II) chloride
CoCl ₃	cobalt(III) ion + three chloride ions = cobalt(III) chloride
Hg ₂ Cl ₂	mercury(I) ion + two chloride ions = mercury(I) chloride or mercurous chloride
AgNO ₃	silver ion + nitrate ion = silver nitrate It is not called silver(I) nitrate because Ag ⁺ is the only stable ion of silver.
(NH ₄) ₂ S	two ammonium ions + sulfide ion = ammonium sulfide
Al(HCO ₃) ₃	aluminum ion + bicarbonate ion = aluminum bicarbonate or aluminum hydrogen carbonate

Chapter 6

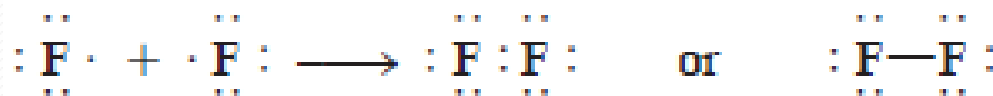
II- The Covalent Bond

Introduction

- **Covalent bond** is a bond in which two electrons are shared by two atoms.
- In a covalent bond, each electron in a shared pair is attracted to the nuclei of both atoms. This attraction holds the two atoms together.
- Covalent bonding between many-electron atoms involves only the valence electrons.
- The formation of these molecules illustrates the octet rule to achieve the stable noble gas configuration by sharing electrons.

Lewis structure

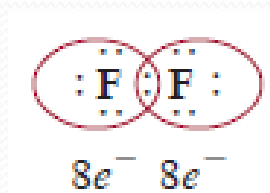
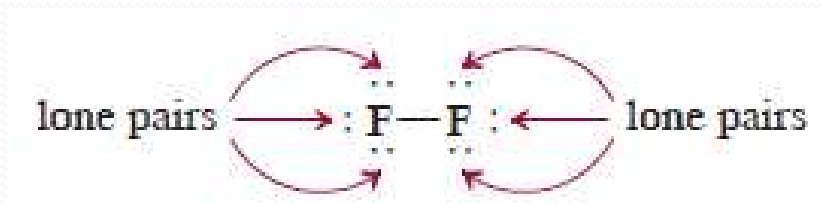
- The structures we use to represent covalent compounds, such as H₂ and F₂, are called Lewis structures.
- A Lewis structure is a representation of covalent bonding in which shared electron pairs are shown either as lines or as pairs of dots between two atoms, and lone pairs are shown as pairs of dots on individual atoms. Only valence electrons are shown in a Lewis structure.
- The formation of the F₂ molecule can be represented as follows:



- For the sake of simplicity, the shared pair of electrons is often represented by a single line.

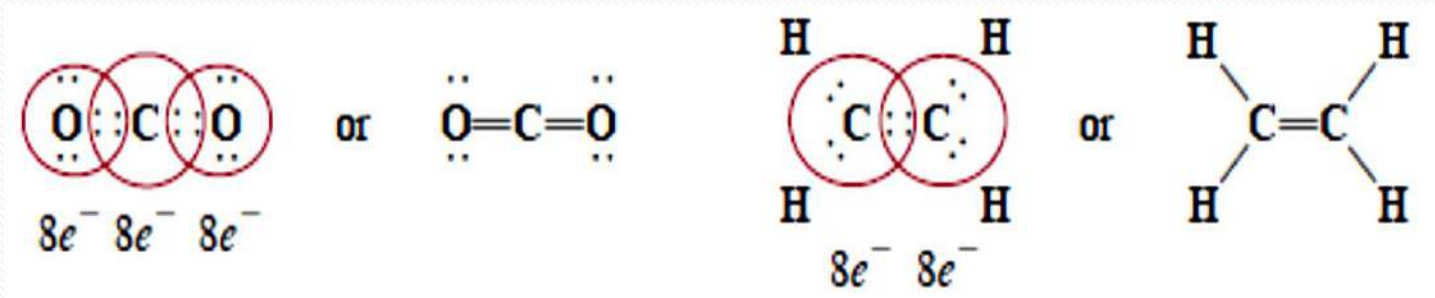
Lone pairs

- Note that only two valence electrons participate in the formation of F_2 . The other, nonbonding electrons, are called lone pairs. (these are pairs of valence electrons that are not involved in covalent bond formation). Thus, each F in F_2 has three lone pairs of electrons.



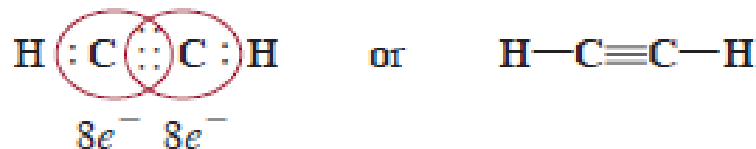
Bond order

- Atoms can form different types of covalent bonds.
- In a single bond, two atoms are held together by one electron pair as F_2 molecule.
- If two atoms share two pairs of electrons, the covalent bond is called a double bond, such as: carbon dioxide (CO_2) and ethylene (C_2H_4):



Bond order

- A triple bond arises when two atoms share three pairs of electrons, as in the nitrogen molecule (N_2) and acetylene molecule (C_2H_2):



Bond length

- Bond length is defined as the distance between the nuclei of two covalently bonded atoms in a molecule.
- Triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds.
- The shorter multiple bonds are also more stable than single bonds.

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C=O	121
C—C	154
C=C	133
C≡C	120
C—N	143
C=N	138
C≡N	116
N—O	136
N=O	122
O—H	96

Electronegativity

- Electronegativity is the ability of an atom to attract the electrons toward itself in a chemical bond.
- Elements with high electronegativity have a greater tendency to attract electrons than do elements with low electronegativity.
- As we might expect, electronegativity is related to electron affinity and ionization energy.
- In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases.
- Within each group, electronegativity decreases with increasing atomic number, and increasing metallic character.

Increasing electronegativity

Increasing electronegativity

Increasing electronegativity							
H 2.1	2A	3A	4A	5A	6A	7A	8A
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9						

Polarity of the bond

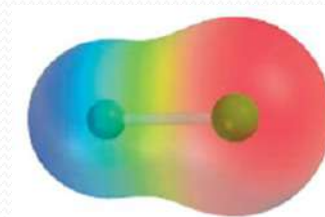
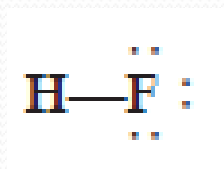
- The electronegativity is one of the factors that contributes to the polarity of the bond.
- Atoms of elements with ***widely*** different electronegativities tend to form ionic bonds. Ionic bonds involve atoms of a metal (low electronegativity) and a non-metal (high electronegativity) elements.
- **Ionic bond is highly polar (complete – or + charges) as the transfer of the electron(s) is nearly complete.**

Polarity of the bond

- Most covalent bonds involve atoms of nonmetallic elements.
- Only atoms of the same element, which have the same electronegativity can be joined by a pure covalent bond (no shift in electrons) as the sharing of an electron pair by two atoms is equal that is, the electrons spend the same amount of time in the vicinity of each atom. This results in **non-polar covalent bond**.

Polarity of the bond

- However, in the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally because H and F are different atoms and hence have different electronegativities. That means, the electrons spend more time in the vicinity of the more electronegative atom than the other. This results in a **polar covalent bond**.
- We can think of this unequal sharing of electrons as a partial electron transfer or a shift in electron density from H to F.



- Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a **dipole** is established. Thus, the HF molecule has a dipole. The size of a dipole is measured by its **dipole moment**.

Polarity of the bond

(a)



Nonpolar covalent bond

Bonding electrons shared equally between two atoms.
No charges on atoms.

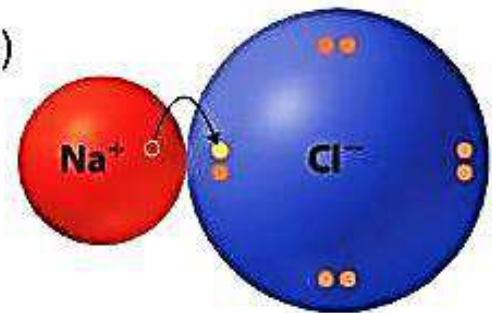
(b)



Polar covalent bond

Bonding electrons shared unequally between two atoms.
Partial charges on atoms.

(c)



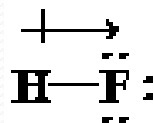
Ionic bond

Complete transfer of one or more valence electrons.
Full charges on resulting ions.

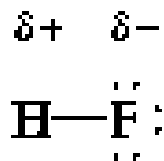
Dipole Moments

- The shift of electron density toward the most electronegative atom is symbolized by placing a crossed arrow (\rightarrow) above the Lewis structure to indicate the direction of the shift.

- For example,



- The consequent charge separation can be represented as:



- Where δ (delta) denotes a partial charge.
- A quantitative measure of the polarity of a bond is its dipole moment (μ) which is the product of the charge Q and the distance r between the charges:

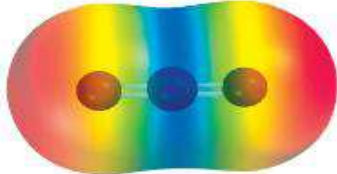
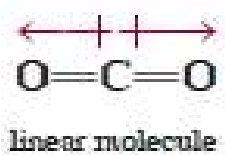
$$\mu = Q \times r$$

Dipole Moments of diatomic molecules

- The following table presents dipole moments of the hydrogen halides. As we proceed from HF to HI, the electronegativity difference decreases. This decreases the amount of charge separated and causes the dipole moment to decrease from HF to HI. For these molecules the change in the difference in electronegativity is the more important factor on the dipole moment.
- The greater the difference between the electron-attracting ability of two atoms joined by a covalent bond, the more polar the bond, and the larger the magnitude of the partial charges.

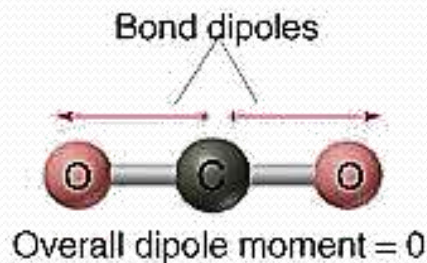
Compound	Electronegativity Difference	Dipole Moment (D)
HF	1.9	1.82
HCl	0.9	1.08
HBr	0.7	0.82
HI	0.4	0.44

Dipole Moments of polyatomic molecules

- For a molecule made up of three or more atoms, both the polarity of the bonds (determined by difference in electronegativity) and the molecular geometry determine whether there is a dipole moment. In this case, even if polar bonds are present, the molecule will not necessarily have a dipole moment.
- Carbon dioxide (CO_2), for example, is a linear triatomic molecule shown in the figure:
- The dipole moment of the entire molecule is made up of two bond moments, that is, individual dipole moments in the polar $\text{C}=\text{O}$ bonds.

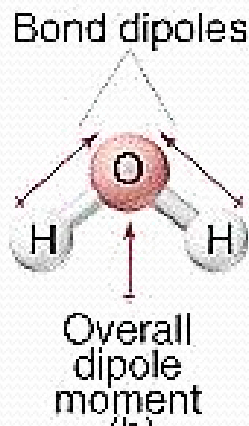
Dipole Moments of polyatomic molecules

- Does the fact that both CO bonds are polar mean that the CO₂ molecule is polar? Not necessarily, why?
- The bond moment is a vector quantity, which means that it has both magnitude and direction. The measured dipole moment is equal to the vector sum of the bond moments.
- The two bond moments in CO₂ are equal in magnitude but they point in opposite directions in a linear CO₂ molecule, so the resultant dipole moment would be zero. So the two bond moments cancel each other.



Dipole Moments of polyatomic molecules

- Now let's consider H_2O , which is a bent molecule with two polar bonds. The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge. Both the bonds are identical, so the bond dipoles are equal in magnitude.
- Because the molecule is bent, however, the bond dipoles do not directly oppose each other and therefore do not cancel each other. Hence, the water molecule has an overall dipole moment.



Writing Lewis Structures

- 1. Write the skeletal structure of the compound**, using chemical symbols and placing bonded atoms next to one another. In general, the least electronegative atom occupies the central position. Hydrogen and fluorine usually occupy the terminal (end) positions in the Lewis structure.
- 2. Count the total number of valence electrons present.** For polyatomic anions, add the number of negative charges to that total. For polyatomic cations, we subtract the number of positive charges from this total.
- 3. Draw a single covalent bond between the central atom and each of the surrounding atoms. Complete the octets of the atoms** bonded to the central atom except a hydrogen atom is complete with only two electrons. Electrons belonging to the central or surrounding atoms must be shown as lone pairs if they are not involved in bonding. The total number of electrons to be used is that determined in step 2.
- 4. After completing steps 1–3, if the central atom has fewer than eight electrons, try adding double or triple bonds between the surrounding atoms and the central atom**, using lone pairs from the surrounding atoms to complete the octet of the central atom.

Examples

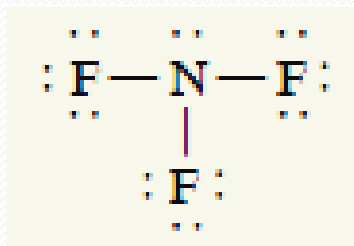
- Write the Lewis structure for nitrogen trifluoride (NF₃)?

Step 1: The N atom is less electronegative than F, so the skeletal structure of NF₃ is



Step 2: There are $5 + (3 \times 7) = 26$, valence electrons to account for in NF₃.

Step 3: We draw a single covalent bond between N and each F, and complete the octets for the F atoms. We place the remaining two electrons on N.



Examples

- Write the Lewis structure for nitric acid (HNO_3)?

Step 1: The skeletal structure of HNO_3 is

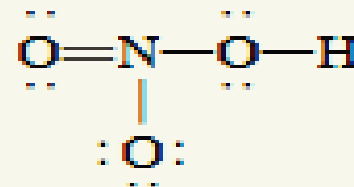


Step 2: There are $5 + (3 \times 6) + 1 = 24$, valence electrons to account for in HNO_3 .

Step 3: We draw a single covalent bond between N and each of the three O atoms and between one O atom and the H atom. Then we fill in electrons to comply with the octet rule for the O atoms:

Step 4: We see that this structure satisfies the octet rule for all the O atoms but not for the N atom. The N atom has only six electrons. Therefore, we move a lone pair from one of the end O atoms to form another bond with N.

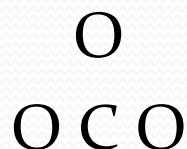
Now the octet rule is also satisfied for the N atom.



Examples

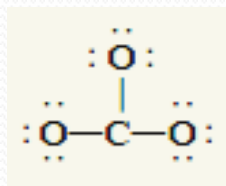
- Write the Lewis structure for the carbonate ion $(\text{CO}_3)^{-2}$

Step 1: C is less electronegative than O. Therefore, it is most likely to occupy a central position as follows:



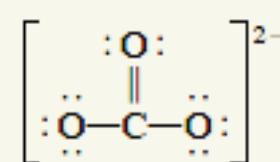
Step 2: Thus, the total number of electrons is $4 + (3 \times 6) + 2 = 24$.

Step 3: We draw a single covalent bond between C and each O and comply with the octet rule for the O atoms. This structure shows all 24 electrons.



Step 4: Although the octet rule is satisfied for the O atoms, it is not for the C atom. Therefore, we move a lone pair from one of the O atoms to form another bond with C.

Now the octet rule is also satisfied for the C atom.



Formal Charges

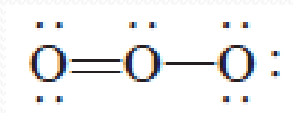
- Sometimes there is more than one acceptable Lewis structure for a given species. In such cases, we can often select the most plausible Lewis structure by using formal charges.
- An atom's formal charge is the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.
- To assign the number of electrons on an atom in a Lewis structure, we proceed as follows:
 1. All the atom's nonbonding electrons (lone pairs) are assigned to the atom.
 2. We break the bond(s) between the atom and other atom(s) and assign half of the bonding electrons to the atom.

Rules of Formal Charges

- When you write formal charges, these rules are helpful:
 1. For molecules, the sum of the formal charges must add up to zero because molecules are electrically neutral species.
 2. For cations, the sum of the formal charges must equal the positive charge.
 3. For anions, the sum of the formal charges must equal the negative charge.
 4. A Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
 5. Lewis structures with large formal charges (-2, -3, and/or +2, +3, and so on) are less plausible than those with small formal charges.
 6. Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

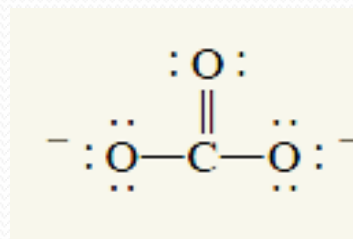
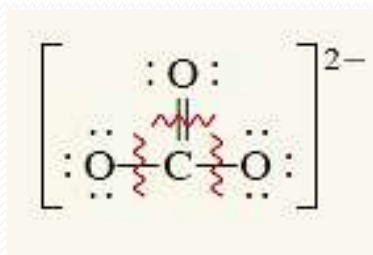
Examples

- The ozone molecule (O_3).



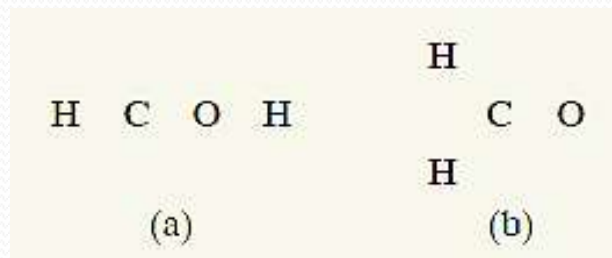
	$\ddot{\text{O}} \text{---} \ddot{\text{O}} \text{---} \ddot{\text{O}} :$		
Valence e^-	6	6	6
e^- assigned to atom	6	5	7
<hr/>			
Difference (formal charge)	0	+1	-1

- The carbonate ion (CO_3)⁻²

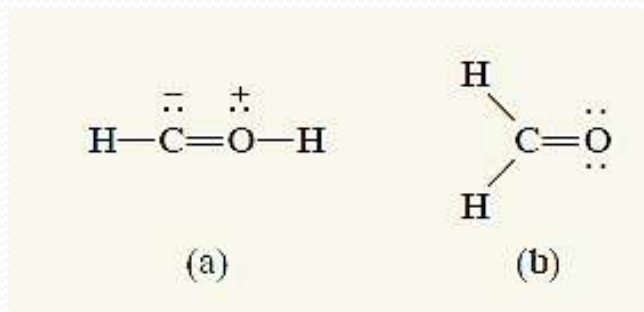


Examples

- Formaldehyde (CH_2O). The two possible skeletal structures



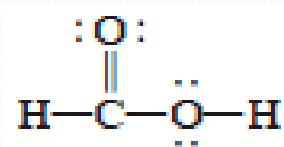
- Although both structures satisfy the octet rule, (b) is the more likely structure because it carries no formal charges, and because in (a) the more electronegative ion (O) carry a positive charge while the less electronegative ion carry a negative charge (less plausible).



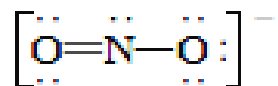
Problems

- Write the Lewis structure and formal charges for the following compounds:

A- Formic acid (HCOOH).



B- The nitrite ion (NO_2)⁻.



C- Carbon disulfide (CS_2).

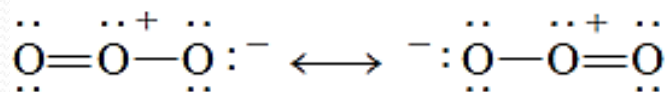


D- Ammonium ion (NH_4)⁺.

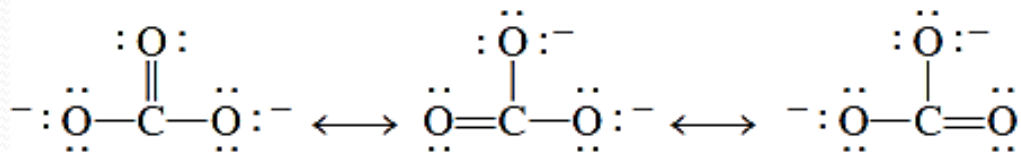
Resonance

- A resonance structure is one of two or more Lewis structures for a particular molecule that cannot be represented accurately by only one Lewis structure. For example:

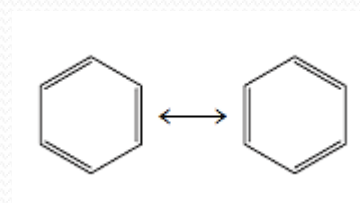
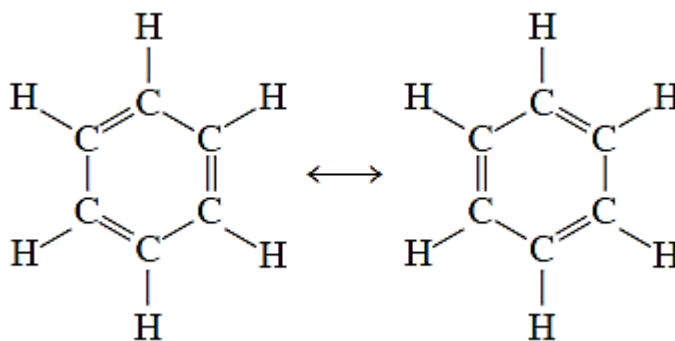
1- Ozone:



2- Carbonate ion:



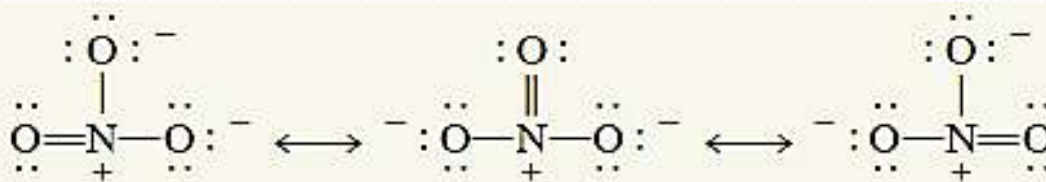
3- Benzene:



- The double-headed arrow indicates that the structures shown are resonance structures.

Resonance

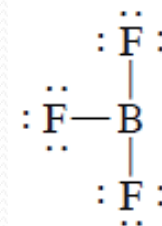
- ***Remember this important rule for drawing resonance structures:*** The positions of electrons (that is, bonds), but not those of atoms, can be rearranged in different resonance structures. In other words, the same atoms must be bonded to one another in all the resonance structures for a given species.
- Draw resonance structures (including formal charges) for the nitrate ion, NO_3^-



Exceptions to the Octet Rule

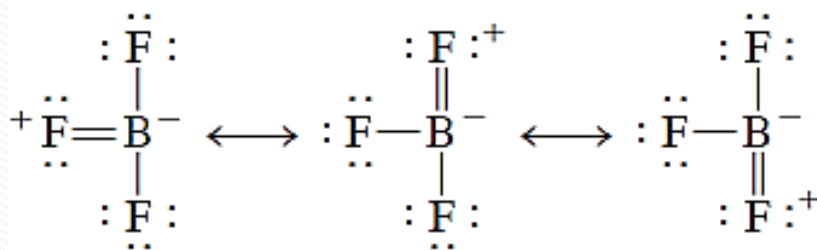
1- The Incomplete Octet

- In some compounds, the number of electrons surrounding the central atom in a stable molecule is fewer than eight.
- The Lewis structure of BeH_2 is
- Elements in Group 3A, particularly boron and aluminum, also tend to form compounds in which they are surrounded by fewer than eight electrons.
- The Lewis structure of boron trifluoride is

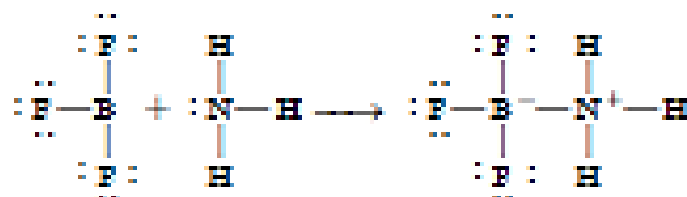


Note

- The following resonance structures all contain a double bond between B and F and satisfy the octet rule for boron:



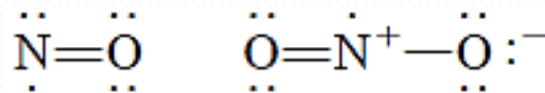
- However, in each case the negative formal charge is placed on the B atom and the positive formal charge on the F atom.*
- Although boron trifluoride is stable, it readily reacts with ammonia to allow boron to reach the octet rule.



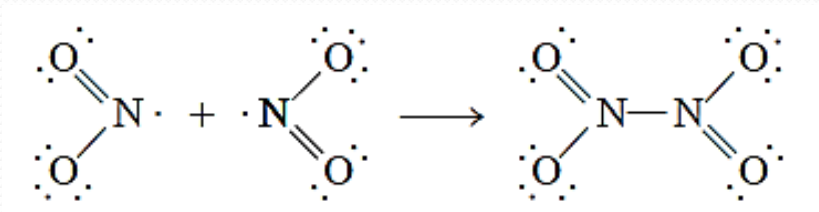
Exceptions to the Octet Rule

2. Odd-Electron Molecules

- Some molecules contain an odd number of electrons. Among them are nitric oxide (NO) and nitrogen dioxide (NO₂): the octet rule clearly cannot be satisfied for all the atoms in any of these molecules.



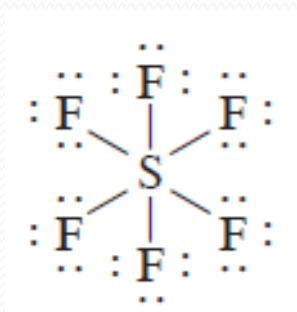
- Odd-electron molecules are sometimes called radicals. Many radicals are highly reactive. The reason is that there is a tendency for the unpaired electron to form a covalent bond with an unpaired electron on another molecule. For example, when two nitrogen dioxide molecules collide, they form dinitrogen tetroxide in which the octet rule is satisfied for both the N and O atoms:



Exceptions to the Octet Rule

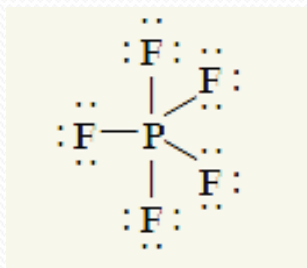
3- The Expanded Octet

- Atoms of the second-period elements cannot have more than eight valence electrons around the central atom, but atoms of elements in and beyond the third period of the periodic table form some compounds in which more than eight electrons surround the central atom.
- One compound in which there is an expanded octet is sulfur hexafluoride, a very stable compound.

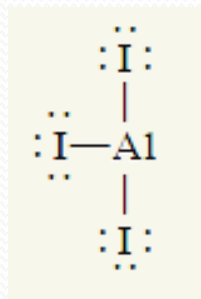


Examples

- Draw the Lewis structure for phosphorus pentafluoride (PF_5).



- Draw the Lewis structure for aluminum triiodide (AlI_3).



- Draw the Lewis structure for POCl_3 .

Bond enthalpy

- The stability and strength of a covalent bond is measured in terms of its bond enthalpy, which is the enthalpy change required to break a particular bond in 1 mole of gaseous molecules.
- As stated earlier, triple bonds are stronger than double bonds, which, in turn, are stronger than single bonds.

Bond	Bond Enthalpy
H—F	568.2
H—Cl	431.9
H—Br	366.1
H—I	298.3
C—H	414
C—C	347
C=C	620
C≡C	812
C—N	276
C=N	615
C≡N	891

Nomenclature

- Naming binary molecular compounds is similar to naming binary ionic compounds.
- We place the name of the first element in the formula first, and the second element is named by adding “-ide” to the root of the element name. Some examples are:
 - HCl: Hydrogen chloride.
 - SiC: Silicon carbide
 - HBr: Hydrogen bromide

Greek Prefixes Used in Naming Molecular Compounds

Prefix	Meaning
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Nomenclature

- It is quite common for one pair of elements to form several different compounds.
- In these cases, confusion in naming the compounds is avoided by the use of Greek prefixes to denote the number of atoms of each element present.
- Consider these examples:
 - CO Carbon monoxide
 - SO₂ Sulfur dioxide
 - NO₂ Nitrogen dioxide
 - CO₂ Carbon dioxide
 - SO₃ Sulfur trioxide
 - N₂O₄ Dinitrogen tetroxide

Notes

- The prefix “mono-” may be omitted for the first element. For example, PCl_3 is named phosphorus trichloride, not monophosphorus trichloride. Thus, the absence of a prefix for the first element usually means that only one atom of that element is present in the molecule.
- For oxides, the ending “a” in the prefix is sometimes omitted. For example, N_2O_4 may be called dinitrogen tetroxide rather than dinitrogen tetraoxide.

Nomenclature

- Exceptions to the use of Greek prefixes are molecular compounds containing hydrogen.
- Traditionally, many of these compounds are called either by their common, nonsystematic names or by names that do not specifically indicate the number of H atoms present:

B_2H_6 Diborane

PH_3 Phosphine

CH_4 Methane

H_2O Water

SiH_4 Silane

H_2S Hydrogen sulfide

NH_3 Ammonia

- Note that even the order of writing the elements in the formulas is irregular. These examples show that H is written first in water and hydrogen sulfide, whereas H is written last in the other compounds.

Problems

- Name the following molecular compounds:

(a) SiCl_4 (b) P_4O_{10} (c) NF_3 and (d) Cl_2O_7 .

- Write chemical formulas for the following molecular compounds:

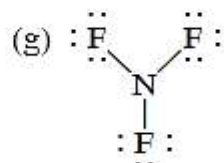
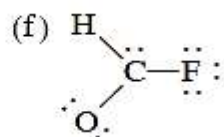
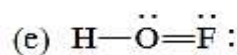
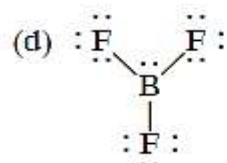
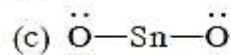
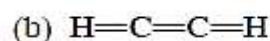
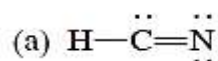
(a) carbon disulfide (b) disilicon hexabromide
(c) sulfur tetrafluoride (d) dinitrogen pentoxide.

9.41 Write Lewis structures for these molecules: (a) ICl , (b) PH_3 , (c) P_4 (each P is bonded to three other P atoms), (d) H_2S , (e) N_2H_4 , (f) HClO_3 , (g) COBr_2 (C is bonded to O and Br atoms).

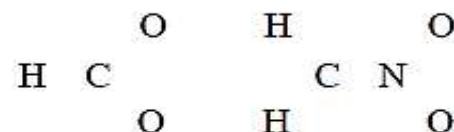
9.42 Write Lewis structures for these ions: (a) O_2^{2-} , (b) C_2^{2-} , (c) NO^+ , (d) NH_4^+ . Show formal charges.

9.43 These Lewis structures are incorrect. Explain what is wrong with each one and give a correct Lewis

structure for the molecule. (Relative positions of atoms are shown correctly.)



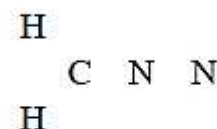
Write Lewis structures for these species, including all resonance forms, and show formal charges: (a) HCO_2^- , (b) CH_2NO_2^- . Relative positions of the atoms are as follows:



Draw three resonance structures for the chlorate ion, ClO_3^- . Show formal charges.

Write three resonance structures for hydrazoic acid, HN_3 . The atomic arrangement is HNNN . Show formal charges.

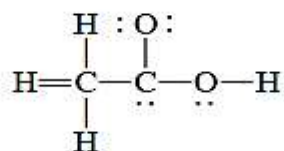
Draw two resonance structures for diazomethane, CH_2N_2 . Show formal charges. The skeletal structure of the molecule is



Draw three reasonable resonance structures for the OCN^- ion. Show formal charges.

Draw three resonance structures for the molecule N_2O in which the atoms are arranged in the order NNO . Indicate formal charges.

9.44 The skeletal structure of acetic acid in this structure is correct, but some of the bonds are wrong. (a) Identify the incorrect bonds and explain what is wrong with them. (b) Write the correct Lewis structure for acetic acid.



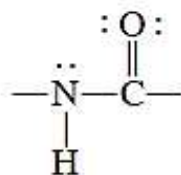
Write a Lewis structure for SbCl_5 . Is the octet rule obeyed in this molecule?

Write Lewis structures for SeF_4 and SeF_6 . Is the octet rule satisfied for Se?

Write Lewis structures for BrF_3 , ClF_5 , and IF_7 . Identify those in which the octet rule is not obeyed.

Write three reasonable resonance structures of the azide ion N_3^- in which the atoms are arranged as NNN. Show formal charges.

The amide group plays an important role in determining the structure of proteins:

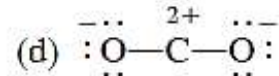
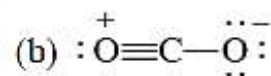
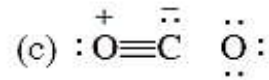
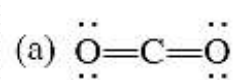


Draw another resonance structure of this group. Show formal charges.

Draw four reasonable resonance structures for the PO_3F^{2-} ion. The central P atom is bonded to the three O atoms and to the F atom. Show formal charges.

Draw reasonable resonance structures for these sulfur-containing ions: (a) HSO_4^- , (b) SO_4^{2-} , (c) HSO_3^- , (d) SO_3^{2-} .

Several resonance structures of the molecule CO_2 are given here. Explain why some of them are likely to be of little importance in describing the bonding in this molecule.



Oxygen forms three types of ionic compounds in which the anions are oxide (O^{2-}), peroxide (O_2^{2-}), and superoxide (O_2^-). Draw Lewis structures of these ions.

Write three resonance structures for the isocyanate ion (CNO^-). Rank them in importance.

Be sure before naming that the compound is ionic or molecular (covalent bonded)

Naming Compounds

Problems

2.47 Name these compounds: (a) Na_2CrO_4 , (b) K_2HPO_4 , (c) HBr (gas), (d) HBr (in water), (e) Li_2CO_3 , (f) $\text{K}_2\text{Cr}_2\text{O}_7$, (g) NH_4NO_2 , (h) PF_3 , (i) PF_5 , (j) P_4O_6 , (k) CdI_2 , (l) SrSO_4 , (m) $\text{Al}(\text{OH})_3$, (n) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

2.48 Name these compounds: (a) KClO , (b) Ag_2CO_3 , (c) FeCl_2 , (d) KMnO_4 , (e) CsClO_3 , (f) HIO , (g) FeO , (h) Fe_2O_3 , (i) TiCl_4 , (j) NaH , (k) Li_3N , (l) Na_2O , (m) Na_2O_2 , (n) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

2.49 Write the formulas for these compounds: (a) rubidium nitrite, (b) potassium sulfide, (c) perbromic acid, (d) magnesium phosphate, (e) calcium hydrogen phosphate, (f) boron trichloride, (g) iodine heptafluoride, (h) ammonium sulfate, (i) silver perchlorate, (j) iron(III) chromate, (k) calcium sulfate dihydrate.

2.50 Write the formulas for these compounds: (a) copper(I) cyanide, (b) strontium chlorite, (c) perchloric acid, (d) hydroiodic acid, (e) disodium ammonium phosphate, (f) lead(II) carbonate, (g) tin(II) fluoride, (h) tetraphosphorus decasulfide, (i) mercury(II) oxide, (j) mercury(I) iodide, (k) cobalt(II) chloride hexahydrate.