1. HOW TO WRITE LEWIS STRUCTURES AND CALCULATE FORMAL CHARGES

The ability to construct Lewis structures is fundamental to writing or understanding organic reaction mechanisms. It is particularly important because lone pairs of electrons frequently are crucial to the mechanism but often are omitted from structures appearing in the chemical literature.

There are two methods commonly used to show Lewis structures. One shows all electrons as dots. The other shows all bonds (two shared electrons) as lines and all unshared electrons as dots.

A. Determining the Number of Bonds

Hint 1.1

To facilitate the drawing of Lewis structures, estimate the number of bonds.

For a stable structure with an even number of electrons, the number of bonds is given by the equation:

(Electron Demand − Electron Supply) / 2 = Number of Bonds

The electron demand is two for each hydrogen and eight for all other atoms usually considered in organic chemistry. (The tendency of most atoms to acquire eight valence electrons is known as the octet rule.) For elements in group IIIA (e.g., B, Al, Ga), the electron demand is six. Other exceptions are noted, as they arise, in examples and problems.

For neutral molecules, the contribution of each atom to the electron supply is the number of valence electrons of the neutral atom. (This is the same as the group number of the element when the periodic table is divided into eight groups.) For ions, the electron supply is decreased by one for each positive charge of a cation and is increased by one for each negative charge of an anion.

Use the estimated number of bonds to draw that number of two-electron bonds in your structure. This may involve drawing a number of double and triple bonds (see the following section).

B. Determining the Number of Rings and / or π Bonds (Degree of Unsaturation)

The total number of rings and/or π bonds can be calculated from the molecular formula, bearing in mind that in an acyclic saturated hydrocarbon the number of hydrogens is $2n + 2$, where n is the number of carbon atoms.

Each time a ring or π bond is formed, there will be two fewer hydrogens needed to complete the structure.

Hint 1.2

On the basis of the molecular formula, the degree of unsaturation for a hydrocarbon is calculated as $(2m + 2 - n)/2$, where m is the number of carbons and n is the number of hydrogens. The number calculated is the number of rings and / or π bonds. For molecules containing heteroatoms, the degree of unsaturation can be calculated as follows:

Nitrogen: For each nitrogen atom, subtract 1 from n.
Halogens: For each halogen atom, add 1 to n.
Oxygen: Use the formula for hydrocarbons.

This method cannot be used for molecules in which there are atoms like sulfur and phosphorus whose valence shell can expand beyond eight.

Example 1.1. ***Calculate the number of rings and/or π bonds corresponding to each of the following molecular formulas.***

a. $C_2H_2Cl_2Br_2$
There are a total of four halogen atoms. Using the formula $(2m + 2 - n)/2$, we calculate the degree of unsaturation to be $[2(2) + 2 - (2 + 4)]/2 = 0$.

b. C_2H_3N
There is one nitrogen atom, so the degree of unsaturation is $[2(2) + 2 - (3 - 1)] = 2$.

C. Drawing the Lewis Structure

Start by drawing the skeleton of the molecule, using the correct number of rings or π bonds, then attach hydrogen atoms to satisfy the remaining valences. For organic molecules, the carbon skeleton frequently is given in an abbreviated form.

Once the atoms and bonds have been placed, add lone pairs of electrons to give each atom a total of eight valence electrons. When this process is complete, there should be two electrons for hydrogen, six for B, Al, or Ga, and eight for all other atoms. The total number of valence electrons for each element in the final representation of a molecule is obtained by counting each electron around the element as one electron, even if the electron is shared with another atom. (This should not be confused with counting electrons for charges or formal charges; see Section 1.D.) The number of valence electrons around each atom equals the electron demand. Thus, when

the number of valence electrons around each element equals the electron demand, the number of bonds will be as calculated in Hint 1.1.

Atoms of higher atomic number can expand the valence shell to more than eight electrons. These atoms include sulfur, phosphorus, and the halogens (except fluorine).

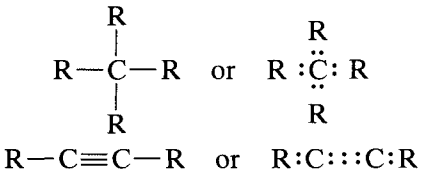
Hint 1.3

When drawing Lewis structures, make use of the following common structural features.

1. Hydrogen is always on the periphery because it forms only one covalent bond.

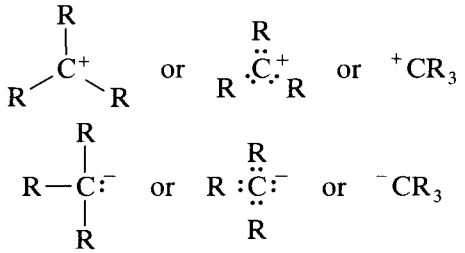
2. Carbon, nitrogen, and oxygen exhibit characteristic bonding patterns. In the examples that follow, the R groups may be hydrogen, alkyl, or aryl groups, or any combination of these. These substituents do not change the bonding pattern depicted.

(a) Carbon in neutral molecules usually has four bonds. The four bonds may all be σ bonds, or they may be various combinations of σ and π bonds (i.e., double and triple bonds).

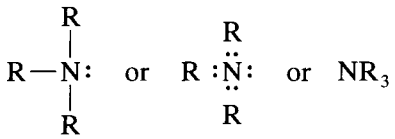


There are exceptions to the rule that carbon has four bonds. These include CO, isonitriles (RNC), and carbenes (neutral carbon species with six valence electrons; see Chapter 4).

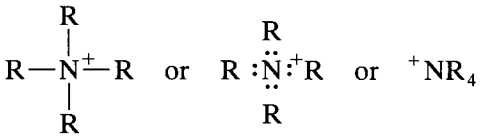
(b) Carbon with a single positive or negative charge has three bonds.



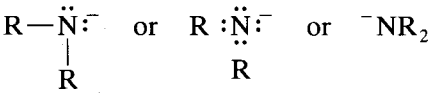
(c) Neutral nitrogen, with the exception of nitrenes (see Chapter 4), has three bonds and a lone pair.



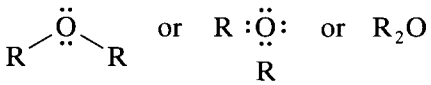
(d) Positively charged nitrogen has four bonds and a positive charge; exceptions are nitrenium ions (see Chapter 4).



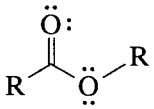
(e) Negatively charged nitrogen has two bonds and two lone pairs of electrons.



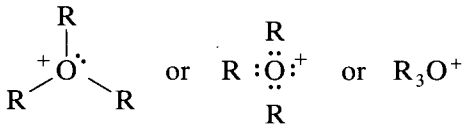
(f) Neutral oxygen has two bonds and two lone pairs of electrons.



(g) Oxygen–oxygen bonds are uncommon; they are present only in peroxides, hydroperoxides, and diacyl peroxides (see Chapter 5). The formula, RCO_2R, implies the following structure:



(h) Positive oxygen usually has three bonds and a lone pair of electrons; exceptions are the very unstable oxenium ions, which contain a single bond to oxygen and two lone pairs of electrons.



3. Sometimes a phosphorus or sulfur atom in a molecule is depicted with 10 electrons. Because phosphorus and sulfur have *d* orbitals, the outer shell can be expanded to accommodate more than eight electrons. If the shell, and therefore the demand, is expanded to 10 electrons, one more bond will be calculated by the equation used to calculate the number of bonds. See Example 1.5.

In the literature, a formula often is written to indicate the bonding skeleton for the molecule. This severely limits, often to just one, the number of possible structures that can be written.

Example 1.2. ***The Lewis structure for acetaldehyde, CH_3CHO.***

	electron supply	electron demand
2C	8	16
4H	4	8
1O	6	8
	18	32

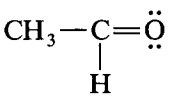
The estimated number of bonds is $(32 - 18)/2 = 7$.

The degree of unsaturation is determined by looking at the corresponding saturated hydrocarbon C_2H_6. Because the molecular formula for acetaldehyde is C_2H_6O and there are no nitrogen, phosphorus, or halogen atoms, the degree of unsaturation is $(6 - 4)/2 = 1$. There is either one double bond or one ring.

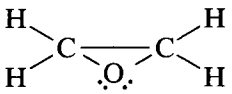
The notation CH_3CHO indicates that the molecule is a straight-chain compound with a methyl group, so we can write

$$CH_3—C—O$$

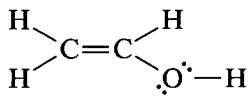
We complete the structure by adding the remaining hydrogen atom and the remaining valence electrons to give



Note that if we had been given only the molecular formula C_2H_6O, a second structure could be drawn



A third possible structure differs from the first only in the position of the double bond and a hydrogen atom.



This enol structure is unstable relative to acetaldehyde and is not isolable, although in solution small quantities exist in equilibrium with acetaldehyde.

D. Formal Charge

Even in neutral molecules, some of the atoms may have charges. Because the total charge of the molecule is zero, these charges are called formal charges to distinguish them from ionic charges.

Formal charges are important for two reasons. First, determining formal charges helps us pinpoint reactive sites within the molecule and can help us

in choosing plausible mechanisms. Also, formal charges are helpful in determining the relative importance of resonance forms (see Section 5).

Hint 1.4

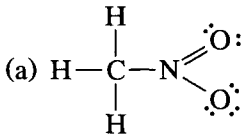
To calculate formal charges, use the completed Lewis structure and the following formula:

$$\text{Formal Charge} = \text{Number of Valence Shell Electrons} - (\text{Number of Unshared Electrons} + \text{Half the Number of Shared Electrons})$$

The formal charge is zero if the number of unshared electrons, plus the number of shared electrons divided by two, is equal to the number of valence shell electrons in the neutral atom (as ascertained from the group number in the periodic table). As the number of bonds formed by the atom increases, so does the formal charge. Thus, the formal charge of nitrogen in $(CH_3)_3\ N$ is zero, but the formal charge on nitrogen in $(CH_3)_4N^+$ is +1.

Note: *An atom always "owns" all unshared electrons.* This is true both when counting the number of electrons for determining formal charge and in determining the number of valence electrons. However, in determining *formal charge*, an atom "owns" *half of the bonding electrons*, whereas in determining the *number of valence electrons*, the atom "owns" *all the bonding electrons*.

Example 1.3. ***Calculation of formal charge for the structures shown.***

(a) 

The formal charges are calculated as follows:

Hydrogen
1 (no. of valence electrons) − 2/2 (2 bonding electrons divided by 2) = 0

Carbon
4 (no. of valence electrons) − 8/2 (8 bonding electrons divided by 2) = 0

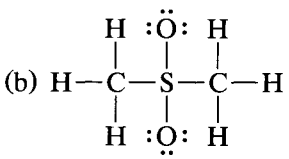
Nitrogen
5 − 8/2 (8 bonding electrons) = +1

There are two different oxygen atoms:

Oxygen (double bonded)
$6 - 4$ (unshared electrons) $- 4/2$ (4 bonding electrons) $= 0$

Oxygen (single bonded)
$6 - 6$ (unshared electrons) $- 2/2$ (2 bonding electrons) $= -1$.

(b)



The calculations for carbon and hydrogen are the same as those for part (a).

Formal charge for each oxygen:
$6 - 6 - (2/2) = -1$

Formal charge for sulfur:
$6 - 0 - (8/2) = +2$

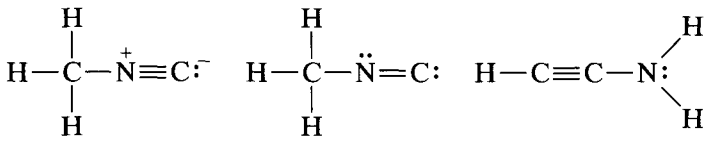
Example 1.4. ***Write possible Lewis structures for C_2H_3N.***

	electron supply	electron demand
3H	3	6
2C	8	16
1N	5	8
	16	30

The estimated number of bonds is $(30 - 16)/2 = 7$.

As calculated in Example 1.1, this molecular formula represents molecules that contain two rings and/or π bonds. However, because it requires a minimum of three atoms to make a ring, and since hydrogen cannot be part of a ring because each hydrogen forms only one bond, two rings are not possible. Thus, all structures with this formula will have either a ring and a π bond or two π bonds. Because no information is given on the order in which the carbons and nitrogen are bonded, all possible bonding arrangements must be considered.

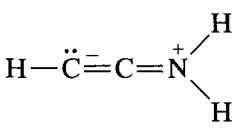
Structures **1-1** through **1-9** depict some possibilities. The charges shown in the structures are formal charges. When charges are not shown, the formal charge is zero.



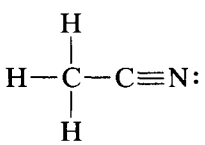
1-1

1-2

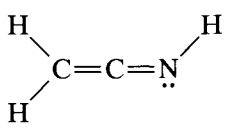
1-3



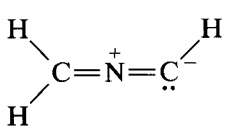
1-4



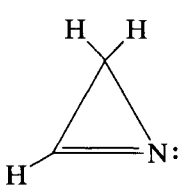
1-5



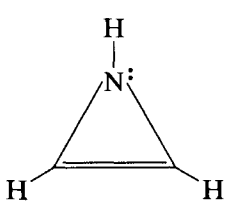
1-6



1-7



1-8



1-9

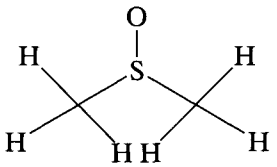
Structure **1-1** contains seven bonds using 14 of the 16 electrons of the electron supply. The remaining two electrons are supplied as a lone pair of electrons on the carbon, so that both carbons and the nitrogen have eight electrons around them. This structure is unusual because the right-hand carbon does not have four bonds to it. Nonetheless, isonitriles such as **1-1** (see Hint 1.3) are isolable. Structure **1-2** is a resonance form of **1-1**. (For a discussion of resonance forms, see Section 5.) Traditionally, **1-1** is written instead of **1-2**, because both carbons have an octet in **1-1**. Structures **1-3** and **1-4** represent resonance forms for another isomer. When all the atoms have an octet of electrons, a neutral structure like **1-3** is usually preferred to a charged form like **1-4** because the charge separation in **1-4** makes this a higher energy (and, therefore, less stable) species. Alternative forms with greater charge separation can be written for structures **1-5** to **1-9**. Because of the strain energy of three-membered rings and cumulated double bonds, **1-6** through **1-9** are expected to be quite unstable.

It is always a good idea to check your work by counting the number of electrons shown in the structure. The number of electrons you have drawn must be equal to the supply of electrons.

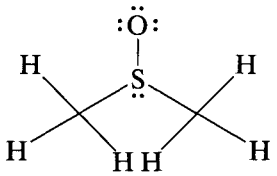
Example 1.5. ***Write two possible Lewis structures for dimethyl sulfoxide, $(CH_3)_2SO$, and calculate formal charges for all atoms in each structure.***

	electron supply	electron demand
2C	8	16
6H	6	12
1S	6	8
1O	6	8
	26	44

According to Hint 1.1, the estimated number of bonds is $(44 - 26)/2 = 9$. Also, Hint 1.3 calculates 0 rings and/or π bonds. The way the formula is given indicates that both methyl groups are bonded to the sulfur, which is also bonded to oxygen. Drawing the skeleton gives the following:



The nine bonds use up 18 electrons from the total supply of 26. Thus there are eight electrons (four lone pairs) to fill in. In order to have octets at sulfur and oxygen, three lone pairs are placed on oxygen and one lone pair on sulfur.



1-10

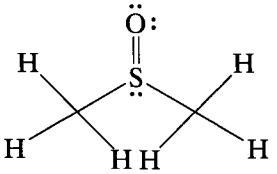
The formal charge on oxygen in **1-10** is -1. There are six unshared electrons and $2/2 = 1$ electron from the pair being shared. Thus, the number of electrons is seven, which is one more than the number of valence electrons for oxygen.

The formal charge on sulfur in **1-10** is $+1$. There are two unshared electrons and $6/2 = 3$ electrons from the pairs being shared. Thus, the number of electrons is five, which is one less than the number of valence electrons for sulfur.

All of the other atoms in **1-10** have a formal charge of 0.

There is another reasonable structure, **1-11**, for dimethyl sulfoxide, which corresponds to an expansion of the valence shell of sulfur to accommodate 10 electrons. Note that our calculation of electron demand counted eight electrons for sulfur. The 10-electron sulfur has an electron demand of 10 and

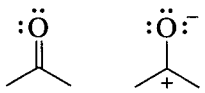
leads to a total demand of 46 rather than 44 and the calculation of 10 bonds rather than 9 bonds. All atoms in this structure have zero formal charge.



1-11

Hint 1.3 does not predict the π bond in this molecule, because the valence shell of sulfur has expanded beyond eight. Structures **1-10** and **1-11** correspond to different possible resonance forms for dimethyl sulfoxide (see Section 5), and each is a viable structure.

Why don't we usually write just one of these two possible structures for dimethyl sulfoxide, as we do for a carbonyl group? In the case of the carbonyl group, we represent the structure by a double bond between carbon and oxygen, as in structure **1-12**.



1-12 **1-13**

In structure **1-12**, both carbon and oxygen have an octet and neither carbon nor oxygen has a charge, whereas in structure **1-13**, carbon does not have an octet and both carbon and oxygen carry a charge. Taken together, these factors make structure **1-12** more stable and therefore more likely. Looking at the analogous structures for dimethyl sulfoxide, we see that in structure **1-10** both atoms have an octet and both are charged, whereas in structure **1-11**, sulfur has 10 valence electrons, but both sulfur and oxygen are neutral. Thus, neither **1-10** nor **1-11** is clearly favored, and the structure of dimethyl sulfoxide is best represented by a combination of structures **1-10** and **1-11**.

Note: No hydrogen atoms are shown in structures **1-12** and **1-13**. In representing organic molecules, it is assumed that the valence requirements of carbon are satisfied by hydrogen unless otherwise specified. Thus, in structures **1-12** and **1-13**, it is understood that there are six hydrogen atoms, three on each carbon.

Hint 1.5

When the electron supply is an odd number, the resulting unpaired electron will produce a radical; that is, the valence shell of one atom, other than hydrogen, will not be completed. This atom will have seven electrons instead of eight. Thus, if