

5.4: Resonance and Formal Charge

Key Concept Video Resonance and Formal Charge

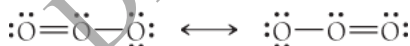
We need two additional concepts to write the best possible Lewis structures for a large number of compounds. The concepts are *resonance*, used when two or more valid Lewis structures can be drawn for the same compound, and *formal charge*, an electron bookkeeping system that allows us to discriminate between alternative Lewis structures.

Resonance

For some molecules, we can write more than one valid Lewis structure. For example, consider writing a Lewis structure for O_3 . The following two Lewis structures, with the double bond on alternate sides, are equally correct:



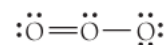
In cases such as this—where we can write two or more valid Lewis structures for the same molecule—we find that, in nature, the molecule exists as an *average* of the two Lewis structures. Both of the Lewis structures for O_3 predict that O_3 contains two different bonds (one double bond and one single bond). However, when we experimentally examine the structure of O_3 , we find that the bonds in the O_3 molecule are equivalent and that each bond is intermediate in strength and length between a double bond and single bond. We account for this by representing the molecule with both structures, called *resonance structures*, with a double-headed arrow between them:

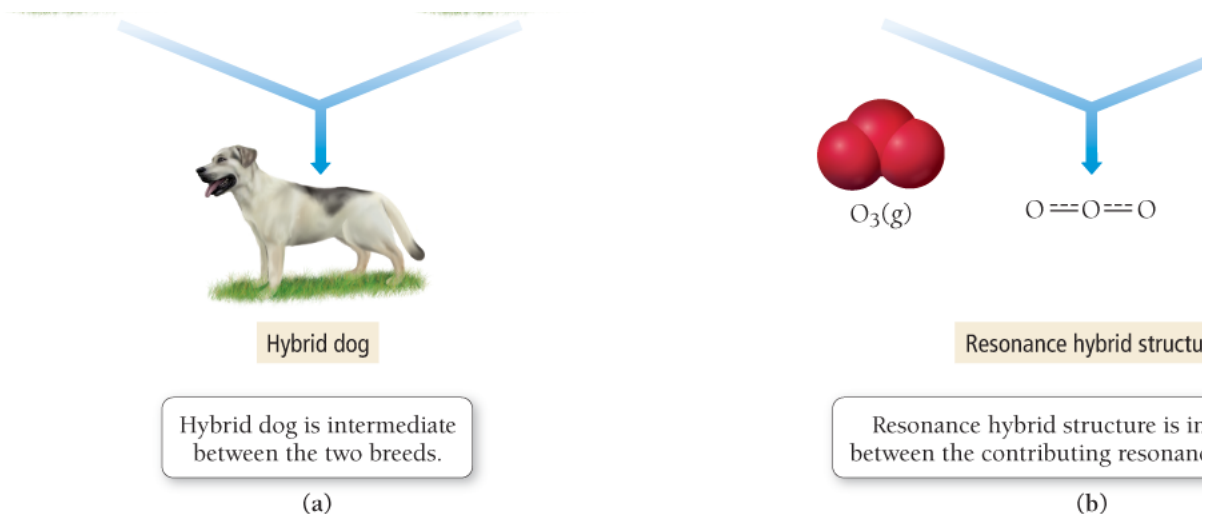


A **resonance structure** is one of two or more Lewis structures that have the same skeletal formula (the atoms are in the same locations) but different electron arrangements. The actual structure of the molecule is intermediate between the two (or more) resonance structures and is called a **resonance hybrid**. The term *hybrid* comes from breeding and means the offspring of two animals or plants of different varieties or breeds. If we breed a Labrador retriever with a German shepherd, we get a *hybrid* that is intermediate between the two breeds (Figure 5.6a). Similarly, the actual structure of a resonance hybrid is intermediate between the two resonance structures (Figure 5.6b). The only structure that actually exists is the hybrid structure. The individual resonance structures do not exist and are merely a convenient way to describe the actual structure. Notice that the actual structure of ozone has two equivalent bonds and a bent geometry (we discuss molecular geometries in more detail later in this chapter).

Figure 5.6 Hybridization

Just as the offspring of two different dog breeds is a hybrid that is intermediate between the two breeds (a), the structure of a resonance hybrid is intermediate between that of the contributing resonance structures (b).





The concept of resonance is an adaptation of the Lewis model that helps account for the complexity of actual molecules. In the Lewis model, electrons are *localized* either on one atom (lone pair) or between atoms (bonding pair). However, in nature, electrons in molecules are often *delocalized* over several atoms or bonds. The delocalization of electrons lowers their energy; it stabilizes them (for reasons that are beyond the scope of this book). Resonance depicts two or more structures with the electrons in different places in an attempt to more accurately reflect the delocalization of electrons. In the real hybrid structure—an average between the resonance structures—the electrons are more spread out (or delocalized) than in any of the resonance structures. The resulting stabilization of the electrons (that is, the lowering of their potential energy due to delocalization) is sometimes called *resonance stabilization*. Resonance stabilization makes an important contribution to the stability of many molecules.

Example 5.5 Writing Resonance Structures

Write the Lewis structure for the NO_3^- ion. Include resonance structures.

SOLUTION

Begin by writing the skeletal structure. Since nitrogen is the least electronegative atom, put it in the central position.



Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons for each atom and adding 1 electron for the 1^- charge.

$$\begin{aligned} &\text{Total number of electrons for Lewis structure} \\ &= (\text{number of valence } e^- \text{ in N}) + 3 (\text{number of valence } e^- \text{ in O}) + 1 \\ &= 5 + 3(6) + 1 \\ &= 24 \end{aligned}$$

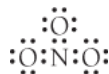
Add 1 e^- to account for 1^- charge of ion.

Place two bonding electrons between each pair of atoms.



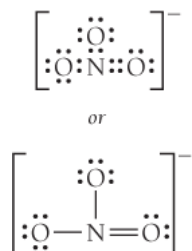
(6 of 24 electrons used)

Distribute the remaining electrons, first to terminal atoms. There are not enough electrons to complete the octet on the central atom.

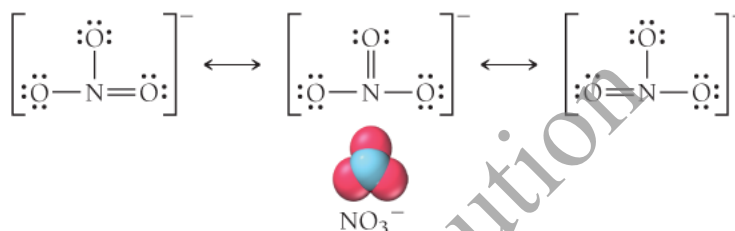


(24 of 24 electrons used)

Form a double bond by moving a lone pair from one of the oxygen atoms into the bonding region with nitrogen. Enclose the structure in brackets and include the charge.



Since the double bond can form equally well with any of the three oxygen atoms, write all three structures as resonance structures. (The actual space-filling model of NO_3^- is shown here for comparison. Note that all three bonds are equal in length.)



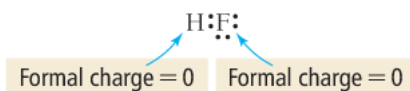
FOR PRACTICE 5.5 Write the Lewis structure for the NO_2^- ion. Include resonance structures.

Interactive Worked Example 5.5 Writing Resonance Structures

In the examples of resonance hybrids that we have examined so far, the contributing structures have been equivalent (or equally valid) Lewis structures. In these cases, the true structure is an equally weighted average of the resonance structures. In some cases, however, we can write resonance structures that are not equivalent. For reasons we cover in the material that follows—such as formal charge, for example—one possible resonance structure may be somewhat better (more closely representative of the actual molecule) than another. In such cases, the true structure is still an average of the resonance structures, but the better resonance structure contributes more to the true structure. In other words, multiple nonequivalent resonance structures may be weighted differently in their contributions to the true overall structure of a molecule (see [Example 5.6](#)).

Formal Charge

Formal charge is a fictitious charge assigned to each atom in a Lewis structure that helps us to distinguish among competing Lewis structures. The **formal charge** of an atom in a Lewis structure is the charge it would have if all bonding electrons were shared equally between the bonded atoms. In other words, formal charge is the calculated charge for an atom in a molecule if we completely ignore the effects of electronegativity. For example, we know that because fluorine is more electronegative than hydrogen, HF has a dipole moment. The hydrogen atom has a slight positive charge, and the fluorine atom has a slight negative charge. However, the *formal charges* of hydrogen and fluorine in HF (the calculated charges if we ignore their differences in electronegativity) are both zero.



We can calculate the formal charge on any atom as the difference between the number of valence electrons in the atom and the number of electrons that it “owns” in a Lewis structure. An atom in a Lewis structure can be thought of as “owning” all of its nonbonding electrons and one-half of its bonding electrons.

$$\text{formal charge} = \text{number of valence electrons} - \left(\text{number of nonbonding electrons} + \frac{1}{2} \text{ number of bonding electrons} \right)$$

So the formal charge of hydrogen in HF is 0:

$$\text{formal charge} = 1 - \left[0 + \frac{1}{2}(2) \right] = 0$$

Number of valence electrons for H Number of electrons that H “owns” in the Lewis structure

Similarly, we calculate the formal charge of fluorine in HF as 0:

$$\text{formal charge} = 7 - \left[6 + \frac{1}{2}(2) \right] = 0$$

Number of valence electrons for F Number of electrons that F “owns” in the Lewis structure

The concept of formal charge is useful because it can help us distinguish between competing skeletal structures or competing resonance structures. In general, these four rules apply:

1. The sum of all formal charges in a neutral molecule must be zero.
2. The sum of all formal charges in an ion must equal the charge of the ion.
3. Small (or zero) formal charges on individual atoms are better than large ones.
4. When formal charge cannot be avoided, negative formal charge should reside on the most electronegative atom.

Let’s apply the concept of formal charge to distinguish between possible skeletal structures for the molecule formed by H, C, and N. The three atoms can bond with C in the center (HCN) or N in the center (HNC). The following table shows the two possible structures and the corresponding formal charges.

	Structure A			Structure B		
	H—C≡N:			H—N≡C:		
number of valence e [−]	1	4	5	1	5	4
− number of nonbonding e [−]	−0	−0	−2	−0	−0	−2
− $\frac{1}{2}$ (number of bonding e [−])	− $\frac{1}{2}(2)$	− $\frac{1}{2}(8)$	− $\frac{1}{2}(6)$	− $\frac{1}{2}(2)$	− $\frac{1}{2}(8)$	− $\frac{1}{2}(6)$
Formal charge	0	0	0	0	+1	−1

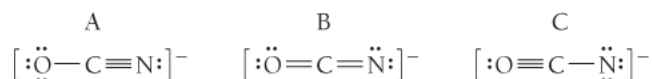
The sum of the formal charges for each of these structures is zero (as it always must be for neutral molecules). However, Structure B has formal charges on both the N atom and the C atom, while Structure A has no formal charges on any atom. Furthermore, in Structure B, the negative formal charge is not on the most electronegative element (nitrogen is more electronegative than carbon). Consequently, Structure A is the better Lewis structure. Since atoms in the middle of a molecule tend to have more bonding electrons and fewer nonbonding electrons, they also tend to have more positive formal charges. Consequently, the best skeletal structure usually has the

least electronegative atom in the central position, as we learned in Step 1 of our procedure for writing Lewis structures in [Section 5.3](#).

Both HCN and HNC exist, but—as we predicted by assigning formal charges—HCN is more stable than HNC.

Example 5.6 Assigning Formal Charges

Assign formal charges to each atom in the resonance forms of the cyanate ion (OCN^-). Which resonance form is likely to contribute most to the correct structure of OCN^- ?



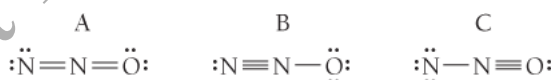
SOLUTION

Calculate the formal charge on each atom by finding the number of valence electrons and subtracting the number of nonbonding electrons and one-half the number of bonding electrons.

	A $\text{[} \ddot{\text{O}} - \text{C} \equiv \text{N:} \text{]}^-$			B $\text{[} \ddot{\text{O}} = \text{C} = \ddot{\text{N}} \text{:} \text{]}^-$			C $\text{[} \text{:O} \equiv \text{C} - \ddot{\text{N}} \text{:} \text{]}^-$		
number of valence e^-	6	4	5	6	4	5	6	4	5
– number of nonbonding e^-	–6	–0	–2	–4	–0	–4	–2	–0	–6
$-\frac{1}{2}(\text{number of bonding } e^-)$	–1	–4	–3	–2	–4	–2	–3	–4	–1
Formal charge	–1	0	0	0	0	–1	+1	0	–2

The sum of all formal charges for each structure is -1 , as it should be for a $1-$ ion. Structures A and B have the least amount of formal charge and are therefore to be preferred over Structure C. Structure A is preferable to B because it has the negative formal charge on the more electronegative atom. You would therefore expect Structure A to make the biggest contribution to the resonance forms of the cyanate ion.

FOR PRACTICE 5.6 Assign formal charges to each atom in the resonance forms of N_2O . Which resonance form is likely to contribute most to the correct structure of N_2O ?



FOR MORE PRACTICE 5.6 Assign formal charges to each of the atoms in the nitrate ion (NO_3^-). The Lewis structure for the nitrate ion is shown in [Example 5.5](#).

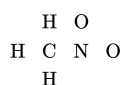
Interactive Worked Example 5.6 Assigning Formal Charges

Example 5.7 Drawing Resonance Structures and Assigning Formal Charge for Organic Compounds

Draw the Lewis structure (including resonance structures) for nitromethane (CH_3NO_2). For each resonance structure, assign formal charges to all atoms that have formal charge.

SOLUTION

Begin by writing the skeletal structure. For organic compounds, the condensed structural formula (in this case CH_3NO_2) indicates how the atoms are connected.

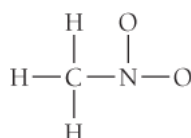


Calculate the total number of electrons for the Lewis structure by summing the valence electrons for each atom.

Total number of electrons for Lewis structure

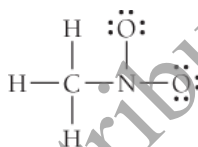
$$\begin{aligned} &= (\# \text{ valence } e^- \text{ in C}) + 3(\# \text{ valence } e^- \text{ in H}) + (\# \text{ valence } e^- \text{ in N}) + \\ &2(\# \text{ valence } e^- \text{ in O}) \\ &= 4 + 3(1) + 5 + 2(6) \\ &= 24 \end{aligned}$$

Place a dash between each pair of atoms to indicate a bond. Each dash counts for two electrons.



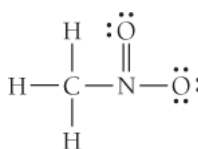
(12 of 24 electrons used)

Distribute the remaining electrons, first to terminal atoms, then to interior atoms.

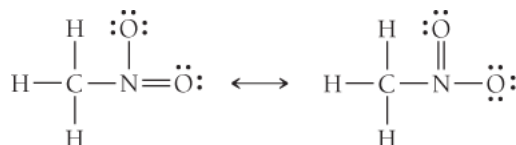


(24 of 24 electrons used)

If there are not enough electrons to complete the octets on the interior atoms, form double bonds by moving lone pair electrons from terminal atoms into the bonding region with interior atoms.



Draw any necessary resonance structures by moving only electron dots. (In this case, you can form a double bond between the nitrogen atom and the other oxygen atom.)



Assign formal charges (fc) to each atom.

$$\text{fc} = \# \text{ valence } e^- - \left(\# \text{ nonbonding } e^- + \frac{1}{2} \# \text{ bonding } e^- \right)$$





Carbon, hydrogen, and the doubly bonded oxygen atoms have no formal charge. Nitrogen has a +1 formal charge $\left[5 - \frac{1}{2}(8)\right]$, and the singly bonded oxygen atom in each resonance structure has a -1 formal charge $\left[6 - \left(6 + \frac{1}{2}(2)\right)\right]$.

FOR PRACTICE 5.7 Draw the Lewis structure (including resonance structures) for diazomethane (CH_2N_2). For each resonance structure, assign formal charges to all atoms that have formal charge.

Not for Distribution

Not for Distribution

Not for Distribution