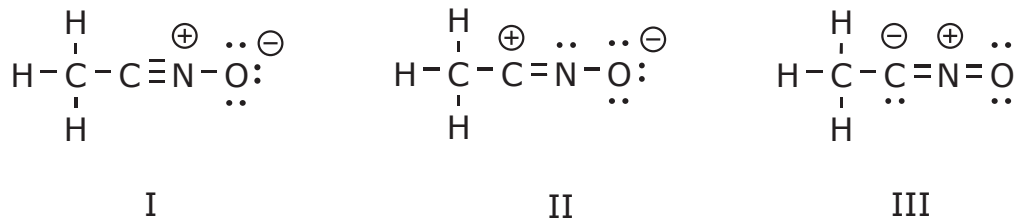


RESONANCE STRUCTURES, ELECTRON MOBILITY AND DELOCALIZATION

I. RESONANCE STRUCTURES. Lewis formulas are misleading in the sense that atoms and electrons are shown as being static. But we know that a given compound can have several valid Lewis formulas. For example CH₃CNO can be represented by at least three different Lewis structures called **resonance forms, or resonance structures**:



However, a stable compound such as the above does not exist in multiple states represented by structures I, or II, or III. The compound exists in a single state called a **hybrid** of all three structures. That is, it contains contributions of all three resonance forms, much like a person might have physical features inherited from each parent to varying degrees.

In the resonance forms shown above the atoms remain in one place, but some electrons have changed locations. The basic bonding pattern that is unique to a specific compound is made up of sigma bonds. This is called the connectivity. The connectivity is the same in all the resonance structures.

II. ELECTRON MOBILITY. Electrons, on the other hand, can be moved around. That is to say, they possess a certain degree of mobility. Further examination of the examples above shows that sigma bonds don't move, for that would amount to destroying the connectivity and therefore the molecule. **Some of the electrons forming part of π -bonds and unshared electron pairs, however, have been moved.**

For example, in structure I a carbon and a nitrogen are joined by a triple bond (that is, a sigma bond and two pi bonds), whereas in structure II the same atoms are joined by a double bond (that is, one sigma bond and one pi bond). Somehow one of the electron pairs that makes up the triple bond in I has been moved to a different location in II, and even in III.

Likewise, a lone pair from oxygen in I and II has been moved in III. The total number of electrons in the various resonance forms cannot change, for that would change the identity of the species. So there must be certain rules by which mobile electrons can be moved to and from certain locations. The strength of the bond determines how mobile the electrons that make it up are. The following criteria apply:

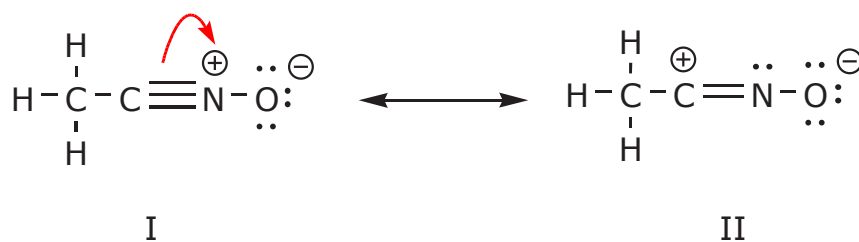
1. **Sigma bonds** are the strongest type of bond and represent the “glue” that holds the atoms together. Therefore, **such electrons are rarely moved**. There are, however, some exceptions.
2. **The π -bonds** in double or triple bonds **can move without destroying the connectivity**, since the σ -bond remains untouched. However, a certain energy investment must be made to break the π -bond before these electrons can be moved.
3. **Unshared electron pairs** (or lone pairs) **represent the most mobile type of electrons**. They do not form part of any bonds and therefore no energy has to be spent breaking a bond before they can be moved.

Therefore, the **order of electron mobility** and/or availability for reactions is:

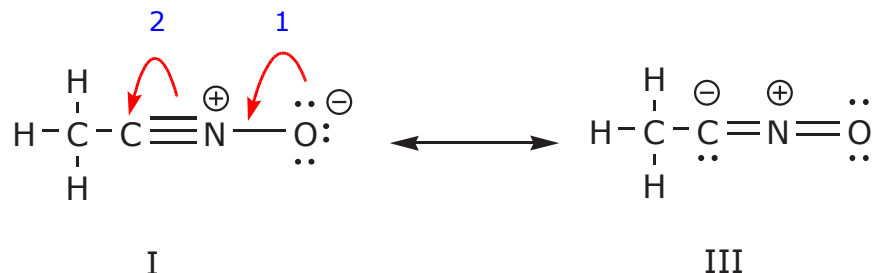


Now, where can those electrons go? Can they move in any direction, or are there rules that govern their movement as well? There is a set of rules, but the most important thing to keep in mind is that **electrons move towards areas of lower electron density, and/or away from negative charges**.

III. ELECTRON “PUSHING” AND THE CURVED ARROW FORMALISM. The movement of mobile electrons in chemical structures and in reaction mechanisms is indicated using the *curved arrow formalism*. Small, curved arrows indicate the movement of **electron pairs**, be it from a bond or an unshared pair. For example, the movement of electrons used to arrive at structure II from I is:



This means that the electrons making up one of the C - N π -bonds are being relocated to the nitrogen atom as an unshared pair. After relocation, the carbon atom is left with a positive charge, the nitrogen atom becomes neutral, and there is now only a double bond between carbon and nitrogen. Here is how to arrive at structure III from I:



First, we move one of the unshared pairs from oxygen to make a new π -bond between N and O. This move would result in a nitrogen atom with 5 bonds, which is impossible. Therefore, as we do step 1 we must also do step 2, that is, move one of the π -bonds between C and N to the carbon atom in order to preserve the octet rule. As carbon gains one extra electron, it also acquires a negative charge. The nitrogen atom gained one electron from oxygen but lost one to carbon, so it retains the same charge. Oxygen lost one electron to make the new bond to nitrogen, so it goes from having a negative charge to being neutral.

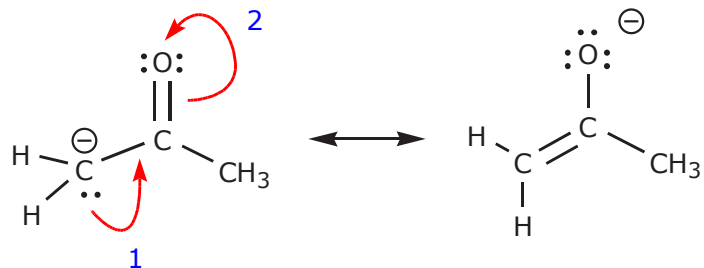
There is no particular order in which resonance structures must be written. Technically, one should be able to go from any resonance structure to any other by pushing mobile electrons using curved arrows. However this can be sometimes trickier than others. Only practice can provide the level of skill needed to do it comfortably.

IV. RULES FOR MOVING ELECTRON PAIRS. There are two basic rules that must be observed when moving electron pairs using curved arrows:

- 1) Electron pairs can only move to adjacent positions. Adjacent positions means neighboring atoms and/or bonds.
- 2) The Lewis structures that result from moving electrons must be valid and must contain the same net charge as the original structure.

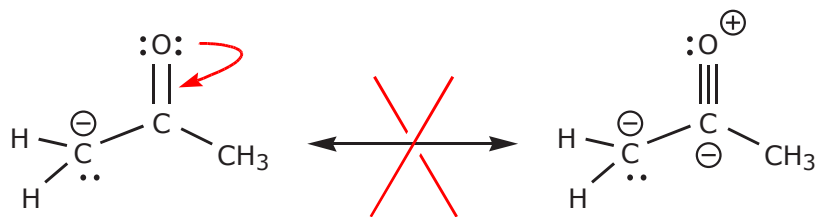
The examples given previously illustrate these two rules. Additional examples are given next.

This example illustrates how a lone pair of electrons (from carbon) can be moved to make a new π -bond (between carbons), and how a π -bond (between carbon and oxygen) can be moved to make a new lone pair (on oxygen):

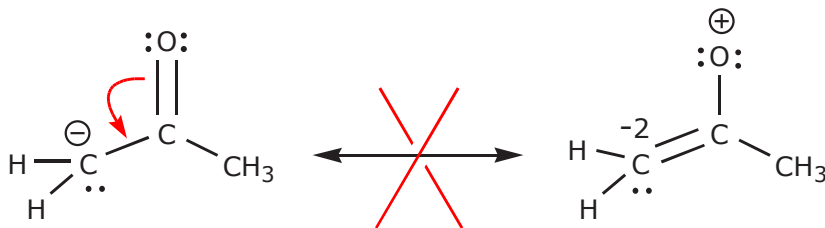


We have observed the two rules for moving electrons in resonance structures. We only moved electron pairs to adjacent, or neighboring positions. The Lewis structure that resulted from steps 1 and 2 is valid, and the net charge in both structures is -1.

Using the same example, but moving electrons in a different way, illustrates how such movement would result in invalid Lewis formulas, and therefore is unacceptable. The resulting structure violates several conventions. First, the central carbon has five bonds and therefore violates the octet rule. Second, the overall charge of the second structure is different from the first.

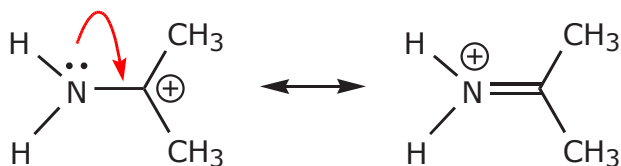


Likewise in the example below. First, electrons are moving towards an area of high electron density (a negative charge). Second, the octet rule is violated for carbon in the resulting structure.

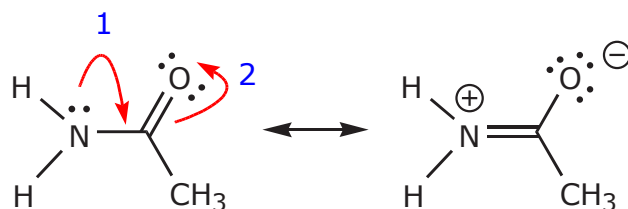


Additional examples illustrate more specific rules that apply to electron movement when writing resonance structures:

- (a) Unshared electron pairs (lone pairs) located on a given atom can only move to an adjacent position to make a new π -bond to the next atom.



- (b) Unless there is a positive charge on the next atom (carbon above), other electrons will have to be displaced to preserve the octet rule. In resonance structures these are almost always π -electrons.

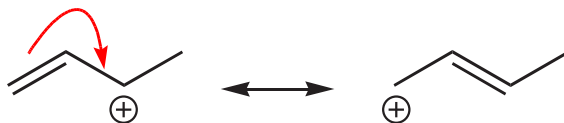


As the electrons from the nitrogen lone pair move towards the neighboring carbon to make a new π -bond, the π -electrons making up the C=O bond must be displaced towards the oxygen to avoid ending up with five bonds to the central carbon.

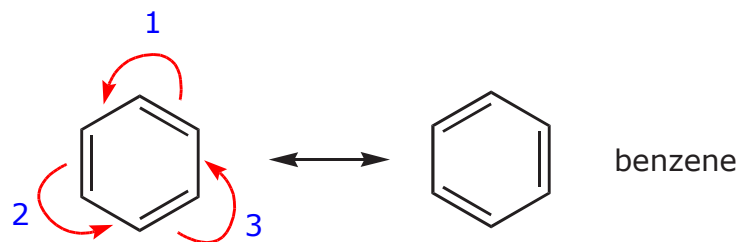
- (c) As can be seen above, π -electrons can move towards one of the atoms they bond to form a new lone pair. In the example above, the π -electrons from the C=O bond moved towards the oxygen to form a new lone pair. Another example is:



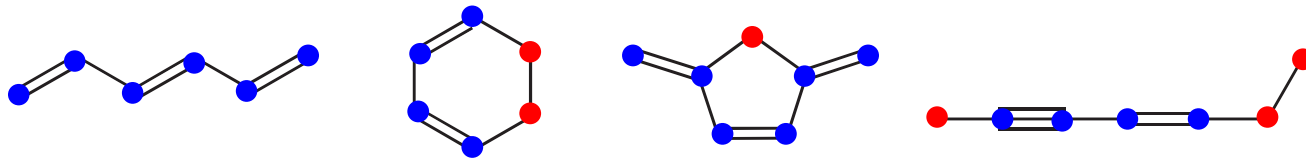
(d) π -electrons can also move to an adjacent position to make new π -bond. Once again, the octet rule must be observed:



One of the most common examples of this feature is observed when writing resonance forms for benzene and similar rings.



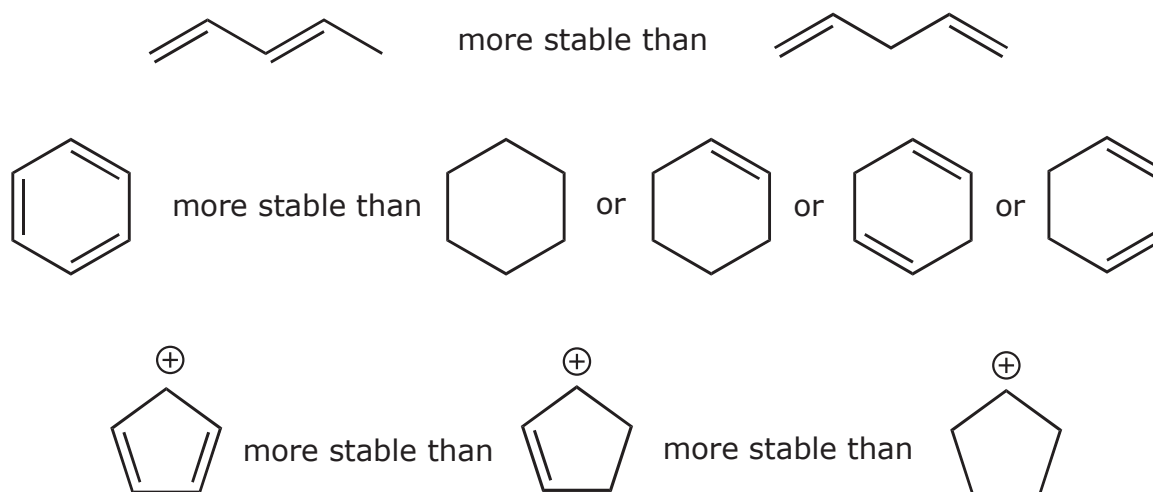
V. DELOCALIZATION, RESONANCE, AND CONJUGATION. The presence of alternating π -bonds and σ -bonds as in benzene is known as a **conjugated system**, or **conjugated π -bonds**. Conjugated systems can extend across the entire molecule, as in benzene, or they can comprise only part of a molecule. A conjugated system always starts and ends with a π -bond (i.e. an sp^2 or an sp -hybridized atom). The atoms that form part of a conjugated system in the examples below are shown in blue, and the ones that do not are shown in red. Most of the times it is sp^3 hybridized atoms that break a conjugated system.



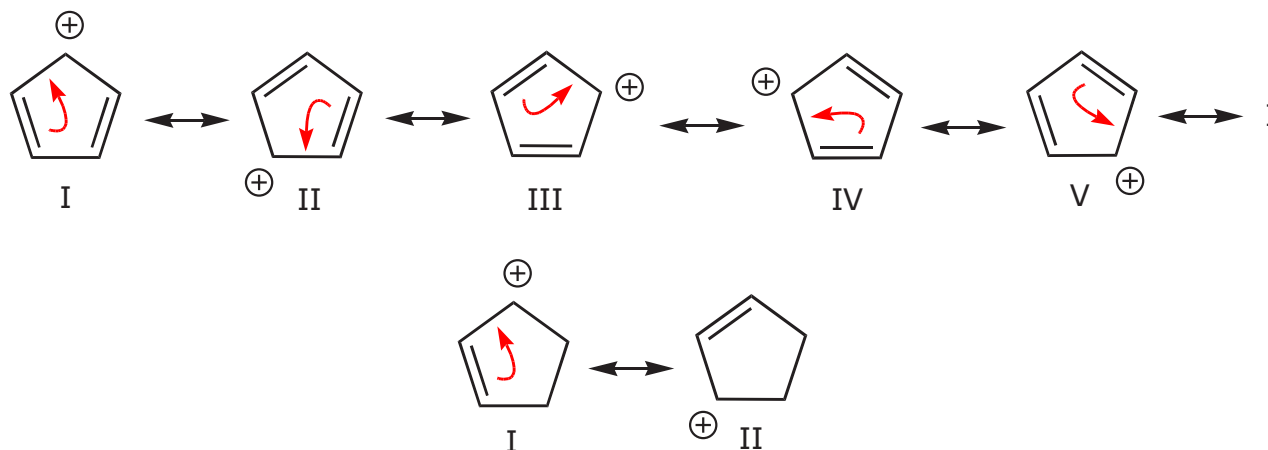
Practically every time there are π -bonds in a molecule, especially if they form part of a conjugated system, there is a possibility for having resonance structures, that is, several valid Lewis formulas for the same compound. What resonance forms show is that there is **electron delocalization**, and sometimes **charge delocalization**. All the examples we have seen so far show that electrons move around and are not static, that is, they are delocalized. **Charge delocalization is a stabilizing force** because it spreads energy over a larger area rather than keeping it confined to a small area. Since electrons are charges, the presence of delocalized electrons brings extra stability to a system compared to a similar system where electrons are localized.

Since conjugation brings up electron delocalization, it follows that **the more extensive the conjugated system, the more stable the molecule** (i.e. the lower its potential energy). If there are positive or negative charges, they also spread out as a result of resonance. The corollary is that **the more resonance forms one can write for a given system, the more stable it is.**

Examine the following examples and write as many resonance structures as you can for each to further explore these points:

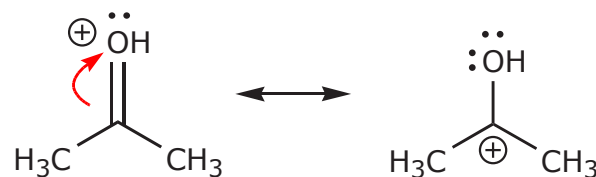


In the last example, the positive charge and the π -bonds are delocalized around the entire ring in the first structure, and over three carbon atoms in the second. The third structure has no delocalization of charge or electrons because no resonance forms are possible.

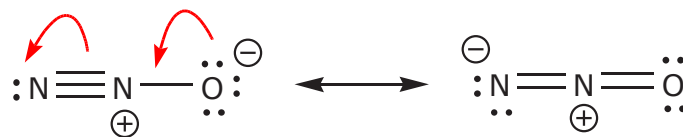
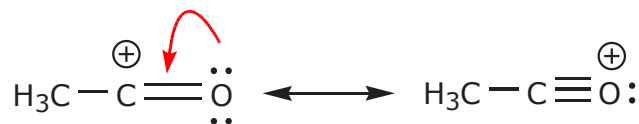


VI. DELOCALIZATION SETUPS. There are specific structural features that bring up electron or charge delocalization. The presence of a conjugated system is one of them. Other common arrangements are:

(a) The presence of a positive charge next to a π -bond. The positive charge can be on one of the atoms that make up the π -bond, or on an adjacent atom.



(b) The presence of a positive charge next to an atom bearing lone pairs of electrons.



(c) The presence of a π -bond next to an atom bearing lone pairs of electrons.

