6.17: Polyatomic Ions

Our discussion of ionic compounds was confined to monatomic ions. However, more complex ions, containing several atoms *covalently bonded* to one another, but having a positive or negative charge, occur quite frequently in chemistry. The charge arises because the total number of valence electrons from the atoms cannot produce a stable structure. With one or more electrons added or removed, a stable structure results. Well-known examples of such **polyatomic ions** are the sulfate ion (SO_4^{2-}),

the hydroxide ion (OH^-),

the hydronium ion (H_3O^+),

and the ammonium ion (NH_4^+).

The atoms in these ions are joined together by covalent electron-pair bonds, and we can draw Lewis structures for the ions just as we can for molecules. The only difference is that the number of electrons in the ion does not exactly balance the sum of the nuclear charges. Either there are too many electrons, in which case we have an anion, or too few, in which case we have a cation.

Consider, for example, the hydroxide ion (OH^-) for which the Lewis structure is

$$\left[:\ddot{O}:H \right]^-$$

O shares a pair of electrons with H. Three pairs of unpaired electrons is also shown. The entire O H molecules is enclosed in a square bracket with a superscript of negative sign.

A neutral molecule containing one O and one H atom would contain only seven electrons, six from O and one from H. The hydroxide ion, though, contains an *octet* of electrons, *one more* than the neutral molecule. The hydroxide ion must thus carry a single negative charge. In order to draw the Lewis structure for a given ion, we must first determine how many valence electrons are involved. Suppose the structure of H_3O^+ is required. The total number of electrons is obtained by adding the valence electrons for each atom, $6 + 1 + 1 + 1 = 9$ electrons. We must now subtract 1 electron since the species under consideration is not H_3O but H_3O^+. The total number of electrons is thus $9 - 1 = 8$. Since this is an octet of electrons, we can place them all around the O atom. The final structure then follows very easily:

$$\left[\begin{array}{c} H \\ H:\ddot{O}:H \end{array} \right]^+$$
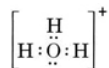
A central O shares three pairs of electrons with three H on the left top and right side. The bottom pair of electron from O is unpaired. The entire O H 3 molecule is enclosed in a square bracket which has a superscript positive sign.

In more complicated cases it is often useful to calculate the number of *shared electron pairs* before drawing a Lewis structure. This is particularly true when the ion in question is an *oxyanion* (i.e., a central atom is surrounded by several O atoms). A well-known oxyanion is the carbonate ion, which has the formula CO_3^{2-}. (Note that the central atom C is written first, as was done earlier for molecules.) The total number of valence electrons available in CO_3^{2-} is

$$4(\text{for C}) + 3 \times 6(\text{for O}) + 2(\text{for the } -2 \text{ charge}) = 24$$

We must distribute these electrons over 4 atoms, giving each an octet, a requirement of $4 \times 8 = 32$ electrons. This means that $32 - 24 = 8$ electrons need to he counted twice for octet purposes; i.e., 8 electrons are shared. The a ion thus contains *four* electron-pair bonds. Presumably the C atom is double-bonded to one of the O's and singly bonded to the other two:
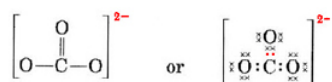
A central C is double bonded to one O and single bonded to two other O. The entire structure is enclosed in a square bracket with superscript of negative 2.

In this diagram the 4C electrons have been represented by dots, the 18 O electrons by ×'s, and the 2 extra electrons by colored dots, for purposes of easy reference. Real electrons do not carry labels like this; they are all the same.

There is a serious objection to the Lewis structure just drawn. How do the electrons know which oxygen atom to single out and form a double bond with, since there is otherwise nothing to differentiate the oxygens? The answer is that they do not. To explain the bonding in the CO_3^{2-} ion and some other molecules requires an extension of the Lewis theory. We pursue this matter further when we discuss resonance. Now we end with an example.

✔ **Example 6.17.1 : Lewis Structure**

Draw a Lewis structure for the sulfite ion, SO_3^{2-}.

Solution The safest method here is to count electrons. The total number of valence electrons available is

6(for S) + 3 × 6(for O) + 2(for the charge) = 26 To make four octets for the four atoms would require 32 electrons, and so the difference, 32 – 26 = 6, gives the number of shared electrons. There are thus only *three* electron-pair bonds in the ion. The central S atom must be linked by a single bond to each O atom.
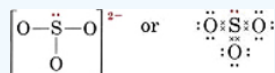
A central S is single bonded to three O. There is a lone pair from S that is not bonded to any other atom. As a result, the overall charge of the molecule is negative 2.

Note that each of the S—O bonds is coordinate covalent.

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