

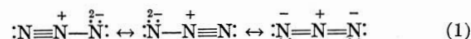
Lewis Structures and the Octet Rule

An automatic procedure for writing canonical forms

Lewis (electron dot) descriptions of the electronic structures of simple, multiple bonded, species such as N_3^- , CO , NO_2^+ , N_2O , NCO^- , O_3 , etc., often cause difficulty. Until expertise has been gained, confusion often arises concerning the correct number of multiple bonds to use, the correct number of valence electrons to use, and the placing of formal charges.

Species formed by the first short period elements generally obey the "Octet Rule" (1). In such species the principal quantum number of the valence shell is 2, and the energy separation between this shell and the $n = 3$ shell is sufficiently great that it is assumed that the latter is not involved in bonding. The $n = 2$ shell can accommodate a maximum of eight electrons, and the "octet rule" recognizes a marked tendency for such species to adopt a configuration which reaches this maximum, i.e., formally has the electron configuration of the inert gas neon.

Thus the azide ion is written



where the three resonance forms in eqn. (1) reflect three ways in which the octet requirement can be met. The ground state of the ion is recognized to be a resonance hybrid of the three canonical forms.

Canonical forms of the type illustrated above may be derived by a simple, almost automatic, procedure, enabling one to write down, correctly and rapidly, the resonance forms of any short period species. This procedure eliminates many of the problems commonly

associated with this topic when first introduced to students.

The procedure is derived as follows. Consider a noncyclic molecule of n atoms composed of elements, to which the octet rule applies. In the absence of any sharing of electrons whatsoever, $8n$ electrons would be required to achieve octets about all n atoms. However, an n atom noncyclic molecule necessarily possesses $(n - 1)$ σ bonds, containing $2(n - 1)$ σ electrons which are shared between the atoms. Because of this sharing of σ electrons the total number of electrons needed to achieve octets about all n atoms is $8n - 2(n - 1)$. If this number is precisely equal to the number of valence electrons (V) present, it follows that the molecule can achieve octets without the need of multiple (π) bonding and will therefore be saturated. If this number is greater than the number of valence electrons available, then additional sharing, through π bonding, will be necessary. The number of electrons which must be shared through π bonding, P , is given by

$$P = 8n - 2(n - 1) - V \\ = 6n + 2 - V \quad (2)$$

V , the number of valence electrons, can be readily determined, in a neutral species, by summing the group numbers of all the elements in the molecule. In a charged species the charge must be taken into account, being subtracted in the case of a cation, and added in the case of an anion. This may be written analytically as

$$V = \left(\sum_i \text{group number} \right) - \text{charge} \quad (3)$$

Consider the azide ion, N_3^-

$$V = (5 + 5 + 5) - (-1) = 16$$

¹ Before beginning this procedure it is necessary to know the basic geometry of the molecule, i.e., whether it is cyclic or noncyclic, and which atoms are connected to which. The procedure cannot be used to determine geometry.

$$n = 3$$

$$P = 18 + 2 - 16 = 4$$

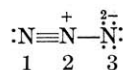
Hence, the azide ion contains 4π electrons which may be present either as two double bonds or one triple bond. These are added to the N—N—N σ framework¹ in the three possible ways illustrated above in eqn. (1). Electrons are added as needed to complete the octets about each atom. By this procedure the structures will automatically be valid with the correct number of valence electrons. However, the inexperienced should count the number of electrons in each canonical form to confirm that the number is indeed correct ($= V$).

The formal charges are calculated in the following manner. (1) Any atom having its normal valency number of bonds will be electrically neutral; any atom which does not have its normal valency number of bonds will carry a formal charge. (2) The formal charge may be calculated by subtracting the number of electrons "owned" by the element from its group number, viz

$$\text{Formal charge} = \text{Group Number} -$$

$$\text{Total number of electrons "owned" by the atom concerned} \quad (4)$$

For example in the structure



nitrogen 1 has its normal valency number (3) and is neutral. Nitrogen 2 shares eight electrons, and may therefore be considered to "own" $\frac{1}{2} \times 8 = 4$. Neutral nitrogen, being group V, has five valency electrons, hence nitrogen 2 carries a positive charge (from eqn. (4), $5 - 4 = +1$). Nitrogen 3 has three lone pairs ($6 e^-$'s) plus a half-share in a σ bond ($\frac{1}{2} \times 1$) for a total of 7 electrons. It therefore has two more electrons than neutral nitrogen and carries two negative charges (from eqn. (4) $5 - 7 = -2$).

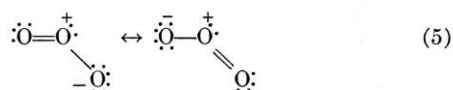
Consider ozone, O_3

$$V = (6 + 6 + 6) = 18$$

$$n = 3$$

$$P = 18 + 2 - 18 = 2$$

Thus, one double bond must be added to the σ framework, O—O—O and electrons added to complete the octets, viz



The formal charges follow logically (from above). The central oxygen shares three bonds (i.e., "owns" three electrons) plus its lone pair for a total of five electrons. Since oxygen belongs to group VI, neutral oxygen has six electrons, thus a positive charge follows from eqn. (4). The single bonded oxygen atom has three lone pairs (6 electrons) plus a half-share in one bond (1 electron) for a total of 7 electrons, hence carries a negative charge (from eqn. (4), $6 - 7 = -1$). The overall charge sums to zero, as it should for neutral ozone. The bent structure may be determined by application of the Gillespie-Nyholm rules (2, 3) which will not be discussed here.

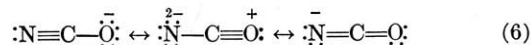
Consider now the cyanate ion, NCO^-

$$V = (5 + 4 + 6) - (-1) = 16$$

$$n = 3$$

$$P = 18 + 2 - 16 = 4$$

Hence two double bonds, or one triple bond, should be added to the N—C—O framework and electrons added to complete the octet, viz



The formal charges follow readily from eqn. (4). Because of the extreme charge separation in the middle canonical form, it probably does not contribute much to the ground state of the molecule which will be dominated by contributions from the outer forms. Note, in passing, that eqn. (6) infers that the cyanate group should be ambidentate, capable of bonding at either nitrogen or oxygen to a metal atom, as indeed is known to occur (4).

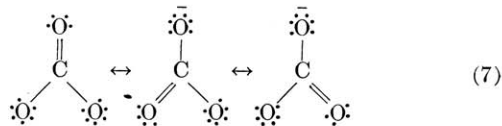
The structure of the carbonate ion, CO_3^{2-} , follows easily by this procedure

$$V = (4 + 6 + 6 + 6) - (-2) = 24$$

$$n = 4$$

$$P = 24 + 2 - 24 = 2 \quad (\text{One double bond})$$

Hence



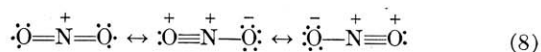
Similarly for NO_2^+

$$V = (5 + 6 + 6) - (+1) = 16$$

$$n = 3$$

$$P = 18 + 2 - 16 = 4$$

Two double bonds or one triple bond are added to the O—N—O σ framework to yield



Clearly, the first canonical form is of lower energy than the remaining two and will therefore make the largest contribution to the ground state.

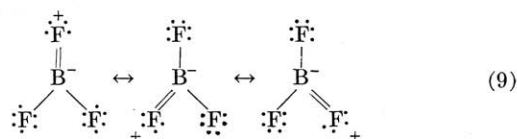
If we consider boron trifluoride, BF_3 we find

$$V = (3 + 7 + 7 + 7) = 24$$

$$n = 4$$

$$P = 24 + 2 - 24 = 2$$

and produce



Boron trifluoride does have B—F bond lengths (5) which may be interpreted in terms of some partial multiple bonding, but the molecule also behaves as an electron deficient species (in common with many other boron derivatives) suggesting that the octet is not complete about the boron atom. Certainly structure 9 is not energetically very favorable placing a positive charge on the highly electronegative fluorine atoms.

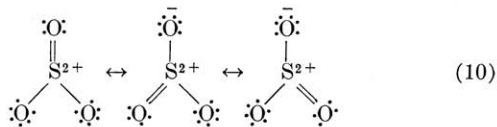
Species such as the thiocyanate ion (NCS^-), con-

taining elements for which the octet rule does not strictly apply, may nevertheless be similarly treated. In the case of NCS^- the canonical forms will be identical with those of NCO^- (5).

Treating sulfur trioxide, SO_3

$$\begin{aligned} V &= (6 + 6 + 6 + 6) = 24 \\ n &= 4 \\ P &= 24 + 2 - 24 = 2 \end{aligned}$$

and hence



In this case the sulfur atom, using valency shell $n = 3$, is not restricted to an octet, and additional double bonds may be generated from the oxygen lone pairs to equalize the charge, viz



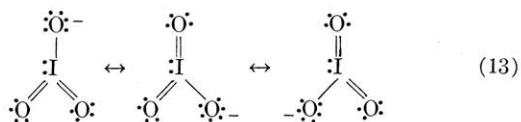
Use of the formula for the iodate ion, IO_3^- , will lead to

$$\begin{aligned} V &= (7 + 6 + 6 + 6) - (-1) = 26 \\ n &= 4 \\ P &= 24 + 2 - 26 = 0 \end{aligned}$$

which gives rise to



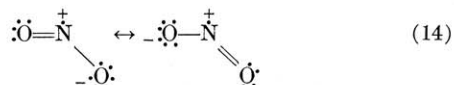
and by equalizing charges to



Odd electron species cannot obey the octet rule on every atom (without dimerizing) but may be treated in the same fashion, e.g., nitrogen dioxide, NO_2

$$\begin{aligned} V &= (5 + 6 + 6) = 17 \\ n &= 3 \\ P &= 18 + 2 - 17 = 3 \end{aligned}$$

The odd electron *must* be considered as a lone electron, not involved in multiple bonding; thus there are only two π electrons and we obtain



Species containing hydrogen atoms can be accommodated if the equation is first modified to account for the fact that a hydrogen atom requires only two rather

than eight electrons, to achieve a pseudo inert gas (helium) configuration. Thus in a noncyclic species of n atoms, q of which are hydrogen, the number of π electrons, P , will be given by

$$\begin{aligned} P &= 8(n - q) + 2q - 2(n - 1) - V \\ &= 6n - 6q + 2 - V \\ &= 6X + 2 - V \end{aligned} \quad (15)$$

where X = number of atoms, *exclusive of hydrogen*, in the molecule ($X = n - q$).

Consider hydrogen cyanide, HCN

$$\begin{aligned} V &= (1 + 4 + 5) = 10 \\ X &= 2 \\ P &= 12 + 2 - 10 = 4 \end{aligned}$$

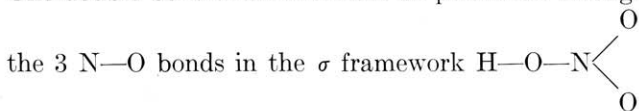
Since only two electrons can be accommodated by the hydrogen atom, the four π electrons must involve a triple bond, namely



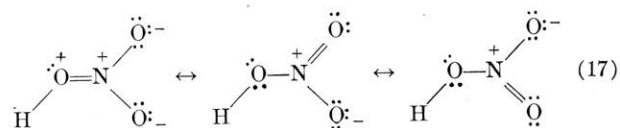
For nitric acid, HNO_3 we have

$$\begin{aligned} V &= (1 + 5 + 6 + 6 + 6) = 24 \\ X &= 4 \\ P &= 24 + 2 - 24 = 2 \end{aligned}$$

One double bond must therefore be permuted through



viz



Clearly cyclic molecules can also be handled by this procedure by taking into account the fact that an n atom cyclic molecules will share $2n$ (rather than $2(n - 1)$) σ electrons. However, once expertise has been achieved with noncyclic molecules, cyclic systems should cause no trouble. Having satisfactorily described the electronic structures of a large number of species by using the simple procedure described here, most students achieve a sufficient understanding of the principles involved to be able to write down simple electronic structures intuitively without the need of formula crutches. (For practice, students should use the procedures outlined above, to determine the electron dot structures of the following species: F_2O , NH_3 , CH_3F , CO_2 , COCl_2 , NO_3^- , SO_2 , NOCl , ClO_2^- , $(\text{CH}_3)_3\text{NO}$, N_2O_4 , NO_2Cl , FNO , N_2F_2 , HN_3 , $(\text{CH}_3)_2\text{SO}$, ClO_2^- , ClO_3^- , etc.)

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