8.9 Formal Charges

- **Formal charge (FC)** – a charge assigned to atoms in Lewis structures assuming that the shared **e^-** are divided equally between the bonded atoms.
  - # of **e^-** assigned to an atom in a Lewis structure – all lone pair **e^-** (**L**) and half of the shared **e^-** (**S**)
  - # of valence **e^-** of an atom (**V**)
  - # of bonds for an atom (**B**) → **B = S/2**

FC = V - [L + S/2] = V - [L + B]

- The **FC** shows the extent to which atoms have gained or lost **e^-** in covalent bond formation

Example: Write the possible resonance structures of the **NCO^-** ion (N-C-O) including the formal charges of all atoms.

$[N–C–O]^-$

n_{tot} = 5 + 4 + 6 + 1 = 16

n_{rem} = 16 - 4 = 12 **n_{need} = 6 + 4 + 6 = 16**

$n_{need} > n_{rem}$ deficiency of **4 e^-** ⇒ add **2** more bonds

a) $[:N=C=O:]^-$ b) $[:N≡C–O:]^-$ c) $[:N–C≡O:]^-$

V	→ **5(N)**	**4(C)**	**6(O)**				
L+B	→ **a) 6(N)**	**4(C)**	**6(O)**	**FC → a) -1(N)**	**0(C)**	**0(O)**
L+B	→ **b) 5(N)**	**4(C)**	**7(O)**	**FC → b) 0(N)**	**0(C)**	**-1(O)**
L+B	→ **c) 7(N)**	**4(C)**	**5(O)**	**FC → c) -2(N)**	**0(C)**	**+1(O)**

- The sum of all **FC**s equals the charge of the species
- Lewis structures with lower **FC**s are more stable

Example: Evaluate the stability of the three possible atomic arrangements of the **NCO^-** ion assuming structures with two double bonds.

a) $[:N=C=O:]^-$ b) $[:C=N=O:]^-$ c) $[:C=O=N:]^-$

V	→ **5(N)**	**4(C)**	**6(O)**			
L+B	→ **a) 6(N)**	**4(C)**	**6(O)**	**FC → a) -1(N)**	**0(C)**	**0(O)**
L+B	→ **b) 4(N)**	**6(C)**	**6(O)**	**FC → b) +1(N)**	**-2(C)**	**0(O)**
L+B	→ **c) 6(N)**	**6(C)**	**4(O)**	**FC → c) -1(N)**	**-2(C)**	**+2(O)**

Structure **(a)** has the lowest formal charges ⇒ **most stable**

Exceptions to the Octet Rule

8.10 Radicals and Biradicals

- **Radicals** – odd electron species **($·CH_3$, ·OH, ·NO, $·NO_2$, …)**
  - highly reactive and short lived species
  - significance to atmospheric chemistry (smog) and human health (antioxidants)

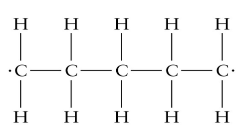
Example: Write the Lewis structure of **NO**.

[N–O] **n_{tot} = 5 + 6 = 11** **n_{rem} = 11 - 2 = 9**

n_{need} = 6 + 6 = 12 ⇒ add **1** more bond

·N=O: ↔ :N=O·

- **Biradicals** – molecules with two unpaired electrons
- The Lewis structures of some biradicals do not show unpaired electrons **(:O=O:)**



27 A biradical

Example: Write the Lewis structure of **NO_2**.

[O–N–O]

n_{tot} = 5 + 2×6 = 17 **n_{rem} = 17 - 4 = 13**

n_{need} = 4 + 2×6 = 16 ⇒ add **1** more bond

:O=N–O·

8.11 Expanded Valence Shells

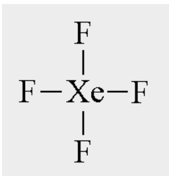
- **Extended octets** – more than eight electrons around a central atom
- Extended octets are formed only by atoms with empty **d**-orbitals in the valence shell (**p-**elements from the third or later periods)
- Extended octets form when:
  - there are too many **e^-** (**$n_{need} < n_{rem}$**) or more than 4 atoms are bonded to the central atom – **electron-rich structures** → place the extra electrons at the central atom
  - structures with lower formal charges can be achieved by forming an extended octet

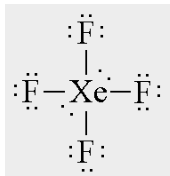
Example: Write the Lewis structure of $\mathbf{XeF_4}$.

$\mathbf{n_{tot} = 8(Xe) + 4 \times 7(F) = 36}$

$\mathbf{n_{rem} = 36 - 8 = 28}$ $\mathbf{n_{need} = 0(Xe) + 4 \times 6(F) = 24}$

$\mathbf{n_{need} < n_{rem}}$ **4** extra $\mathbf{e^-}$ ⇒ add **2** lone pairs at **Xe**





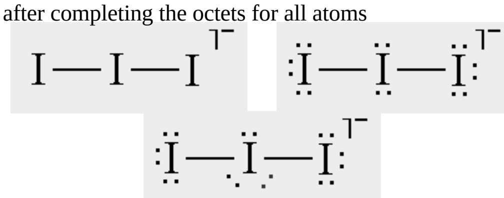
Example: Write the Lewis structure of $\mathbf{I_3^-}$.

$\mathbf{n_{tot} = 3 \times 7(I) + 1(charge) = 22}$

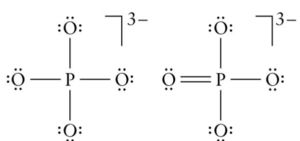
$\mathbf{n_{rem} = 22 - 4 = 18}$ $\mathbf{n_{need} = 4(I) + 2 \times 6(I) = 16}$

$\mathbf{n_{need} < n_{rem}}$

2 extra $\mathbf{e^-}$ ⇒ add **1** extra lone pair at the central **I** atom after completing the octets for all atoms



Example: Select the favored resonance structure of the $\mathbf{PO_4^{3-}}$ anion.



(a) (b)

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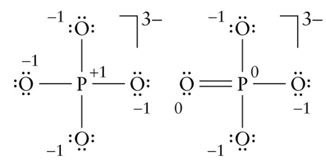
Formal charges:

(a) O → 6-(6+1)=-1 P → 5-(0+4)=+1

(b) O– → 6-(6+1)=-1 P → 5-(0+5)=0

O= → 6-(4+2)=0



(a) (b)

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- Structure (**b**) has an extended octet (10 $\mathbf{e^-}$) at the **P** atom
- Structure (**b**) is more favored (contributes more to the resonance hybrid) due to the lower formal charges