Inorganic Chemistry with Doc M.

Day 3. Covalent bonding: Lewis dot structures and Molecular Shape.

Topics:

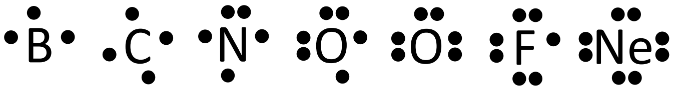
1. Covalent bonding, Lewis dot structures in review, formal charges
2. VSEPR
3. Expanded octets
4. On bulkiness of electrons and bonding groups
5. On formal charge and bond order (BO)
6. Resonance
7. Paramagnetism
8. Polarity
9. subvalent central atom species

1. Covalent bonding occurs between two non-metals. The metalloids are also included. Once in awhile it is extended to a metal and non-metal, especially if considerable covalent character is expected (e.g. $AlCl_3$)

1.1. Procedure for drawing Lewis dot structures:

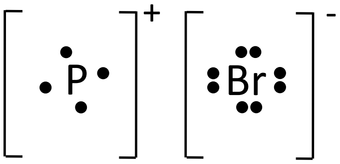
1. Determine the central atom. This is normally given the formula. Typically, the central atom is written first and is often the least electronegative of the atoms. For simple molecules/ions, there is only one of them. Things get weird when there is more than one central atom, such as S_2Cl_2. Often you can figure out how the atoms are connected, but sometimes, the structure will have to be given.

2. Start with the central atom and sketch the central atom with its valence electrons in Lewis format. Note that oxygen has two forms:

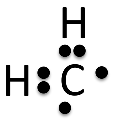


3. All the members of the same group look the same: for example, phosphorus and arsenic would look the same as nitrogen.

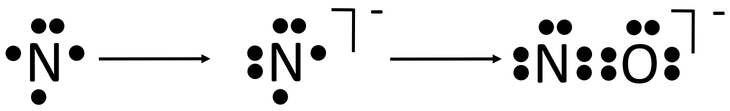
4. Adjust central atom for the charge if the species is ionic. So PCl_4^+ and BrO_4^- would start out as shown at right.



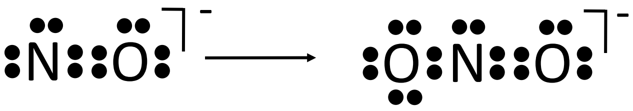
5. Some atoms, specifically hydrogen and fluorine, can only go on the ends and make one bond. Add these next: For example, CH_2O would go through:



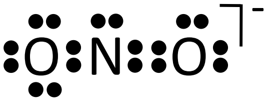
6. After H and F (or terminal halogens) have been added, add the remaining B groups (bonding groups) one at a time with the goal of completing the octet for both A and B as soon as possible. So, building nitrite from atoms would proceed as: 1. Nitrogen atom → 2. Nitrogen adjusted for charge of ion → 3. Add the first B-group while trying to get both A and B to octet if possible:



7. Finally, keep adding B groups until all have been added. This time with oxygen, we used the second form of oxygen, the one with the three pairs and "snapped" the oxygen onto the existing pair of electrons on nitrogen. This approach prevents exceeding the octet.



Going from nitrite to nitrate is done in a similar way. Convert nitrite to nitrate:

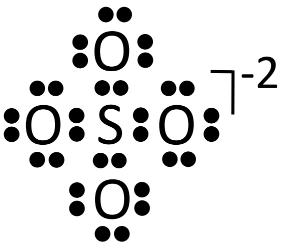


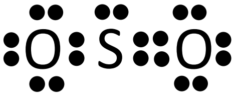
8. Structures produced in this way should always satisfy the octet rule (except for odd electron species.) When you are done, double-check the electron count around each atom: everybody should have 8 e^-. If there is an odd number of electrons, settle on 7 e^-, but never 9 e^-.

9. If your molecule/ion contains a second row central atom (B, C, N, O, F), you are done with the Lewis drawing and can now consider resonance forms and formal charges. The main purpose of sketching the Lewis structure is to establish the ABE formula so we can determine shape and polarity when appropriate.

1.2. Formal Charge Issues.

For central atoms with $n \geq 3$, the octet on the central atom can expand to some extent in order to reduce the formal charge on the central atom to zero. This involved converting a single bond between the central atom and oxygen into a double bond. Let's look at sulfate and sulfur dioxide as two examples. Sketched according to the above octet-driven rules, we come up with:





Assign formal charges to each atom in the above structures. (Note that the Lewis sketch for SO_2 represents only one of two resonance forms.)

By converting sulfur-oxygen single bonds into double bonds, we can reduce the "separation of charge" between A and B groups. It is important not to overdo it, however. Reducing the formal charge on the central atom, A, to zero is all that should be done. Sketch these two species again with formal charges on the central atom of zero.

So which is right: expand octet in order to reduce formal charges or not? Some things are certain: Never expand for n = 2 elements (B, C, N, O, F). The "jury is out" on to whether or not to expand the octet by making double bonds (almost always involving oxygen atoms.) Here are some things to consider:

- The Lewis of Lewis dot fame never ever expanded the octet. Never. Prior to xenon-fluorine chemistry, no one expanded the octet. When XeF_2 and XeF_4 were reported, one needed to expand the octet to create the single bonds needed. The resulting drawings correctly predicted molecular geometries (shapes) and so, octet expanding quickly became fashionable. It wasn't long before compounds with oxygen atoms for B groups were involved in double bonds to the A atoms for formal charge reasons.

- Most general chemistry books expand the octet by using double bonding to oxygen B groups as a method to lower formal charges.

- Double-bonding involving n $\geq$ 3 elements is considered rare by most inorganic chemists. For example, SiO_2 is not like CO_2. The former has single bonds only in a network covalent structure (quartz) while CO_2 is covalent molecular.

- There is growing theoretical evidence (*ab inition* calculations, etc.) that reducing formal charge by expanding octets may not be all that important (Suidan, Budenhoop, Glendening and Weinhold, J. Chem. Educ., 1995, **72** 583 – 586.)

Soooo, what to do? First of all, one does not need to expand the octet in order to get the correct ABE formula. If you are concerned about formal charges, well go ahead and make a few double bonds. But only make as many as are needed in order to give the central atom a FC = 0. Even if you do this, you will still have the same ABE formula as the one predicted by the non-expanded structure.

2. Geometries and their name and angles

2 groups	name	sketch	angles	example
AB_2				
ABE				

3 groups	name	sketch	angles	example
AB_3				
AB_2E				
ABE_2				

4 groups	name	sketch	angles	example
AB_4				
AB_3E				
AB_2E_2				
ABE_3				

3. Expanding octets:

- never occurs for n = 2 elements as central elements (B, C, N, O, F) — only n = 3 and higher
- almost always involves the elements that form the strongest bonds: F, O, Cl.
- All known examples are diamagnetic

5 groups	name	sketch	angles	example
AB_5				
AB_4E				
AB_3E_2				
AB_2E_3				

6 groups	name	sketch	angles	example
AB_6				
AB_5E				
AB_4E_2				

7 groups	name	sketch	angles	example
AB_7				

8 groups	name	sketch	angles	example
AB_8				

Predicting structures of expanded octet molecules:

Step 1. Count the valence electrons around central atom (P: 5; S: 6, Br: 7, Xe: 8)

Step 2. Adjust for charge if it is ionic

Step 3. Add one for each atom bonded-to-central atom that needs only one electron: H, F, etc.

Step 4. The total will tell you how many pairs of electrons will be around the central atom and hence the general geometry.

Step 5. The ABE formula is AB_xE_y where x equals the number of atoms bonded to the central atom and y is the number of electron pairs on central atom. Determine the ABE formula for each of these: (not all of these have expanded octets)

PCl_6^-	PCl_4^+	PCl_5
SF_6	SF_4	ClF_3

Step 6. Oxygen atoms bonded to central atom. Oxygen atoms can (a) form double bonds with two single electrons on the central atom or can simply coordinate to an available electron pair (E group) on the central atom. For example, if there are 5 valence electrons on the central atom and there are three bonding groups, the oxygen atom can form coordinate covalent bonds (can coordinate to the electron pair groups.) Determine the ABE formula for each of these: (not all of these have expanded octets)

PCl_3O	IO_4^-	BrO_3^-
SO_3	SF_4O	ClO_2F_3

4. On bulkiness of electrons and bonding groups

Electron pairs (and unpaired, electrons) on the central atom reside in orbitals on the central atom and thus, seem bulkier than single-bonded groups when it comes to determining bond angles. For example, CH_4 has the ideal tetrahedral angle while NH_3 (AB_3E) has a slightly reduced HNH angle (107^o) and water, OH_2, has AB_2E_2 and an even more reduced BAB angle (104^o). Estimate the bond angles for these:

PCl_3	SCl_2	OH_3^+
BrF_5	SF_4	CH_3^-

For species with 5 structural groups, the E groups prefer the equatorial positions. For species with 6 structural groups, two of which are E groups, the E groups prefer *trans* positions. Sketch these and estimate (<, > or =) the bond angles for these:

SbF_4^-	ClF_3	ICl_4^+
PCl_5	SF_4	ICl_2^-

Similarly, for species with 5 structural groups, oxygen groups prefer the equatorial positions. Sketch these and estimate (<, > or =) the bond angles for these:

SF_4O	ClO_2F_3	SeF_3O^-
$SeF_3O_2^-$	$IF_2O_3^-$	Free space ☺

5. On formal charge and bond order (BO)

Formal charges should

(a) be as small as possible
(b) should avoid "separation of charge"
(c) must add up to the charge on the ion or to 0 for molecules
(d) negative FC go with electronegative atoms.

Separation of charge can be minimized in species with coordinate covalent oxygen atoms by making one of the lone pairs on oxygen into a bonding pair (thus creating a double bond, but at the same time expanding the octet on the central atom — something n = 2 elements cannot do.). This is done until the FC on the central atom is 0. KEEP IN MIND: Second row elements (B, C, N, O, and F as central elements cannot expand the octet!

Another dilemma: third row elements (and beyond) are not known for their ability to make good double bonds to oxygen (unless it is require to achieve the octet.) Thus, it is best to show a range of bond orders and sometimes formal charges that indicate the two extremes: the extreme that minimizes the electrons around the central element and the extreme that minimizes separation of charge (FC = 0 on central element)

Optimized/Assign formal charges to each atom in the following while obeying all rules. In some cases, you will need to draw two figures for each: one that does not expand the octet unless absolutely necessary and a second one that reduces the FC on the central atom to zero. In other cases, only one figure is necessary as per the rules above.

SO_2	SO_4^{-2}	SO_3^{-2}
NO_3^-	PO_4^{-3}	SbF_4^-
XeO_4	ClO_2^-	CO_3^{-2}

6. On resonance

Look for resonance when you can draw structures more than one acceptable way with different arrangements of bond orders. The number of resonance forms equals the number of acceptable structures. Purists require the structures to be identical. Determine if resonance forms exist in the structures. Sketch a Lewis dot structure and add something such as “+ 2 other res forms,” when appropriate.

SO_2	SO_4^{-2}	SO_3^{-2}
NO_3^-	PO_4^{-3}	SbF_4^-
XeO_4	ClO_2^-	CO_3^{-2}

7. On paramagnetic substances.

Paramagnetic substances have generally one unpaired electron (although molecular oxygen has two). For n = 2 elements, the least electronegative element settles on 7 valence electrons (never 9). Draw suitable Lewis dot structures for each of the following, all of which exist, albeit sometimes fleetingly.

ClO_2	NO_2	CH_3
NO	NO_3	BrO_3

8. On polarity.

There are several simple considerations that save time when determining if a molecule is polar or not.

a. don't worry about polarity with anything ionic — it's like worrying about the 25 cents it costs to park in front of a pricy restaurant that you plan to eat at…

b. molecules with all equivalent B groups and no E groups are non-polar.

c. ALL molecules with two types of B groups are polar unless the B groups are balanced by equivalent symmetry (e.g. PCl_2F_3 with all 3 F equatorial)

d. ALL molecules with E groups are polar unless the E groups are balanced by equivalent symmetry. This only occurs for the expanded octet structures AB_2E_3 and AB_4E_2.

e. Central atoms with two or more different B groups are technically polar (See 'c' above), however if the two B groups have similar electronegativities, the central atom may be effectively non-polar for all intents and purposes. For example, the middle carbon in propane is bonded to two H atoms (EN = 2.1) and carbon groups (EN = 2.5). We usually do not think of propane as polar even though it technically is.

Which of these molecules, all used in previous examples, are polar?

SO_2	SO_3	SF_4
SF_6	SF_4O	SO_2Cl_2
XeO_4	ClO_2	PF_5

9. On sub-valent central atom species

This mostly pertains to boron where a very few six valence electron species are known. In other "similar cases," the electron pairs on terminal elements donate to the vacant site on the central atom. Thus $AlCl_3$ is actually Al_2Cl_6. Even BH_3 forms a dimer with bridging hydrogen atoms. What is the structure of each of these?

BF_3	Al_2Cl_6	B_2H_6

Review for ACS Final Exam in Inorganic Chemistry

Lewis dots, molecular shape, formal charges, polarity, hybridization

1. Which of these compounds is non-polar?
   - (a) NH_3
   - (b) PF_3
   - (c) SO_3
   - (d) SeF_2
   - (e) CH_3F

2. Which of these compounds is not trigonal planar?
   - (a) BF_3
   - (b) CO_3^{-2}
   - (c) SO_3
   - (d) ClF_3
   - (e) NO_3^-

3. What is the molecular shape, formal charge, and hybridization of phosphorus in PCl_4^+?
   - (a) square plane, +1, sp^3
   - (b) tetrahedral, +1, dsp^3
   - (c) square plane, -1, sp^2
   - (d) tetrahedral, +1, sp^3
   - (e) tetrahedral, 0, sp^2

4. Which species is incorrectly paired with its hybridization?
   - (a) $AsCl_3$, sp^3
   - (b) PF_6^-, d^2sp^3
   - (c) SO_2, sp^2
   - (d) SO_3, sp^3
   - (e) O_3, sp^2

5. Formal charges predict the best linkage in the ion NCS^- is:
   - (a) N—S—C
   - (b) N—C—S
   - (c) C—N—S
   - (d) two of the above are equally favorable.
   - (e) Choices (a), (b) and (c) are equivalent.

6. The geometry XeF_4 is explained by the hybridization:
   - (a) sp^2d^2
   - (b) sp^3
   - (c) sp^2d
   - (d) sp^3d^2
   - (e) sp^2d^3

7. Which these compounds is paramagnetic?
   - (a) ClO_2
   - (b) Cl_2O
   - (c) N_2O_4
   - (d) SO_3
   - (e) BrF_5

Answers: C, D, D, D, B, D, A

Answers from Day 2.

1a. a. P $(1s)^2\ (2s2p)^8\ (3s3p)^5$
b. F $(1s)^2\ (2s2p)^7$
c. Cl $(1s)^2\ (2s2p)^8\ (3s3p)^7$
d. Mg $(1s)^2\ (2s2p)^8\ (3s3p)^2$
e. C $(1s)^2\ (2s2p)^4$

1b. a. P $(1s)^2\ (2s2p)^8\ (3s3p)^4$
b. F $(1s)^2\ (2s2p)^6$
c. Cl $(1s)^2\ (2s2p)^8\ (3s3p)^6$
d. Mg $(1s)^2\ (2s2p)^8\ (3s3p)^1$
e. C $(1s)^2\ (2s2p)^3$

1c. a. P S = 2 x 1 + 8 x 0.85 + 4 x 0.35 = 10.2
b. F S = 2 x 0.85 + 6 x 0.35 = 3.8
c. Cl S = 2 x 1 + 8 x 0.85 + 6 x 0.35 = 10.9
d. Mg S = 2 x 1 + 8 x 0.85 + 1 x 0.35 = 9.15
e. C S = 2 x 0.85 + 3 x 0.35 = 2.75

1d. a. P Z_{eff} = N - S = 15 - 10.2 = 4.8
b. F Z_{eff} = N - S = 9 – 3.8 = 5.2
c. Cl Z_{eff} = N - S = 17 - 10.9 = 6.1
d. Mg Z_{eff} = N - S = 12 – 9.15 = 2.85
e. C Z_{eff} = N - S = 6 – 2.75 = 3.25

1e. a. a 2s electron on P S = 2 x 0.85 + 7 x 0.35 = 4.15 Z_{eff} = 15 – 4.15 = 10.85
b. a 2p electron on Mg S = 2 x 0.85 + 7 x 0.35 = 4.15 Z_{eff} = 12 – 4.15 = 7.85
c. a 2s electron on Cl S = 2 x 0.85 + 7 x 0.35 = 4.15 Z_{eff} = 17 – 4.15 = 12.85

1f. a. a 1s electron on He S = 1 x 0.30 = 0.30 Z_{eff} = 2 – 0.30 = 1.70
b. a 1s electron on MgS = 1 x 0.30 = 0.30 Z_{eff} = 12 – 0.30 = 11.70

2. a. a 2s electron on Na^+ S = 2 x .85 + 7 x 0.35 = 4.15 Z_{eff} = N - S = 11 – 4.15 = 6.85
b. a 3p electron on Cl^-S = 2 x 1.0 + 8 x 0.85 + 7 x 0.35 = 11.25 Z_{eff} = 17 – 11.25 = 5.75
c. a 2p electron on Mg^{+2} S = 2 x .85 + 7 x 0.35 = 4.15 Z_{eff} = 12 – 4.15 = 7.85
d. a 1s electron on Li^+ (See 1f above!) S = 1 x 0.30 = 0.30 Z_{eff} = 3 – 0.30 = 2.70

3. a. a 4p electron on As $(1s)^2\ (2s2p)^8\ (3s3p)^8\ (3d)^{10}\ (4s4p)^4$
S = 10 x 1.00 + 18 x 0.85 + 4 x 0.35 = 26.7 Z_{eff} = N - S = 33 – 26.7 = 6.3

b. a 5s electron on Sr $(1s)^2\ (2s2p)^8\ (3s3p)^8\ (3d)^{10}\ (4s4p)^8\ (4d)^0\ (4f)^0\ (5s5p)^1$
S = 28 x 1.00 + 8 x 0.85 + 1 x 0.35 = 35.15 Z_{eff} = 38 – 35.15 = 2.85

c. a 5p electron on Cs^+ $(1s)^2\ (2s2p)^8\ (3s3p)^8\ (3d)^{10}\ (4s4p)^8\ (4d)^{10}\ (4f)^0\ (5s5p)^7$
S = 28 x 1.00 + 18 x 0.85 + 7 x 0.35 = 45.75 Z_{eff} = 55 – 45.75 = 9.25

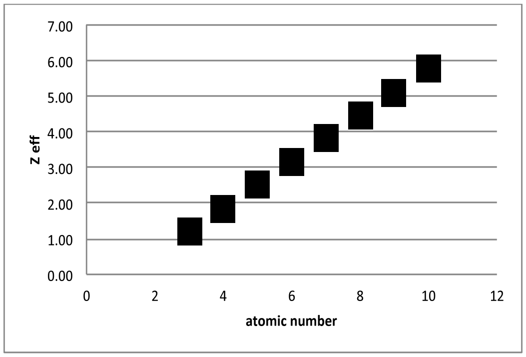
4. a. a 3d electron on Ni $(1s)^2\ (2s2p)^8\ (3s3p)^8\ \underline{(3d)}^7\ (4s4p)^2$
S = 18 x 1.00 + 7 x 0.35 = 20.45 Z_{eff} = N - S = 28 – 20.45 = 7.55

b. a 3d electron on Mn $(1s)^2\ (2s2p)^8\ (3s3p)^8\ \underline{(3d)}^4\ (4s4p)^2$
S = 18 x 1.00 + 4 x 0.35 = 19.4 Z_{eff} = N - S = 25 – 19.4 = 5.6

c. a 4d electron on Ru $(1s)^2\ (2s2p)^8\ (3s3p)^8\ (3d)^{10}\ (4s4p)^8\ \underline{(4d)}^5\ (5s5p)^2$
S = 36 x 1.00 + 5 x 0.35 = 37.75 Z_{eff} = N - S = 44 – 37.75 = 6.25

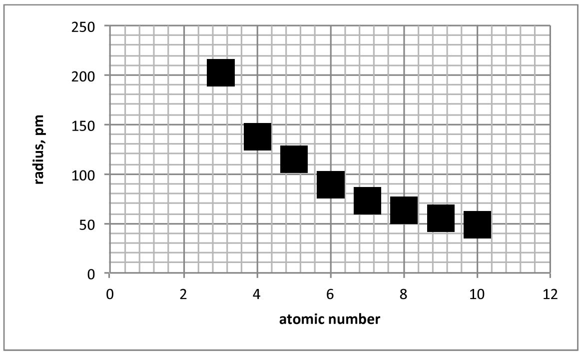
5a.

	x1	x.85	x.35	S	Z	Zeff
Li	0	2	0	1.70	3	1.30
Be	0	2	1	2.05	4	1.95
B	0	2	2	2.40	5	2.60
C	0	2	3	2.75	6	3.25
N	0	2	4	3.10	7	3.90
O	0	2	5	3.45	8	4.55
F	0	2	6	3.80	9	5.20
Ne	0	2	7	4.15	10	5.85



5b.

Z	r
3	205
4	140
5	117
6	91
7	75
8	65
9	57
10	51



5c.

	1s	2s2p	3s3p	3d	4s4p	x1	x.85	x.35	S	Z	Zeff
Li	2	0				0	2	0	1.70	3	1.90
Na	2	8	0			2	8	0	8.80	11	2.20
K	2	8	8	0		10	8	0	16.80	19	2.20
Rb	2	8	8	10	8	28	8	0	34.80	37	2.20

5d. 1. Atomic radius (size): (Li → Cs) is explained by increasingly larger shells being occupied.

2. First ionization energy ($E \rightarrow E^+$) (Li → Cs) decreases because the valence electrons are in shells with larger n values.

5e. Na $(1s)^2 (2s)^2 (2p)^6 (3s)^1 + e^- \rightarrow Na^- (1s)^2 (2s)^2 (2p)^6 (3s)^2$

Sodium has a $Z_{eff} = 2.20$, so electrons are attracted to it and since we are not starting a new subshell (3p), the process is exothermic.

5f. Elements with filled subshells, ns^2, np^6, or nd^{10} do not want an additional electron.

5g. B $(1s)^2 (2s)^2 (2p)^1 \rightarrow B^+ (1s)^2 (2s)^2 (2p)^0 + e^-$ Vacating the 2p orbital requires energy (boron has $Z_{eff} = 2.6$), but it does not take as much energy as would have been expected because we are emptying a subshell. Oxygen works the same way, but with half-filled subshells (also pairing energy that goes with $2p^4$).

6a. Circle the species with the largest radius and draw a box around the smallest radius in each series.

(i) largest: Se^{-2} smallest: Sr^{+2} (ii) largest: Y^{+3} smallest: Nb^{+5}

(iii) largest: Co smallest: Co^{+4} (iv) largest: F^- smallest: Na^+