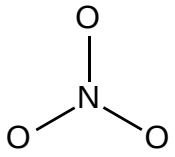
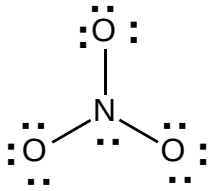
Solutions to Problem Assignment 4 (bonding)

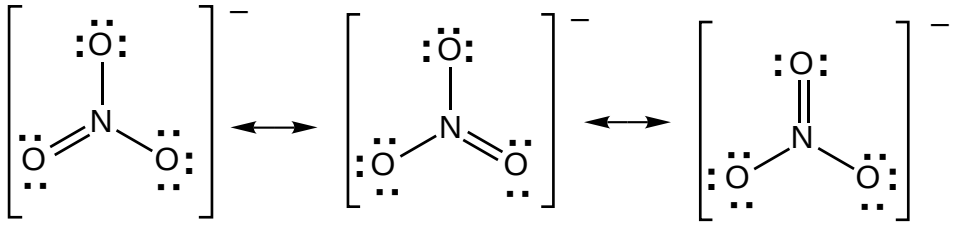
1. The approach is shown in detail for NO_3^- only. The SKELETAL structure i.e. which atoms are CONNECTED, is shown below.



Total Number of Valence Electrons = 5 (from N) + 3(6 from each O) + 1 (from the net negative charge) = 24. A trial structure uses 26 electrons, so eliminate the 2-electron surplus by introducing one double bond.



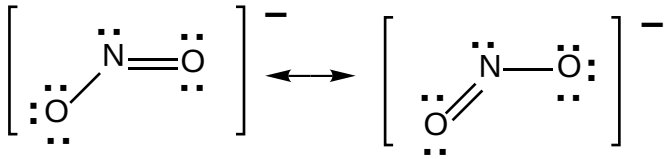
Acceptable resonance structures are:



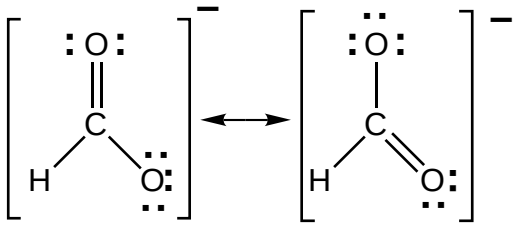
The actual structure of NO_3^- is an EQUAL mixture of all three resonance structures; i.e. a HYBRID--each NO bond is 1.333 times the strength of a normal NO single bond.

For the following examples, the valence electron count is placed in parentheses after the empirical formula and only the resonance structures which satisfy the octet rule are given.

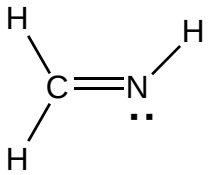
NO_2^- (18)



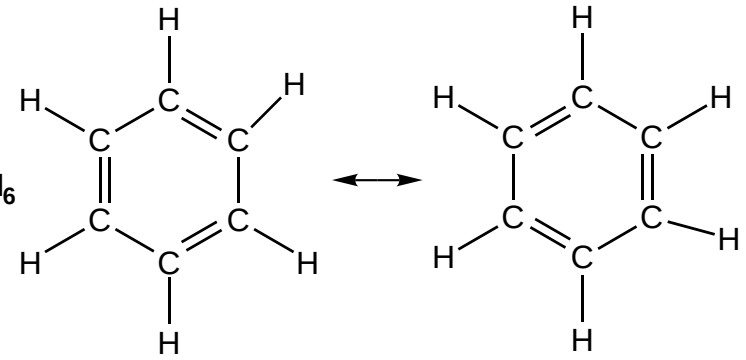
3. HCO_2^-
(18)



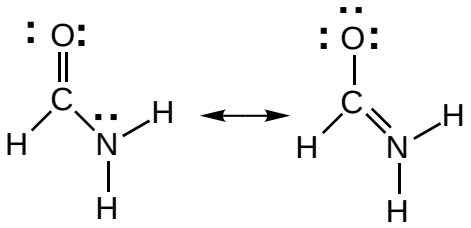
4. $H_2C{=}NH$ (12)



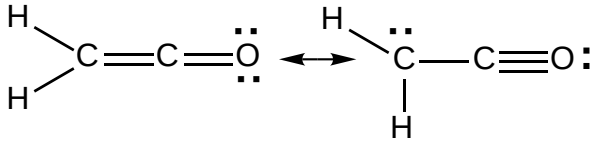
5. C_6H_6 (30)



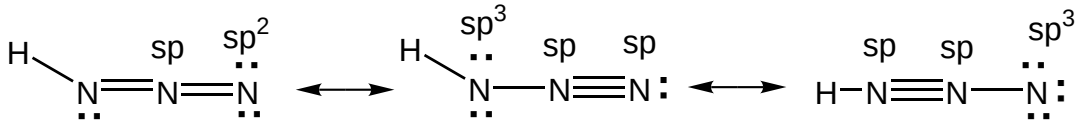
6. $HCONH_2$ (18)



7. H_2CCO (16)



7. HN_3 (16)



2) **NO_3^-** There are 3 possible resonance structures that satisfy the octet rule. In each resonance structure, the FORMAL CHARGE on N = +1; the FORMAL CHARGE on the N=O oxygen = 0; and the FORMAL CHARGE on each of the N – O oxygens = –1. The actual structure is an EQUAL mixture of the 3 RESONANCE structures.

NO_2^- There are 2 possible resonance structures. In each resonance structure, the FORMAL CHARGE on N = 0; the FORMAL CHARGE on the N = O oxygen =

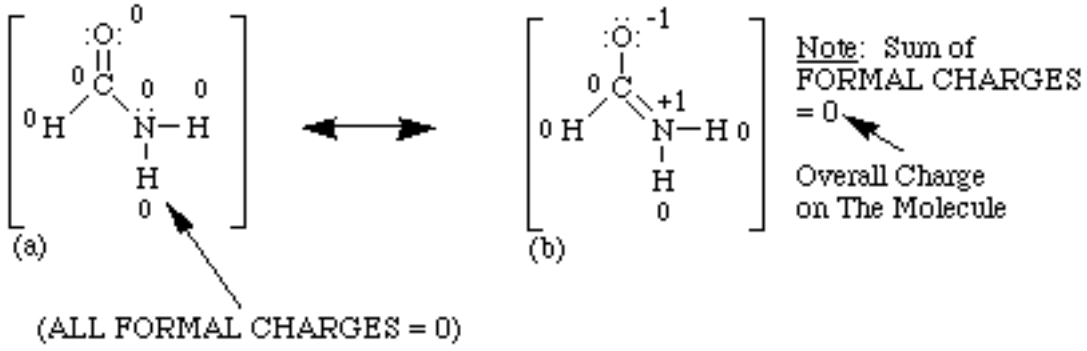
0; and the FORMAL CHARGE on the N – O oxygen = –1. The actual structure is an EQUAL mixture of the 2 RESONANCE structures.

HCO_2^- There are 2 possible resonance structures. In each resonance structure, the FORMAL CHARGE on C = 0; the FORMAL CHARGE on the C = O oxygen = 0; the FORMAL CHARGE on the C – O oxygen = –1; and the FORMAL CHARGE on H = 0. The actual structure is an EQUAL Mixture of the 2 RESONANCE structures.

H_2CNH -- Only 1 resonance structure: the FORMAL CHARGES on all the atoms = 0.

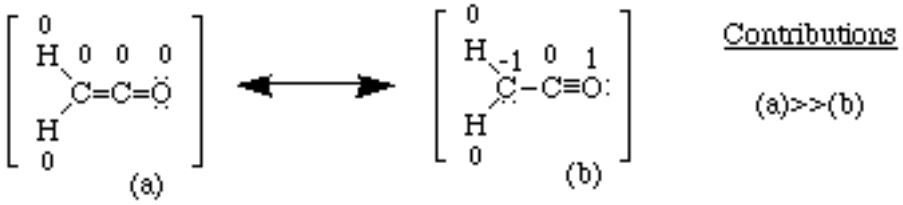
C_6H_6 -- 2 possible resonance structures: the FORMAL CHARGES on all the atoms = 0. The actual structure is an EQUAL MIXTURE of the 2 RESONANCE structures.

$HC(O)NH_2$

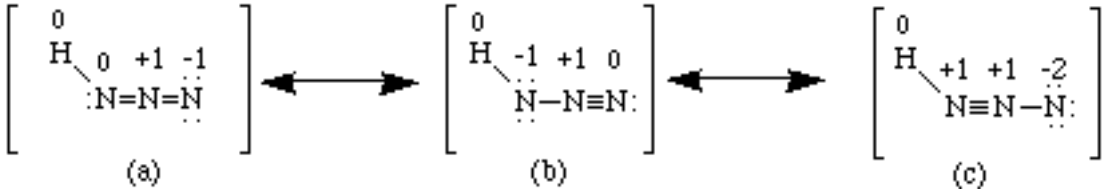


Since (a) involves no separation of FORMAL CHARGE, it makes a much larger contribution to the actual structure of $HC(O)NH_2$ than does (b).

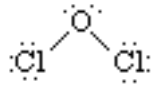
H_2CCO



HN_3

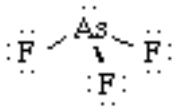


Since structure (c) involves (i) separating larger FORMAL CHARGES of opposite sign and (ii) placing LIKE FORMAL CHARGES at a separation corresponding to the N≡N bond length, it will make a much smaller contribution than either (a) or (b). Structure (a) involves separating +1 and –1 FORMAL CHARGES to an N=N distance; structure (b) involves separating +1 and –1 FORMAL CHARGES to an N–N distance. Since the N=N distance (a DOUBLE BOND) is considerably SHORTER than the N–N distance (a SINGLE BOND) we expect resonance structure (a) to make a larger contribution to the actual structure of HN_3 than does resonance structure (b).

3a) 

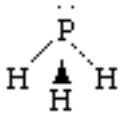
Bent

∢ ClOCl = 109.5°

h) 

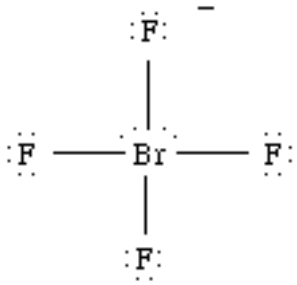
Pyramidal

∢ FAsF = 109.5°

b) 

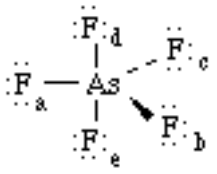
Pyramidal

∢ HPH = 109.5°

i) 

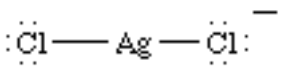
Square Planar

∢ FBrF = 90°

c) 

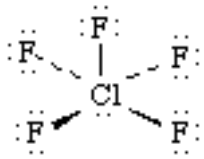
Trigonal bipyramidal

$\measuredangle F_a As F_b = 120^\circ$
$\measuredangle F_a As F_d = 90^\circ$
$\measuredangle F_d As F_e = 180^\circ$

j) 

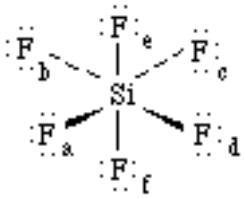
Linear

$\measuredangle$ ClAgCl = 180°

d) 

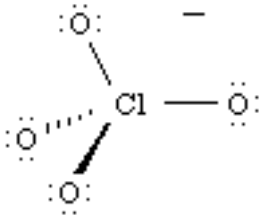
Square-based pyramidal

$\measuredangle$ FClF = 90°

k) 

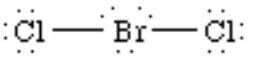
Octahedral

$\measuredangle F_b SiF_a = 90^\circ$
$\measuredangle F_a SiF_e = 90^\circ$
$\measuredangle F_e SiF_f = 180^\circ$

e) 

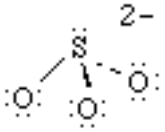
Tetrahedral

$\measuredangle$ O Cl O = 109.5°

l) 

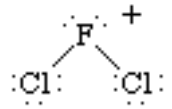
Linear

$\measuredangle$ ClBrCl = 180°

f) 

Pyramidal

$\measuredangle$ OSO = 109.5°

g)  Bent

∠ ClFCl = 109.5°

4a) BeH_4^{2-} - TETRAHEDRAL b) H_2O - BENT; (∠ HOH < 109.5°)

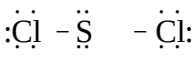
c) NO_3^- - TRIGONAL PLANAR d) NF_3 - PYRAMIDAL; ∠ FNF < 109.5°)

e) PCl_4^+ - TETRAHEDRAL f) XeF_4 - SQUARE PLANAR

g) HCN - LINEAR h) S_3^{2-} - BENT; ∠ SSS < 109.5°)

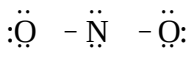
5. SCl_2 -- The Central Atom is S.

The number of valence Electrons = 6(from S) +2(7 from each Cl) = 20.

Trial structure:  -- uses 20 electrons so we're O.K.

Thus, there are 4 Electron Pairs around S. Since there are two LIGANDS (Cl) there must be 2 BONDING PAIRS of electrons and 2 NON-BONDING PAIRS. By VSEPR theory, the electron pair geometry will be TETRAHEDRAL. However ∠ Cl–S–Cl will be somewhat less than 109.5° because of the larger size of the non-bonding pairs. Recall, non-bonding–bonding pair repulsion > bonding pair–bonding pair repulsion. This result is consistent with the experimental bond angle of 100.3°.

6. NO_2^+: No. of valence of electrons = 2 (6) + 5 – 1(for the positive charge) = 16.

Trial structure:  -- uses 20 electrons.

Introduce 1 triple bond or 2 double bonds. Possible resonance structures are:

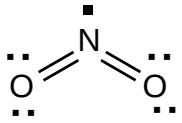
 (a) is preferred

(a) (b)

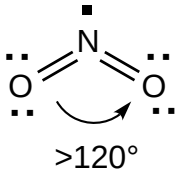
In (a) there are 4 pairs of valence electrons around the central atom N. Since the N=O bonds are DOUBLE BONDS there are only 2 ELECTRON GROUPS around

the central atom. The ELECTRON GROUP geometry around N is LINEAR. All electron groups are bonding so the molecular geometry is LINEAR.

In NO_2, there are 9 valence electrons around N -- the main resonance structure is

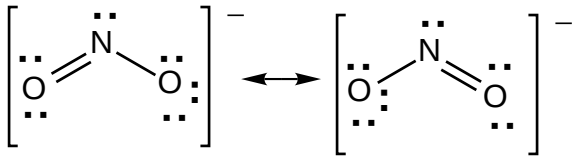


Thus, there are 4 pairs of electrons and one odd electron around N but only 3 Groups. i.e. 2 $4e^-$ groups associated with 2 double bonds, and 1 $1e^-$ group. The Idealized electron group geometry is TRIGONAL PLANAR



Since the size of a $4e^-$ group > the size of a $1e^-$ group, the O–N–O angle will increase somewhat to a value $>120^{o}$.

In NO_2^-, there are 18 valence electrons: the actual structure is a resonance hybrid (equal mixture of (a) and (b) taken together). For a discussion of the angle consider (a). There are 8 valence electrons around N:



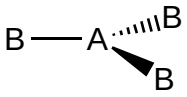
There are 4 electron pairs but since there is one double bond there are only 3 electron Groups -- 1 $4e^-$ group, 1 $2e^-$ group and 1 unshared electron pair. The idealized electron group geometry is TRIGONAL PLANAR. Strong repulsion between the non-bonding electron pair and the bonding pairs will result in a decrease of the O–N–O angle to a value somewhat smaller than 120^{o}.

7a) 2 electron pairs: Linear electron pair geometry

180° angle

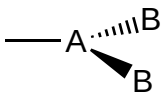
b) 3 electron pairs: Trigonal planar electron pair geometry

(i) All electron pairs bonding - Trigonal planar molecular geometry



120° angles

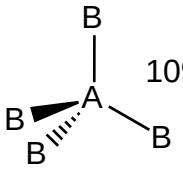
(ii) 2 bonding pairs, 1 non-bonding pair - Bent molecular geometry



idealized 120° angle
"bent" geometry

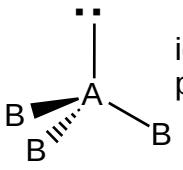
c) 4 electron pairs: Tetrahedral electron pair geometry

(i) All electron pairs bonding - Tetrahedral molecular geometry



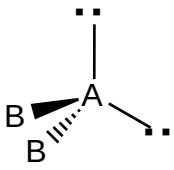
109.5° angles

(ii) 3 bonding pairs, 1 non-bonding pair - Pyramidal molecular geometry



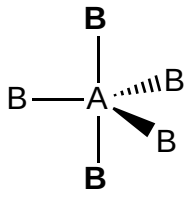
idealized 109.5° angles
pyramidal geometry

(iii) 2 bonding pairs, 2 non-bonding pairs - Bent molecular geometry



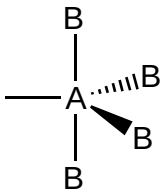
idealized 109.5° angles
bent geometry

d) 5 electron pairs - Trigonal bipyramidal electron pair geometry



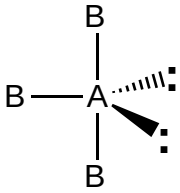
90, 180, and 120° angles
trigonal bipyramidal geometry
"axial" B atoms in bold **B**A**B** angle 180°
"equatorial" B atoms BAB angle 120°
BAB angle 90°

(ii) 4 bonding pairs, 1 non-bonding pair - "Saw horse" molecular geometry



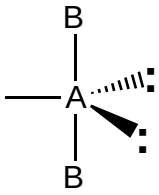
idealized 90, 180, and 120° angles

(iii) 3 bonding pairs, 2 non-bonding pairs - T-shape molecular geometry.



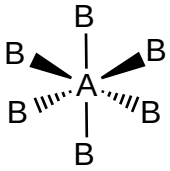
idealized 90, 180° angles
T-shaped

(iv) 2 bonding pairs, 3 non-bonding pairs - Linear molecular geometry.



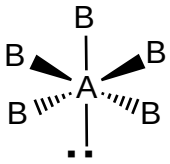
180° angle
linear

e) 6 electron pairs - Octahedral electron pair geometry



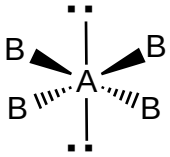
180 and 90° angles

(ii) 5 bonding pairs, 1 non-bonding pair - Square-based pyramidal molecular geometry



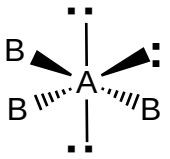
square pyramid idealized 90, 180° angles

(iii) 4 bonding pairs, 2 non-bonding pairs - Square planar molecular geometry



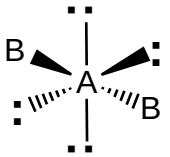
square planar 90° angles

(iv) 3 bonding pairs, 3 non-bonding pairs - T-shaped molecular geometry.



T-shaped 180 and 90° angles

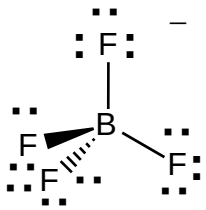
(v) 2 bonding pairs, 4 non-bonding pairs - Linear molecular geometry.



linear 180° angle

8. BF_4^-

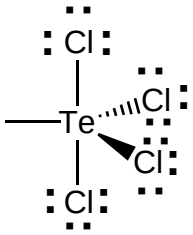
The Central Atom is B: The number of valence electrons = 3+4(7)+1=32. Thus there are 6 lone pair electrons on each F atom, and 8 more electrons in the 4 B-F bonds.



Thus, there are 4 electron pairs around B, and since there are no multiple bonds, there are 4 2 electron groups around B. Thus, we have tetrahedral electron pair geometry. Since all the electron pairs are bonding pairs and are equivalent, the molecular geometry is also TETRAHEDRAL; no deviations from ideal geometry.

$TeCl_4$ The Central Atom is Te:

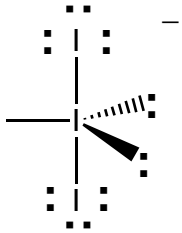
The number of valence electrons = 6+4(7)=34. (Note the filled $4d^{10}$ shell is NOT counted). Lewis Electron Dot Structure



Thus, there are 5 electron pairs around Te; since there is no multiple bonding, there are 5 electron groups around Te. The idealized electron group geometry is TRIGONAL BIPYRAMIDAL. Four groups are BONDING and one group is NON-BONDING; the NON-BONDING group goes into an EQUATORIAL POSITION. Therefore, the Idealized Molecular Geometry is SAWHORSE

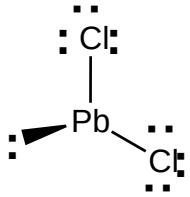
Since lone-pair–bonding pair repulsions are greater than bonding pair–bonding pair repulsions, there will be small deviations from this idealized structure. Thus the Cl_{axial}-Te-Cl_{axial} angle will be > 180 °, and the Cl_{eq}-Te-Cl_{eq} angle will be <120°.

I_3^- The number of valence electrons = 3(7)+1=22



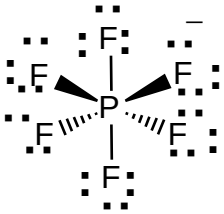
There are 5 electron pairs around the central atom--since there is no multiple bonding there are 5 electron groups around the central atom; 3 GROUPS are NON-BONDING; 2 GROUPS are BONDING. The NON-BONDING groups go into the EQUATORIAL POSITIONS of the TRIGONAL BIPYRAMID. The BONDING groups go into the AXIAL POSITIONS. Thus, the Molecular Geometry is LINEAR--no deviations from this ideal structure.

$PbCl_2$ The Central Atom is Pb; the number of valence electrons = 4+2(7)=18
Lewis Electron Dot Structure. (Note filled $4f^{14}$ and $5d^{10}$ shells are not counted.)



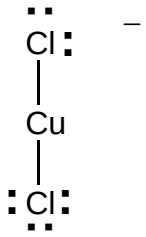
There are 3 electron pairs around Pb. Thus, we find trigonal planar Electron Pair Geometry. Since one groups is NON-BONDING, the Molecular Geometry is BENT. Since lone pair–bonding pair repulsions > bonding pair–bonding pair repulsions, the Cl-Pb-Cl angle will be <120°.

PF_6^- -- The Central atom is P; the number of valence electrons = 5+6(7)+1=48



There are 6 electron pairs around P, and since there is no multiple bonding there are 6 electron groups around P. Thus, we have OCTAHEDRAL Electron Pair Geometry; since all electron pairs are BONDING, the Molecular Geometry is OCTAHEDRAL -- no deviations from the idealized structure. The angles as usual in the octahedron will be 90 and 180°.

$CuCl_2^-$ The Central atom is Cu; the number of valence electrons = 1+2(7)+1=16
The Lewis electron dot structure is:



There are 2 electron Groups around Cu. Since both are BONDING, we have a LINEAR electron pair geometry and a LINEAR molecular geometry. Later in the course we will discuss electron counting and Lewis structures for such metal complexes in more detail. As a preview, this is Cu(I), d^{10}, so we can ignore the filled shell of d-electrons for our VSEPR assignment.