3.4 Covalent Bonds and Lewis Structures

The Lewis Model of Chemical Bonding

• In 1916 G. N. Lewis proposed that atoms combine in order to achieve a more stable electron configuration.

• Maximum stability results when an atom is isoelectronic with a noble gas.

• An electron pair that is shared between two atoms constitutes a covalent bond.



Two hydrogen atoms, each with 1 electron,

Н• •Н

can share those electrons in a covalent bond. H:H

• Sharing the electron pair gives each hydrogen an electron configuration analogous to helium.



Two fluorine atoms, each with 7 valence electrons,



can share those electrons in a covalent bond. : F:F:

• Sharing the electron pair gives each fluorine an electron configuration analogous to neon.

The Octet Rule

In forming compounds, atoms gain, lose, or share electrons to give a stable electron configuration characterized by 8 valence electrons.

• The octet rule is the most useful in cases involving covalent bonds to C, N, O, and F.



Combine carbon (4 valence electrons) and four fluorines (7 valence electrons each)



to write a Lewis structure for CF_4 .

The octet rule is satisfied for carbon and each fluorine.



It is common practice to represent a covalent bond by a line. We can rewrite



3.4 Double Bonds and Triple Bonds







Carbon dioxide

H: C::: N: $H-C \equiv N$: Hydrogen cyanide



H H H H Ethylene H C = C H H

H:C:::C:H Acetylene $H-C \equiv C-H$

3.4 Formal Charges

• Formal charge is the charge calculated for an atom in a Lewis structure on the basis of an equal sharing of bonded electron pairs.



Formal charge of H



• We will calculate the formal charge for each atom in this Lewis structure.



Formal charge of H



- Hydrogen shares 2 electrons with oxygen.
- Assign 1 electron to H and 1 to O.
- A neutral hydrogen atom has 1 electron.
- Therefore, the formal charge of H in nitric acid is 0.



Formal charge of O



- Oxygen has 4 electrons in covalent bonds.
- Assign 2 of these 4 electrons to O.
- Oxygen has 2 unshared pairs. Assign all 4 of these electrons to O.
- Therefore, the total number of electrons assigned to O is 2 + 4 = 6.



Formal charge of O



- Electron count of O is 6.
- A neutral oxygen has 6 electrons.
- Therefore, the formal charge of O is 0.



Formal charge of O j: H-Ö-N ; O:

- Electron count of O is 6 (4 electrons from unshared pairs + half of 4 bonded electrons).
- A neutral oxygen has 6 electrons.
- Therefore, the formal charge of O is 0.



Formal charge of O



- Electron count of O is 7 (6 electrons from unshared pairs + half of 2 bonded electrons).
- A neutral oxygen has 6 electrons.
- Therefore, the formal charge of O is -1.



Formal charge of N



- Electron count of N is 4 (half of 8 electrons in covalent bonds).
- A neutral nitrogen has 5 electrons.
- Therefore, the formal charge of N is +1.



Formal charges



• A Lewis structure is not complete unless formal charges (if any) are shown.

Formal Charge

An arithmetic formula for calculating formal charge.

Formal charge =

group numbernumber ofnumber ofin periodic tablebondsunshared electrons

"Electron counts" and formal charges in NH₄⁺ and BF₄⁻



3.5 Drawing Lewis Structures

Constitution

- The order in which the atoms of a molecule are connected is called its *constitution* or *connectivity*.
- The constitution of a molecule must be determined in order to write a Lewis structure.

• Step 1: The molecular formula and the connectivity are determined by experiment.

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 Example: Methyl nitrite has the molecular formula CH₃NO₂. All hydrogens are bonded to carbon, and the order of atomic connections is CONO.

• Step 2:

Count the number of valence electrons. For a neutral molecule this is equal to the number of valence electrons of the constituent atoms.

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 Example (CH₃NO₂): Each hydrogen contributes 1 valence electron. Each carbon contributes 4, nitrogen 5, and each oxygen 6 for a total of 24.

• Step 3:

Connect the atoms by a covalent bond represented by a dash.

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• Example: Methyl nitrite has the partial structure:



• Step 4:

Subtract the number of electrons in bonds from the total number of valence electrons.



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Subtract the number of electrons inbonds from the total number ofvalence electrons.

 Example: 24 valence electrons – 12 electrons in bonds. Therefore, 12 more electrons to assign.

• Step 5:

Add electrons in pairs so that as many atoms as possible have 8 electrons.
Start with the most electronegative atom.

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• Example:

The remaining 12 electrons in methyl nitrite are added as 6 pairs.



• Step 6:

If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

• Example:

Nitrogen has only 6 electrons in the structure shown.



• Step 6:

If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

• Example:

All the atoms have octets in this Lewis structure.



• Step 7:

Calculate formal charges.

• Example:

None of the atoms possess a formal charge in this Lewis structure.


- Step 7:
 - Calculate formal charges.

- Example:
 - This structure has formal charges; is less stable Lewis structure.



Condensed structural formulas

• Lewis structures in which many (or all) covalent bonds and electron pairs are omitted.



3.5 Constitutional Isomers

Constitutional isomers

- Isomers are different compounds that have the same molecular formula.
- Constitutional isomers are isomers that differ in the order in which the atoms are connected.
- An older term for constitutional isomers is "structural isomers."

A Historical Note

NH₄OCN Ammonium cyanate



- In 1823 Friedrich Wöhler discovered that when ammonium cyanate was dissolved in hot water, it was converted to urea.
- Ammonium cyanate and urea are constitutional isomers of CH_4N_2O .
- Ammonium cyanate is "inorganic." Urea is "organic." Wöhler is credited with an important early contribution that helped overturn the theory of "vitalism."

Examples of constitutional isomers



Nitromethane

Methyl nitrite

• Both have the molecular formula CH_3NO_2 but the atoms are connected in a different order.

3.5 Resonance

Resonance

two or more acceptable octet Lewis structures

may be written for certain compounds (or ions)

Table 1.4 How to Write Lewis Structures

• Step 6:

If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.

• Example:

Nitrogen has only 6 electrons in the structure shown.



- Step 6:
 - If an atom lacks an octet, use electron pairs on an adjacent atom to form a double or triple bond.
- Example:
 - All the atoms have octets in this Lewis structure.



• Step 7:

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None of the atoms possess a formal charge in this Lewis structure.



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 - This structure has formal charges; is less stable Lewis structure.



Resonance Structures of Methyl Nitrite

•same atomic positions

•differ in electron positions



Resonance Structures of Methyl Nitrite

•same atomic positions

•differ in electron positions



Why Write Resonance Structures?

• Electrons in molecules are often delocalized between two or more atoms.

• Electrons in a single Lewis structure are assigned to specific atoms-a single Lewis structure is insufficient to show electron delocalization.

• Composite of resonance forms more accurately depicts electron distribution.

Example

•Ozone (O_3)

Lewis structure of ozone shows one double bond and one single bond



Expect: one short bond and one long bond

Reality: bonds are of equal length (128 pm)

Example

•Ozone (O_3)

Lewis structure ofozone shows onedouble bond andone single bond



Resonance:



3.7 The Shapes of Some Simple Molecules





Methane

•tetrahedral geometry •H-C-H angle = 109.5°



Methane

•tetrahedral geometry •each H-C-H angle = 109.5°



Valence Shell Electron Pair Repulsions

• The most stable arrangement of groups attached to a central atom is the one that has the maximum separation of electron pairs (bonded or nonbonded).



but notice the tetrahedral arrangement of electron pairs

Ammonia

•trigonal pyramidal geometry •H-N-H angle = 107°



but notice the tetrahedral arrangement of electron pairs

Boron Trifluoride

F-B-F angle = 120°
trigonal planar geometry allows for maximum separation of three electron pairs



Multiple Bonds

• Four-electron double bonds and six-electron triple bonds are considered to be similar to a two-electron single bond in terms of their spatial requirements.

Formaldehyde: CH₂=O

H—C—H and H—C—O angles are close to 120°
trigonal planar geometry





Figure 1.12: Carbon Dioxide

•O—C—O angle = 180° •linear geometry







27 Carbon dioxide, CO₂



28 Water, H₂O

3.7: Polar Covalent Bonds and Electronegativity



Electronegativity is a measure of an element to attract electrons toward itself when bonded to another element.

An electronegative element attracts electrons.
An electropositive element releases electrons.

Pauling Electronegativity Scale

Li	Be	В	С	Ν	0	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	Р	S	C1
0.9	1.2	1.5	1.8	2.1	2.5	3.0

•Electronegativity increases from left to right in the periodic table.

•Electronegativity decreases going down a group.



Generalization

• The greater the difference in electronegativity between two bonded atoms; the more polar the bond.



nonpolar bonds connect atoms of the same electronegativity
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• The greater the difference in electronegativity between two bonded atoms; the more polar the bond.

 d_{+} ... d_{-} d_{+} d_{+} d_{-} d_{+} d_{-} d_{+} d_{-} d_{+} d_{-} d_{+} d_{-} d_{+} d_{-} d_{+} d_{+} d_{-} d_{+} d_{-} d_{+} d_{-} d_{+} d_{+}

polar bonds connect atoms of different electronegativity

3.7 Molecular Dipole Moments

Dipole Moment

• A substance possesses a dipole moment if its centers of positive and negative charge do not coincide.

m= e x d

• (expressed in Debye units)









Dipole Moment

- A substance possesses a dipole moment if its centers of positive and negative charge do not coincide.
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 - (expressed in Debye units)



Molecular Dipole Moments

•molecule must have polar bonds

-necessary, but not sufficient

•need to know molecular shape

-because individual bond dipoles can cancel

Molecular Dipole Moments



Carbon dioxide has no dipole moment; m= 0 D

Comparison of Dipole Moments





Carbon tetrachloride

m= 0 D

Dichloromethane

m= 1.62 D



Carbon tetrachloride has no dipole moment because all of the individual bond dipoles cancel.

Dichloromethane

Resultant of these two bond dipoles is



Resultant of these two bond dipoles is

m= 1.62 D

The individual bond dipoles do not cancel in dichloromethane; it has a dipole moment.