Bonding and Molecular Structure: Fundamental Concepts

Structure refers to the ways atoms are arranged in a compound

Bonding describes the forces that hold together adjacent atoms in a compound

The structure and bonding in a compound determines its chemical and physical properties

Chemical Bonding

Problems and questions —
How is a molecule or polyatomic ion held together?
Why are atoms distributed at strange angles?
Why are molecules not flat?
Can we predict the structure?
How is structure related to chemical and physical properties?
Valence Electrons

Electrons in an atom can be divided into

Core electrons
These are the inner electrons and they don't
Participate in chemical reactions

Valence electrons
These are the outermost electrons and they
are involved in chemical reaction

Electrons are divided between Core and
valence electrons.
Na  1s² 2s² 2p⁶ 3s¹
Core = [Ne] and valence = 3s¹

Br  [Ar] 3d¹⁰ 4s² 4p⁵
Core = [Ar] 3d¹⁰ and valence = 4s² 4p⁵

Number of valence electrons is equal to
Group number.

<table>
<thead>
<tr>
<th>Element</th>
<th>Period</th>
<th>Group</th>
<th>Core</th>
<th>Valence</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>3</td>
<td>1</td>
<td>1s² 2s² 2p⁶</td>
<td>3s¹</td>
<td>[Ne]3s¹</td>
</tr>
<tr>
<td>Br</td>
<td>4</td>
<td>17</td>
<td>[Ar] 3d¹⁰ 4s² 4p⁵</td>
<td>4s² 4p⁵</td>
<td>[Ar]3d¹⁰ 4s² 4p⁵</td>
</tr>
</tbody>
</table>
Lewis Symbols for Atoms

Proposed by G.N. Lewis (1875-1946)
Referred to as the Lewis Electron Dot Symbol

Rules:
- Use the element symbol to represent the nucleus and core electrons
- Represent each electron with a dot.
- Place up to 4 electrons around the symbol, one at a time. If there are more electrons then begin to pair them up.
- Maximum of 4 pairs around the symbol representing the octet of electrons

Lewis Symbols for Atoms

Draw the Lewis electron dot structures for the following elements:

- Li
- F
- N
- Ne
- C

Chemical Bond Formation

When two atoms react, they reorganize their valence electrons so that there is a net attractive force between them.

This net attractive force is called a chemical bond.
There are 2 extreme forms of connecting or bonding atoms:

**Ionic**—complete transfer of electrons from one atom to another

**Covalent**—electrons shared between atoms

Most bonds are somewhere in between.

Ionic and covalent bonding occur because of the tendency of atoms to achieve the noble gas configuration.

Essentially complete electron transfer from an element of low IE (metal) to an element of high affinity for electrons (nonmetal)

\[ \text{Na.} + \cdot\text{Cl}: \rightarrow [\text{Na}^+ :\text{Cl}^-] \]

Ionic compounds form primarily between metals at left of periodic table (Grps 1A and 2A and transition metals) and nonmetals at right (O and halogens).

### Ionic Bonds: Energy of Ion-Pair Formation

Most important factor in the formation of ionic compound is their energetics:
- the new compound must have a lower energy than the reactants

\[
\begin{align*}
\text{Na}(g) \rightarrow \text{Na}^+(g) + e^- & \quad \text{IE}_{\text{Na}} = +502 \text{ kJ/mol} \\
\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g) & \quad \text{- EA}_{\text{Cl}} = -349 \text{ kJ/mol} \\
\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(g) & \quad \text{E}_{\text{ion pair}} = -552 \text{ kJ/mol} \\
\text{Na} (g) + \text{Cl} (g) \rightarrow \text{NaCl}(g) & \quad \Delta E = -399 \text{ kJ/mol}
\end{align*}
\]

Note
formation of the ions is actually endothermic (IE + EA) = 153kJ/mol. It is the E_{ion pair} that makes the reaction Favorable.
Ionic Bonds: Energy of Ion-Pair Formation

$E_{_{\text{ion pair}}} = \frac{(n^+e^-)(n^-e^+)}{d}$

$E_{_{\text{ion pair}}}$ for the formation of Metal halides, $MX(g)$. The energy was calculated from the equation:

$E = (138,900n^+n^-) \text{kJ/mol}$

where $n$ is the ionic charge and $d$ is the interionic distance.

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Energy of Ion Pair Formation

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Ionic Bonds: Lattice Energy

Ionic compounds are solids, and their structures contain positive and negative charges arranged in a 3-dimensional lattice.

Note:
There are no ion pairs in these structures.
Ionic Bonds: Lattice Energy

Lattice energy, $E_{\text{lattice}}$, is the energy of formation of one mole of a solid crystalline ionic compound when ions in gas phase combine:

$$\text{Na} (g) + \text{Cl} (g) \rightarrow \text{NaCl} (g) \quad E_{\text{lattice}} = -786 \text{ kJ/mol}$$

Lattice energy is a measure of bonding energy in a crystalline compound. Lattice energy results from attractive forces between the cations and anions in a crystal.

Lattice energy varies with the charge and size of the ions in a similar way like $E_{\text{ion pair}}$, e.g. $\Delta H_{\text{lattice}}$ for MgO = -4050kJ/mol, for NaF = -926 kJ/mol

Table 9.3: Lattice Energies of Some Ionic Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_{\text{lattice}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>-1107</td>
</tr>
<tr>
<td>LiCl</td>
<td>-915</td>
</tr>
<tr>
<td>LiBr</td>
<td>-761</td>
</tr>
<tr>
<td>NaF</td>
<td>-961</td>
</tr>
<tr>
<td>NaCl</td>
<td>-766</td>
</tr>
<tr>
<td>NaBr</td>
<td>-702</td>
</tr>
<tr>
<td>KCl</td>
<td>-911</td>
</tr>
<tr>
<td>KBr</td>
<td>-717</td>
</tr>
<tr>
<td>KI</td>
<td>-689</td>
</tr>
<tr>
<td>KF</td>
<td>-640</td>
</tr>
</tbody>
</table>

Ionic Bonds: Why Compounds Like NaCl$_2$ and NaNe Don’t Exist

Formation of NaCl$_2$ will involve initial formation of Na$^{2+}$, i.e.:

$$\text{Na}(g) + 2 \rightarrow \text{Na}^+(g) \rightarrow \text{Na}^{2+}(g)$$

$1s^22s^22p^63s^1 \rightarrow 1s^22s^22p^6 \rightarrow 1s^22s^22p^5$

This will involve 1$^{\text{st}}$ and 2$^{\text{nd}}$ IE (496+4562 kJ/mol) which is a huge amount of energy thus resulting in a $\Delta H_{\text{f}}$ that is positive — an unfavorable reaction !!.

Similar argument holds true for Ne
Covalent Bonding

Covalent bond forms by the sharing of VALENCE ELECTRONS, the electrons at the outer edge of the atom.

The bond arises from the mutual attraction of 2 nuclei for the same electrons (see Screen 9.9):

Bond is a balance of attractive and repulsive forces.

Electron Distribution in Molecules

- Electron distribution is depicted with Lewis electron dot structures
- Electrons are distributed as shared or BOND PAIRS and unshared or LONE PAIRS.
Bond and Lone Pairs

- Electrons are distributed as shared or BOND PAIRS and unshared or LONE PAIRS (NON BONDING PAIRS).

\[ \text{H} + \cdot \text{Cl} \rightarrow \text{H} \cdot \text{Cl} \]

shared or bond pair

lone pair (LP)

This is called a LEWIS ELECTRON DOT structure.

Bond Formation

A bond can result from a “head-to-head” overlap of atomic orbitals on neighboring atoms.

\[ \text{H} \cdot \cdot \text{Cl} \rightarrow \text{H} \cdot \cdot \text{Cl} \]

Overlap of H (1s) and Cl (2p)

This type of overlap places bonding electrons in a MOLECULAR ORBITAL along the line between the two atoms and forms a SIGMA BOND (\(\sigma\)).

Bond Formation

There are cases in which two or more atoms are multiply bonded

\[
\begin{array}{c}
\text{Double Bond} \\
:O=O:
\end{array}
\quad
\begin{array}{c}
\text{Triple Bond} \\
:N=N:
\end{array}
\]
Rules of the Game

No. of valence electrons of an atom = Group number
For Groups 1A-4A, no. of bond pairs = group number
For Groups 5A-7A, no. of bond pairs = 8 - Grp. No.
Except for H (and atoms of 3rd and higher periods),
BP's + LP's = 4
This observation is called the OCTET RULE

Building a Dot Structure

Ammonia, NH₃
1. Decide on the central atom; never H.
   Central atom is atom of lowest affinity for electrons.
   Therefore, N is central
   (Most common central atoms – C,N,P,S)
   Cl is typically a terminal atom except when connected to O

2. Count valence electrons
   Nitrogen (Grp 5A) contributes 5e⁻  1 x 5 = 5
   Hydrogen (Grp 1A) contributes 1e⁻  3 x 1 = 3
   8e⁻
Building a Dot Structure

3. Place 2e⁻ in each bond to form a sigma bond between the central atom and surrounding atoms.

H—N—H
H

4. Remaining electrons form LONE PAIRS to complete the Octet as needed. 3 BOND PAIRS and 1 LONE PAIR

Note: Hydrogen does not need lone pair of electrons

Sulfite ion, SO₃²⁻

1. Choose central atom (Lowest EA) = S

2. Count valence electrons
   Sulfur (Grp 6A) contributes 6e⁻  1 x 6 = 6
   Oxygen (Grp 6A) contributes 6e⁻  3 x 6 = 18
   Add 2e⁻ for 2⁻ charge = 2
   Total = 26e⁻

3. Form sigma bonds
   10 pairs of electrons are now left.

    O
    O—S—O

Remaining pairs become lone pairs, first on outside atoms and then on central atom.

    O
    O—S—O

Each atom is surrounded by an octet of electrons
**NH₄⁺ (Ammonium Ion)**

1. Central atom is N
2. Number of valence electrons
   - Nitrogen (Grp 5A) contributes 5e⁻: \[1 \times 5 = 5\]
   - Hydrogen (Grp 1A) contributes 1e⁻: \[4 \times 1 = 4\]
   - Subtract 1e⁻ for 1+ charge: \[-1\] \[\text{Total} = 8e⁻\]

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**Carbon Dioxide, CO₂**

1. Central atom = _______
2. Valence electrons = ___ or ___ pairs
3. Form sigma bonds.

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**Carbon Dioxide, CO₂**

1. Central atom = ___C____
2. Valence electrons = ___16__ or ___8__ pairs
3. Form sigma bonds.
   \[\text{O}--\text{C}--\text{O}\]

   This leaves 6 pairs.
Carbon Dioxide, CO₂

1. Central atom = __C_____
2. Valence electrons = _16_ or _8_ pairs
3. Form sigma bonds.
   O—C—O
   This leaves 6 pairs.
4. Place lone pairs on outer atoms.
   O=C=O
4. Place lone pairs on outer atoms.

5. So that C has an octet, we shall form DOUBLE BONDS between C and O.

The second bonding pair forms a \( \pi \) (pi) bond.
Double and even triple bonds are commonly observed for C, N, P, O, and S.

Sulfur Dioxide, SO₂
1. Central atom = S
2. Valence electrons = 18 or 9 pairs
**Sulfur Dioxide, SO₂**

1. Central atom = S
2. Valence electrons = 18 or 9 pairs

\[ \text{O} \quad \text{S} \quad \text{O} \]

3. Form pi (\(\pi\)) bond so that S has an octet — but note that there are two ways of doing this.

\[ \text{O} \quad \text{S} \quad \text{O} \]

- **bring in left pair**
- **OR bring in right pair**

\[ \text{O} \quad \text{S} \quad \text{O} \]
This leads to the following structures.

These equivalent structures are called RESONANCE STRUCTURES. The true electronic structure is a HYBRID of the two.
1. Number of valence electrons = 24 e-
2. Draw sigma bonds.
3. Place remaining electron pairs in the molecule.

\[
\begin{array}{c}
\text{Urea, } (\text{NH}_2)_2\text{CO} \\
\text{H} \quad \text{N} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{N} \quad \text{C} \quad \text{H}
\end{array}
\]


\[
\begin{array}{c}
\text{Urea, } (\text{NH}_2)_2\text{CO} \\
\text{H} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{H} \\
\text{H} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{H}
\end{array}
\]

Violations of the Octet Rule

Exceptions to the octet rule include molecules or ions:
- that have less than four pair of electrons (e.g. B compounds)
- That have more than four pairs of electrons (e.g. >3rd period)
- That have odd number of electrons (some oxides of nitrogen)
Violations of the Octet Rule
Usually occurs with B and elements of higher periods.

Boron Trifluoride
- Central atom = B
- Valence electrons = 24 or electron pairs = 12
- Assemble dot structure

The B atom has a share in only 6 pairs of electrons (or 3 pairs). B atom in many molecules is electron deficient.
Electron deficient compounds such as BF$_3$ are very reactive. They accept pair of electron from other molecules that can donate pair of electrons

This kind of bonding in which the pair of electron that is shared originates from one molecule is called Coordinate covalent bond.

**Boron Trifluoride**

**Sulfur Tetrafluoride, SF$_4$**

- Central atom = S
- Valence electrons = _34_ or _17_ pairs.
- Form sigma bonds and distribute electron pairs.

Sulfur Tetrafluoride, SF$_4$

- Central atom = S
- Valence electrons = _34_ or _17_ pairs.
- Form sigma bonds and distribute electron pairs.

5 pairs around the S atom. A common occurrence outside the 2nd period.

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Molecules With Odd Number of Electrons

Examples:

\[ \text{NO} \quad 11e^- \]
\[ \text{NO}_2 \quad 17e^- \]

Odd electron molecules are called free radicals (chemical species with unpaired electron).

It is impossible to draw a structure that obeys the octet rule.