Carbonyl chloride

$\text{COCl}_2$

1. # of valence electrons =

2. connect atoms

3. distribute electrons
Deciding between alternate Lewis Structures

Use FORMAL CHARGE (FC):

\[ FC = VE - LSE \]

**VE** = number of valence electrons in an isolated atom

**LSE** = number of electrons on the atom in the Lewis structure

**LSE** = lone pair electrons + \( \frac{1}{2} \) shared electrons

The most stable structure is the one in which the atoms bear the smallest formal charge.

Example: COCl\(_2\)
NITRATE ION: NO$_3^-$

Valence electrons:

Connect atoms, distribute electron pairs

What does the Lewis structure indicate about bond lengths and strengths in NO$_3^-$?
Some molecules cannot be represented by a single Lewis structure.

\[ \text{NO}_3^- \]

3 resonance structures
All 3 are proper and equal Lewis structures.

Together, they represent the best picture of bonding.

Molecule does not flip-flop: the TRUE structure is a MIXTURE of the resonance structures.
Molecule has **RESONANCE** when more than 1 Lewis structure can be drawn for a fixed nuclear arrangement.

Different Lewis structures are equally good (usually).

Molecules with resonance exhibit **extra stability**

**Properties** (e.g. bond length, bond strength) are **averaged over resonance structures**

Aromatic hydrocarbons have resonance
Aromatic Hydrocarbons

Contain alternating single and double C-C bonds

Benzene is prototypical molecule

Usually written:

Aromatic hydrocarbons are less reactive than alkenes:
Special kind of bonding
Have “delocalized” $\pi$ electrons
Results in added stability
Reactivity of Hydrocarbons

Do same reaction:
hydrocarbon + Br₂
  colorless red

ALKANE
Heptane + Br₂ →
CH₃-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃

ALKENE (and ALKYNES)
2-pentene + Br₂ →

AROMATIC
toluene + + Br₂ →
Review Lewis structures

What is the Lewis structure for

$\text{C}_2\text{H}_4$

$\text{SiF}_4$

$\text{XeF}_4$

$\text{TeF}_4$
EXCEPTIONS TO OCTET RULE

1. Odd # of electrons (rare)
   E.g. NO, NO₂, ClO₂
   \[ \begin{array}{c}
   7 \\
   17 \\
   19 \\
   \end{array} \]
   # of valence e⁻
   
   .. 

   \[ \begin{array}{c}
   :N=O: \\
   \end{array} \]
   octet on O
   unpaired electron on N
   (free radical)

2. Incomplete octet (# e⁻ < 8)
   Rare: Be, B

   Example: BF₃
   Formal charges
   = zero
   F is too electronegative

   BF₃ reacts readily with electron pair donors (like NH₃).
3. Molecule with atom having more than 8 electrons

fairly common

**never occurs with period 2 atoms**
occurs with atoms in period 3 and below

**WHY??** Atoms in period 3 and below are:
- larger
- have available (empty) d-orbitals

**Conditions**
- large central atom
- highly electronegative atoms attached to it: eg. F, Cl, O
- attached atoms can’t be too large

**Examples**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF₅</td>
<td>does not exist</td>
</tr>
<tr>
<td>PF₅</td>
<td>stable</td>
</tr>
<tr>
<td>PF₅</td>
<td>stable</td>
</tr>
<tr>
<td>AsF₅</td>
<td>stable</td>
</tr>
<tr>
<td>PCl₅</td>
<td>less stable</td>
</tr>
<tr>
<td>PBr₅</td>
<td>unstable</td>
</tr>
<tr>
<td>PI₅</td>
<td>does not exist</td>
</tr>
</tbody>
</table>
## Bond properties

**COVALENT BOND LENGTHS** and **ENERGIES**

**Bond length**: distance between nuclei

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (kJ/mol)</th>
<th>Bond length (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C−C</td>
<td>348</td>
<td>154</td>
</tr>
<tr>
<td>C=O</td>
<td>614</td>
<td>134</td>
</tr>
<tr>
<td>C≡C</td>
<td>839</td>
<td>121</td>
</tr>
</tbody>
</table>

More electrons shared, shorter bond length

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (kJ/mol)</th>
<th>Bond length (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C−H</td>
<td>413</td>
<td>110</td>
</tr>
<tr>
<td>C−Cl</td>
<td>328</td>
<td>176</td>
</tr>
<tr>
<td>C−Br</td>
<td>276</td>
<td>196</td>
</tr>
</tbody>
</table>

Shorter bond length, stronger the bond

*Table 8.4 and 8.5*
**BOND ENERGY**

**bond (dissociation) energy:** $D$

enthalpy of bond breaking reaction in the gas phase.

$D > 0 \quad (\Delta H > 0)$

for diatomics, $D$ is $\Delta H$ of one reaction:

$$
\text{H–H(g) → 2H(g)}
$$

$D_{\text{H–H}} = \Delta H_{\text{rxn}} = 436\text{kJ/mol}$

for polyatomics, $D$ is an averaged quantity

$$
\text{H–O–H(g) → HO(g) + H(g) + 494kJ/mol}
$$

$$
\text{H–O(g) → H(g) + O(g) + 424kJ/mol}
$$

$D_{\text{O–H}} = 463 \text{kJ/mol}$ *

* value obtained from averaging over many molecules

not exact for any one case (like $\Delta H_{f}^\circ$)