- **Expanded valence shells (extended octets)** – more than $8e^-$ around a central atom
  - Extended octets are formed only by atoms with vacant **d**-orbitals in the valence shell (**p**-elements from the **third or later periods**)
  - Extended octets form when:
    - There are too many electrons ($n_{need} < n_{rem}$) or more than 4 atoms are bonded to the central atom – **electron-rich structures → place the extra electrons at the central atom**
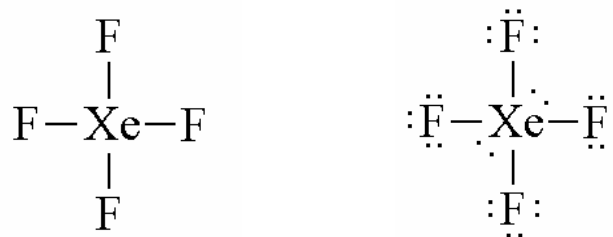   - Structures with **lower formal charges** can be achieved by forming an extended octet

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Example: Write the Lewis structure of XeF_4.

$n_{tot} = 8(Xe) + 4 \times 7(F) = 36$

$n_{rem} = 36 - 8 = 28$ $n_{need} = 0(Xe) + 4 \times 6(F) = 24$

$n_{need} < n_{rem}$

4 extra $e^- \Rightarrow$ add **2** lone pairs at **Xe**

Example: Write the Lewis structure of I_3^-.

$n_{tot} = 3 \times 7(I) + 1(charge) = 22$

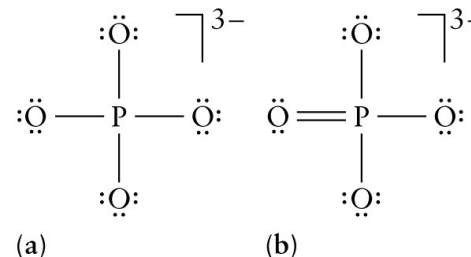$n_{rem} = 22 - 4 = 18$ $n_{need} = 4(I) + 2 \times 6(I) = 16$

$n_{need} < n_{rem}$ **2** extra e^-

$\Rightarrow$ add **1** <u>extra</u> lone pair at the central **I** atom after completing the octets for all atoms

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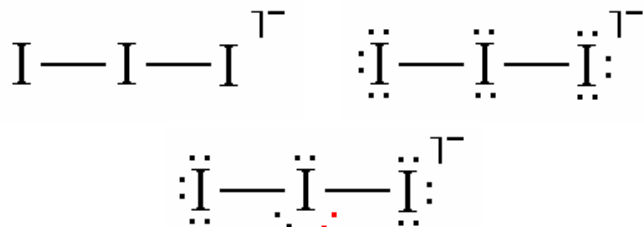
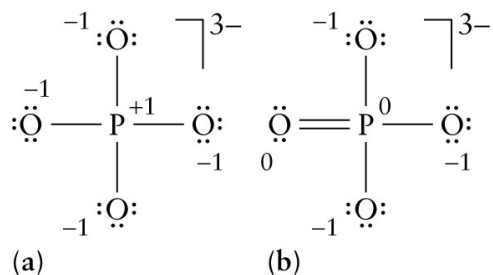**Example:** Select the favored resonance structure of the PO_4^{3-} anion.

(a)   (b)

Formal charges:
(a) O   →   6-(6+1)=-1   P → 5-(0+4)=+1
(b) O−   →   6-(6+1)=-1   P → 5-(0+5)=0
   O=   →   6-(4+2)=0

(a)   (b)

– Structure (**b**) has an extended octet (10 **e$^-$**) at the **P** atom

– Structure (**b**) is more favored (contributes more to the resonance hybrid) due to the lower formal charges

# 9.4 Using Lewis Structures and Bond Energies to Calculate *ΔH* of Reaction

• Any reaction can be represented as a two step process in which:

  – All **reactant bonds break** to give individual atoms
  – All **product bonds form** from the individual atoms
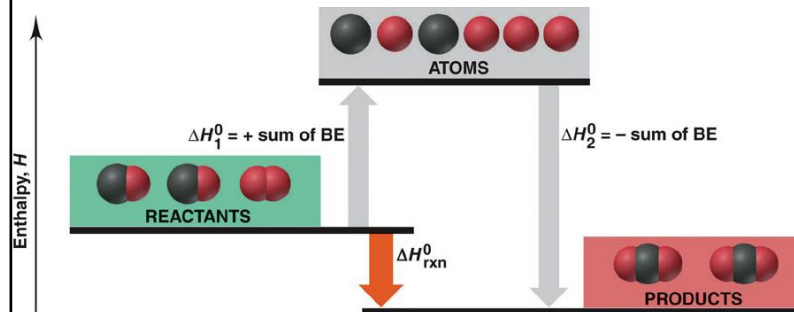
⇒ Average bond enthalpies can be used to estimate the enthalpy changes of reactions in the gas phase (only approximate values)

$$\Delta H_r^o = \Delta H_B(\text{broken}) - \Delta H_B(\text{formed})$$

– Energy is absorbed (+) to break the bonds of the reactants and emitted (-) during forming the bonds of the products
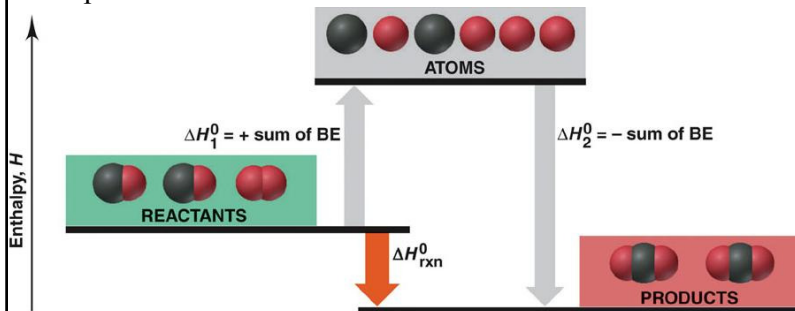
Example: Estimate the standard enthalpy of the reaction $CH_4(g) + 2F_2(g) \rightarrow CH_2F_2(g) + 2HF(g)$

1. Lewis structures are needed to get the bond order

2. Bonds broken (reactants):

  4 C–H (412 kJ/mol), 2 F–F (158 kJ/mol)

3. Bonds formed (products):

  2 C–H (412 kJ/mol), 2 C–F (484 kJ/mol), 2 H–F (565 kJ/mol)

$\Delta H^o = \Delta H_B(\text{broken}) - \Delta H_B(\text{formed}) = [4\times412 + 2\times158]$
 $- [2\times412 + 2\times484 + 2\times565] = \text{-958 kJ}$

(this value is only an estimate, the exact value can be calculated using ΔH_f^o data)

## 10.2 Molecular Shape and the Valence-Shell Electron-Pair Repulsion Model

- The chemical and physical properties of compounds are intimately related to their molecular shapes
  - **Molecular shapes** (geometries) depend on the three-dimensional arrangement of atoms in space
    - Bond **distances**, bond **angles, …**
  - Lewis structures do not represent the true shape of molecules
  - Molecular shapes are studied experimentally, but can be predicted using various theoretical models

- **Valence-shell electron-pair repulsion (VSEPR) model** – the electron-groups around a central atom are arranged as far from one another as possible in order to minimize the repulsion between them
  - **Electron-groups** are regions with high **e⁻** density (lone pairs or bonds) around the central atom
  - The **electron-group arrangement** that minimizes the repulsion depends on the number of electron-groups that repel each other:

| 2 | 3 | 4 | 5 | 6 |
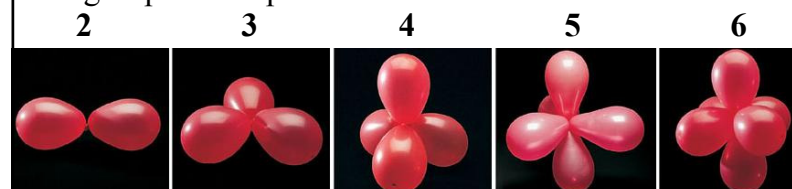
- The five most common **electron-group arrangements** and their characteristic angles:
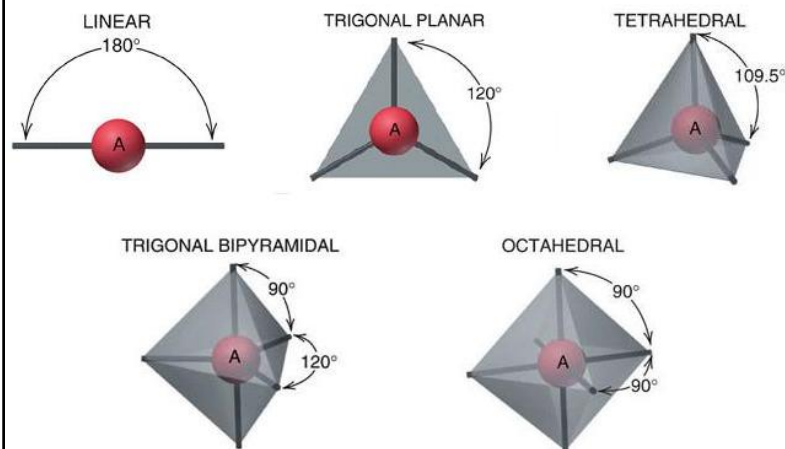
- **Both** bonding and nonbonding **e⁻** groups are considered in the **electron-group arrangement**
  - **Only** the bonding **e⁻** groups are considered in the **molecular shape** since they determine the positions of the atoms (lone pairs are ignored)
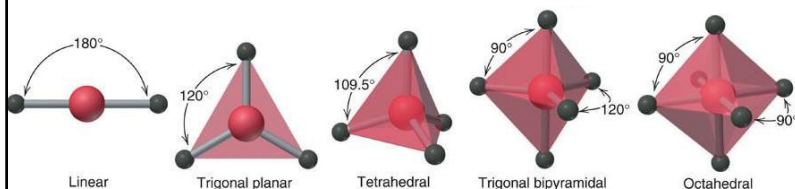- **VSEPR classes** – representations in the form AX_mE_n , where **A** is the central atom, **X** is an atom attached to it, and **E** is a nonbonding group (lone pair)
  $\Rightarrow$ *n* is the number of non-bonding groups (lone pairs) and *m* is the number of bonding groups (atoms attached to the central atom)
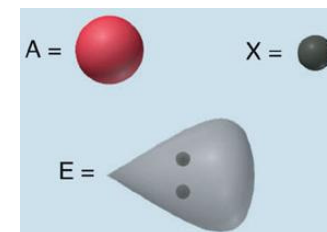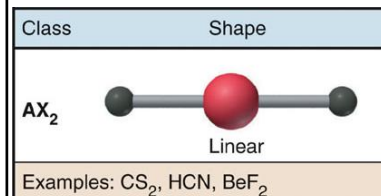
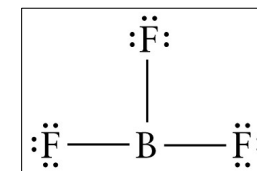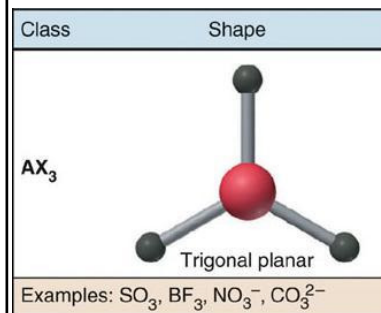- VSEPR classes AX_2, AX_3, AX_4, AX_5 & AX_6
  - All electron-groups surrounding the central atom are **bonding groups**
  - If all surrounding atoms (**X**) are the same, the **bond angles** are equal to the characteristic angles of the arrangement
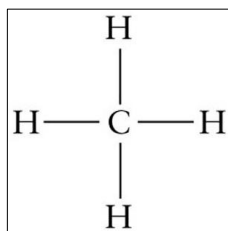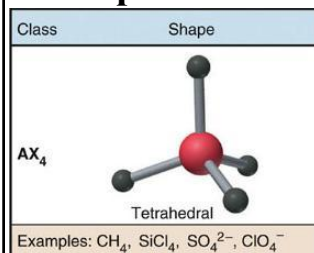 - The **molecular shape** and electron-group arrangement have the same name:

Linear · Trigonal planar · Tetrahedral · Trigonal bipyramidal · Octahedral
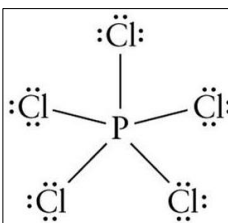

Examples:

Class	Shape
AX_2	Linear

Examples: CS_2, HCN, BeF_2

Linear shape, bond angle of 180°

Class	Shape
AX_3	Trigonal planar

Examples: SO_3, BF_3, NO_3^-, CO_3^{2-}

Trigonal planar shape, bond angles of 120°

Examples:

Class	Shape
AX_4	Tetrahedral

Examples: CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-

Tetrahedral shape, bond angles of 109.5°

Class	Shape
AX_5	Trigonal bipyramidal

Examples: PF_5, AsF_5, SOF_4
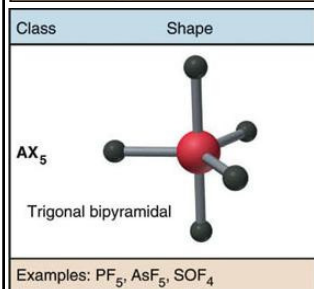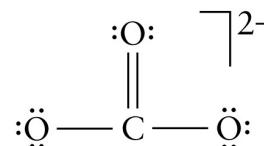
Trigonal bipyramidal shape, bond angles of 120 and 90°

- The VSEPR model treats multiple bonds in the same way as single bonds (a single bonding electron-group)

Example: CO_3^{2-}
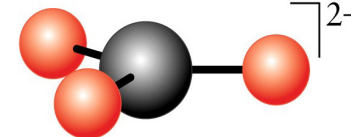
→**Three** atoms attached to a central atom (AX_3) → **Trigonal planar shape,** bond angles of 120°

→Any one of the resonance structures can be used to predict the molecular shape

- The effect of **double bonds** on **bond angles**

Example: Cl$_2$CO

→**Three** atoms attached to the central atom, no lone pairs (**AX$_3$**)

⇒**Trigonal-planar shape**

→The **bond angles deviate** from the ideal values

→The double bond has greater **e$^-$** density and repels the single bonds stronger

⇒∠ Cl-C-Cl < 120°
   ∠ Cl-C-O > 120°