Molecular Structure

– the chemical and physical properties of compounds are intimately related to their molecular shapes
– molecular shapes (geometries) depend on the electron arrangement of molecules

The Shapes of Molecules and Ions

– Lewis structures do not represent the true shape of molecules
– molecular shapes are studied experimentally, but can be predicted using various theoretical models

9.1 The VSEPR Model

- **Molecular shape (geometry)** – three-dimensional arrangement of the atoms in space
  - bond **distances**, bond **angles**
  - basic geometrical shapes

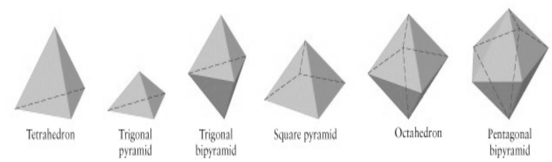


Fig. 9.1

- **Valence-shell electron-pair repulsion (VSEPR) model** – the bonding and lone e^- pairs around a central atom are arranged as far from one another as possible so that the repulsion between them is minimized
- The **electron pair arrangement** that minimizes the repulsion depends on the number of regions of high e^- density (lone pairs and bonds) that repel each other

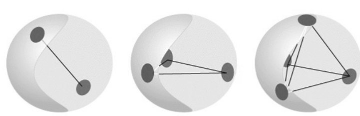


Fig. 9.4

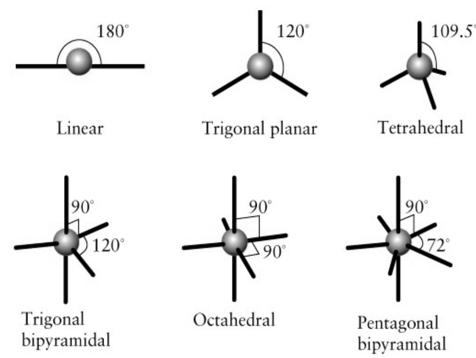
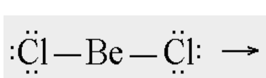
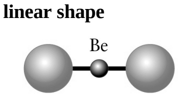


Fig. 9.5

- Molecules and polyatomic ions with **no lone pairs** at the central atom

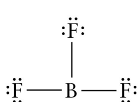
Two atoms attached to a central atom - **linear shape**



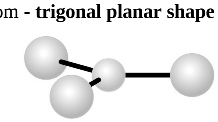


3 Beryllium chloride, $BeCl_2$

Three atoms attached to a central atom - **trigonal planar shape**

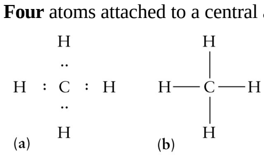


4 Boron trifluoride, BF_3

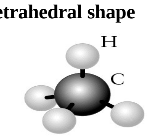


5 Boron trifluoride, BF_3

Four atoms attached to a central atom - **tetrahedral shape**

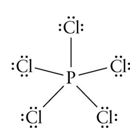


3 Methane, CH_4

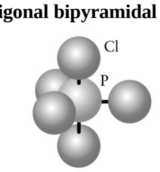


1 Methane, CH_4

Five atoms attached to a central atom - **trigonal bipyramidal shape**



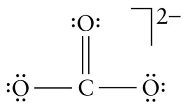
6 Phosphorus pentachloride, PCl_5



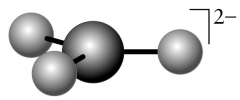
7 Phosphorus pentachloride, PCl_5

9.2 Molecules with Multiple Bonds

- The VSEPR model treats multiple bonds in the same way as single bonds (a single region of high electron density)



9 Carbonate ion, CO_3^{2-}



10 Carbonate ion, CO_3^{2-}

Three atoms attached to a central atom - **trigonal planar shape**

Example: Predict the molecular shape of **HCN**.

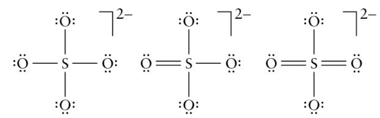
Lewis structure → **H–C≡N:**

The triple bond is counted as one

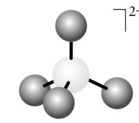
Two atoms attached to a central atom, no lone pairs

⇒ **linear shape**

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



33 Sulfate ion, SO_4^{2-}

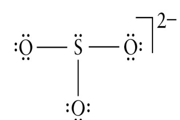


14 Sulfate ion, SO_4^{2-}

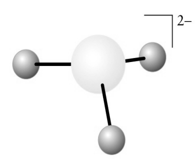
9.3 Molecules with Lone Pairs at the Central Atom

- **Electron arrangement** – a three-dimensional arrangement of the regions with high electron density (bonds and lone pairs)
  - single and multiple bonds as well as lone pairs are treated equally
- **VSEPR formulas** (**A** – central atom; **X** – atom bonded to the central atom; **E** – lone pair on the central atom)

AX_2E_2 → **2** lone pairs **+ 2** bonded atoms **= 4** → **tetrahedral electron arrangement**



15 Sulfite ion, SO_3^{2-}



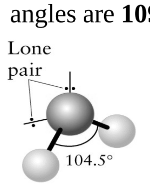
16 Sulfite ion, SO_3^{2-}

AX_3E → **1** lone pair **+ 3** bonded atoms **= 4** → **tetrahedral electron arrangement**

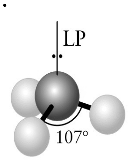
- Only the positions of atoms are considered in describing the molecular shape (lone pairs are ignored)
  - both **H_2O** and **SO_3^{2-}** have **tetrahedral** electron arrangements
  - the shape of **H_2O** is **bent** and that of **SO_3^{2-}** is **trigonal pyramidal**

- Bond angles can be predicted from the electron arrangements, but for some molecules they differ slightly from the experimental values

Example: Both **H_2O** and **NH_3** have **tetrahedral** electron arrangements and their expected bond angles are **109.5°**.



18 Water, H_2O



19 Ammonia, NH_3

The **experimental bond angles** are **smaller** when lone pairs are present at the central atom

- Lone pairs are bulkier than bonding pairs and tend to have a greater repelling effect
- If **more lone pairs** are present, the repelling effect is stronger and the **bond angles** become **smaller** →107° for **NH_3** (1 lone pair); 104.5° for **H_2O** (2 lone pairs)

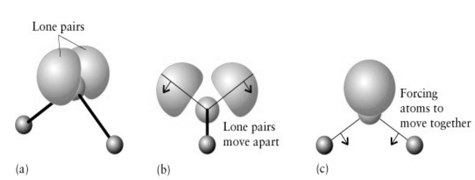


Fig. 9.5