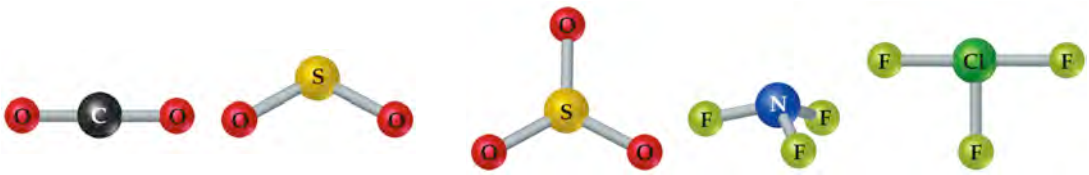
Chapter 9 Molecular Geometry and Bonding Theories

9.1 Molecular Shapes

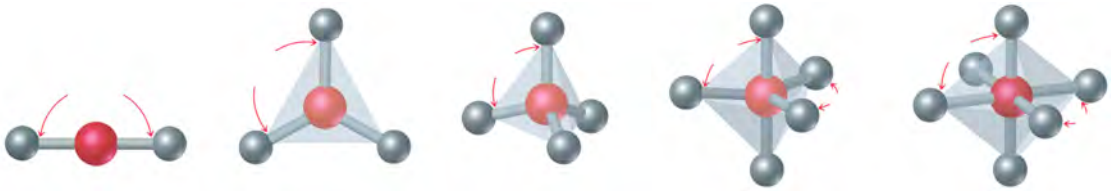
Lewis structures give atomic **connectivity** (which atoms are physically connected).

By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule

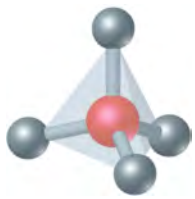


In order to predict molecular shape, we assume that the valence electrons repel each other.

For molecules of the general form $\mathbf{AB}_n$ there are 5 fundamental shapes:



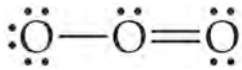
The shape of any particular AB_n molecule can usually be derived from one of these shapes. For example, starting from a tetrahedron:



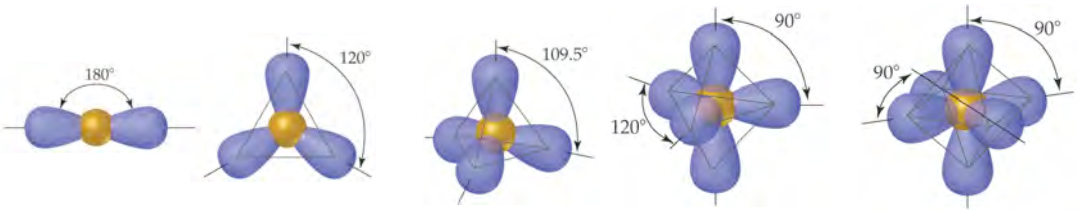
9.2 The VSEPR Model

What determines the shape of a molecule? Electron pairs, whether bonding or nonbonding, repel each other.

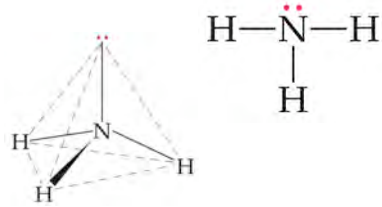
Each **nonbonding pair**, **single bond** or **multiple bond** produces an electron domain about the central atom.

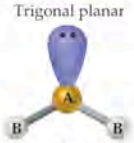


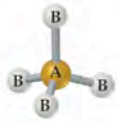
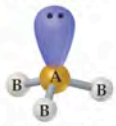
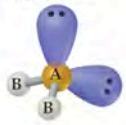
VSEPR predicts that



We use the electron-domain geometry to help us predict the molecular geometry.

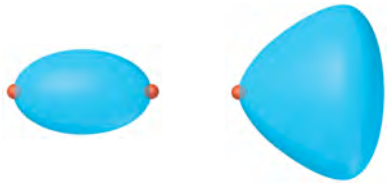


Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	 Linear			 Linear	
	 Trigonal planar			 Trigonal planar	
				 Bent	

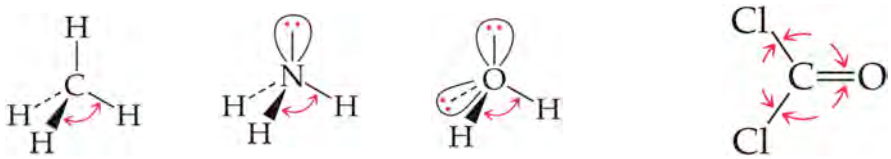
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	 Tetrahedral			 Tetrahedral	
				 Trigonal pyramidal	
				 Bent	

Effect of nonbonding electrons and multiple bonds on bond angles

Nonbonding pairs are physically larger than bonding pairs.

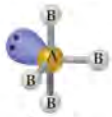


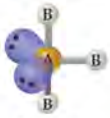
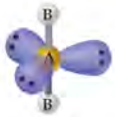
Electrons in nonbonding pairs and in multiple bonds repel **more** than electrons in single bonds:



Molecules with Expanded Valence Shells

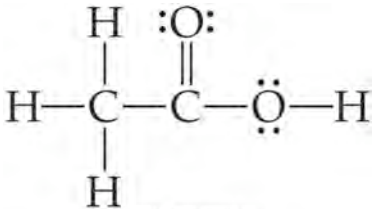
Atoms that have expanded octets have **five** electron domains (*trigonal bipyramidal*) or **six** electron domains (*octahedral*) electron-domain geometries.

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	 Trigonal bipyramidal			 Trigonal bipyramidal	
				 Seesaw	

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
	 Trigonal bipyramidal			 T-shaped	
				 Linear	
	 Octahedral			 Octahedral	
				 Square pyramidal	
				 Square planar	

Shapes of larger molecules

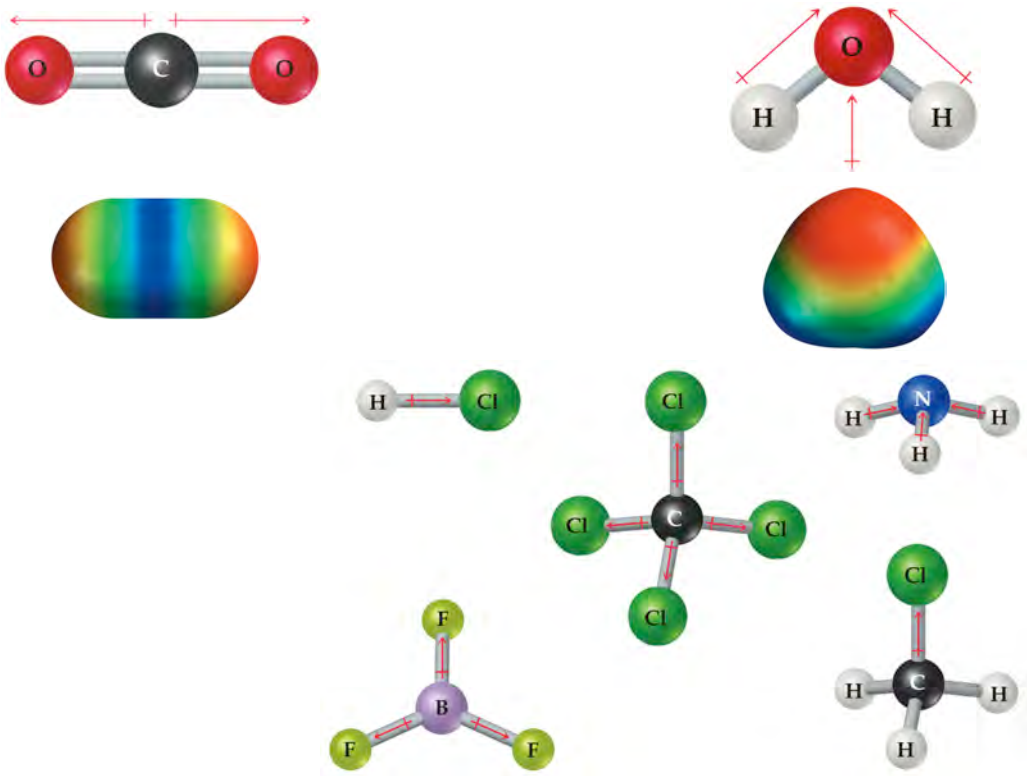
The interior atoms of more complicated molecules can be dealt with in turn using the VSEPR model.



Q. Give the electron-domain and molecular geometries for the following molecules and ions: (a) HCN, (b) SO_3^{2-}.

9.3 Molecular Shape and Molecular Polarity

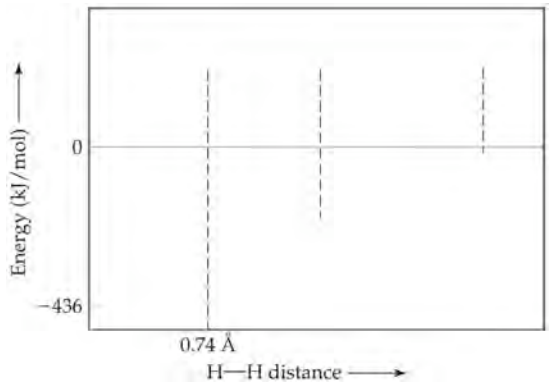
Polar molecules interact with electric fields. Binary compounds are polar if their centers of negative and positive charge **do not** coincide.



9.4 Covalent Bonding and Orbital Overlap

Covalent bonds form through sharing of electrons by adjacent atoms.

The change in potential energy as two hydrogen atoms combine to form the H_2 molecule:

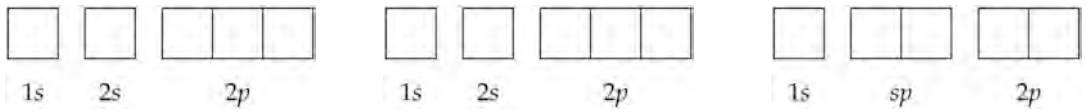


9.5 Hybrid Orbitals

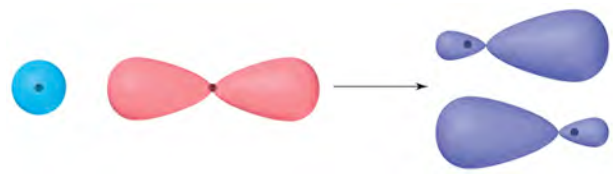
To apply the ideas of orbital overlap and valence-bond theory to polyatomic molecules, we need to introduce the concept of **hybrid orbitals**.

sp hybrid orbitals

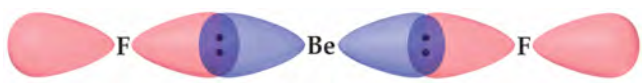
Consider beryllium: in its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals:



Mixing the *s* and *p* orbitals yields two degenerate orbitals

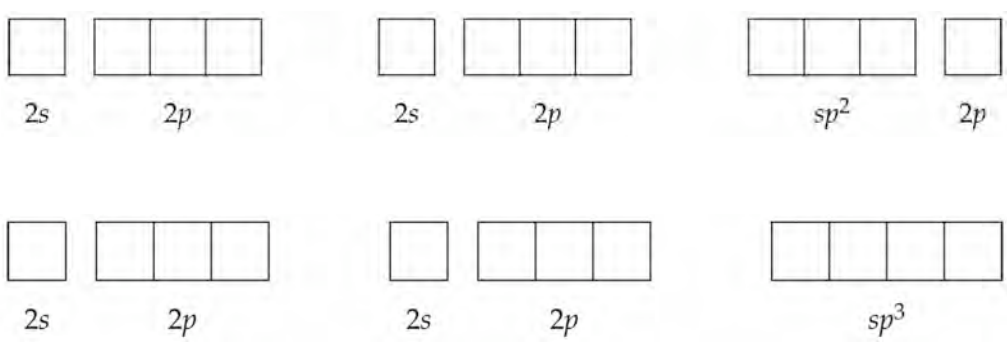


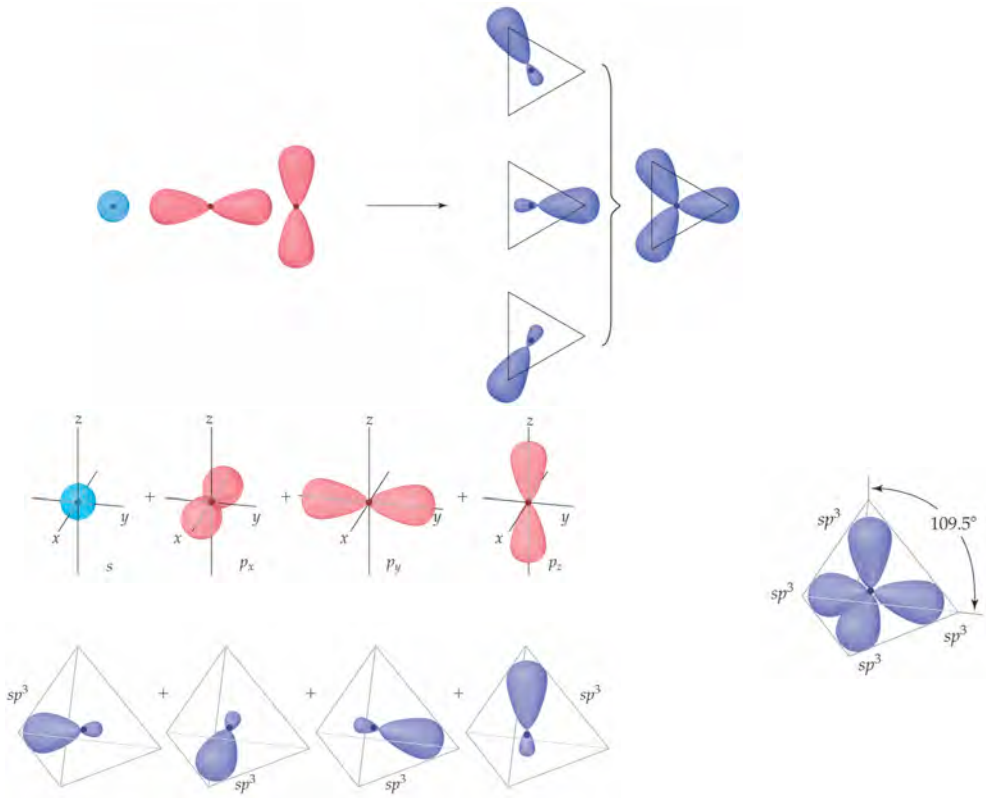
These two degenerate orbitals align themselves 180° from each other, and 90° from the two remaining unhybridized *p* orbitals.



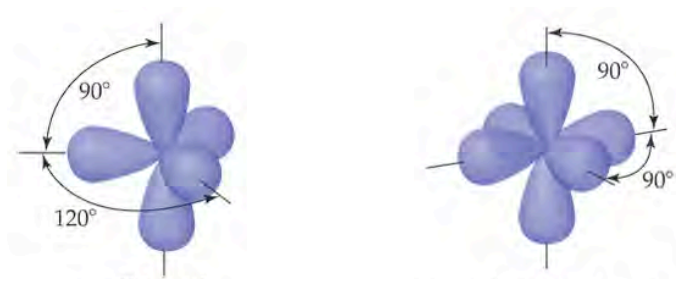
sp^2 and sp^3 hybrid orbitals

Three sp^2 hybrid orbitals are formed from hybridization of one *s* and two *p* orbitals;





For geometries involving expanded octets on the central atom, we use *d* orbitals in our hybrids:



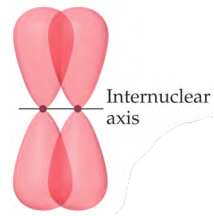
Once you know the electron-domain geometry, you know the hybridization state of the atom

9.6 Multiple Bonds

The covalent bonds we have seen so far are **sigma** (σ) bonds, characterized by:

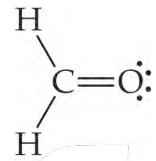
To describe multiple bonding, we must invoke **pi** (π) bonds.

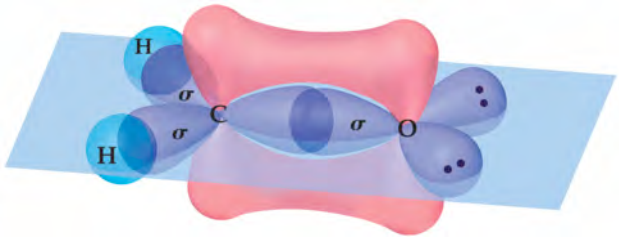
Pi (π) bonds are characterized by:



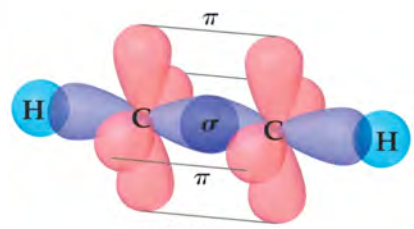
Single bonds are ***always*** σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering.

In a molecule like formaldehyde an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.



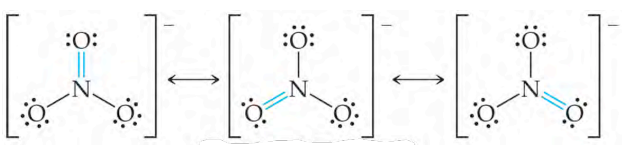


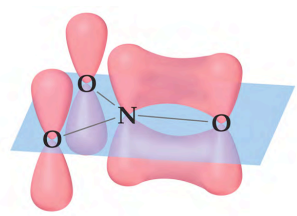
In triple bonds, e.g. acetylene, two *sp* orbitals form a σ bond between the carbons

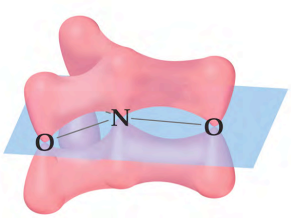


Delocalized π Bonding

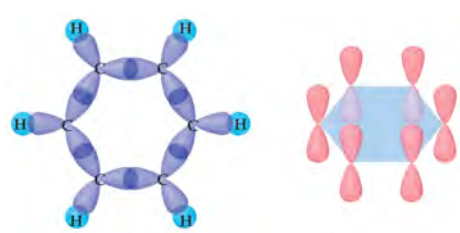
When writing Lewis structures for species like the nitrate ion, we draw resonance structures to more accurately reflect the structure of the molecule or ion







The *p* orbitals on all three oxygens overlap with the *p* orbital on the central nitrogen



9.7 Molecular Orbitals

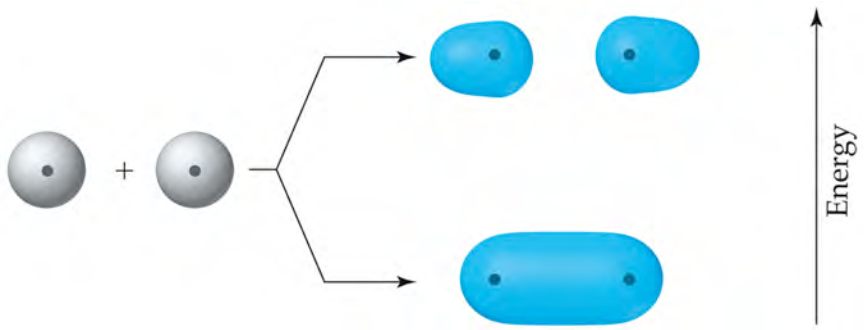
Some aspects of bonding are not explained by Lewis structures, VSEPR theory, and hybridization.

We can use molecular orbital (MO) theory to explain some of these observations.

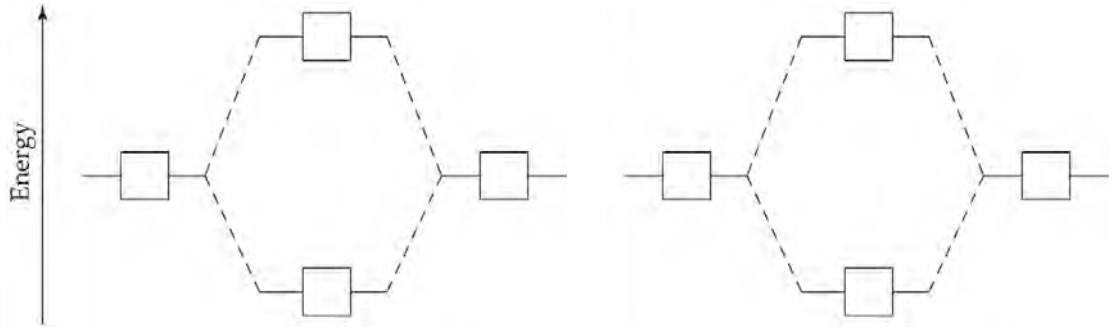
Molecular orbitals have some characteristics are similar to those of atomic orbitals.

The hydrogen molecule

When ***n*** AOs overlap, ***n*** MOs form. For H_2, 1*s* (H) + 1*s* (H) must result in 2 MOs:



Both bonding and antibonding molecular orbitals have electron density centered around the internuclear axis



Note similarity to mixing of atomic orbitals to make hybrid atomic orbitals: the difference here is that the orbitals used are on two different nuclei.

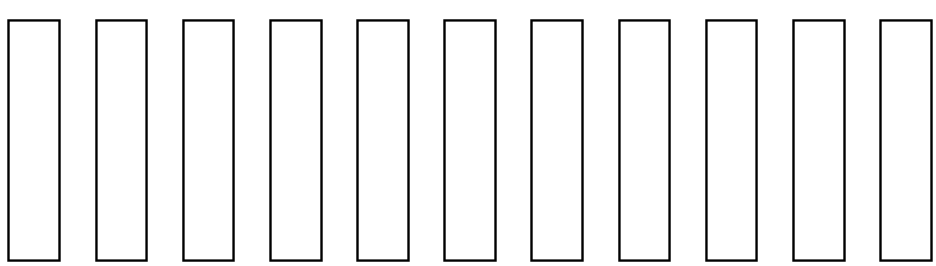
Bond order

Bond order

23.5 Metallic Bonding

MO theory helps us explain the bonding in metals. Recall that *n* AOs are used to make *n* MOs.

The energy differences between orbitals are small, so promotion of electrons requires little energy: electrons readily move through the metal.

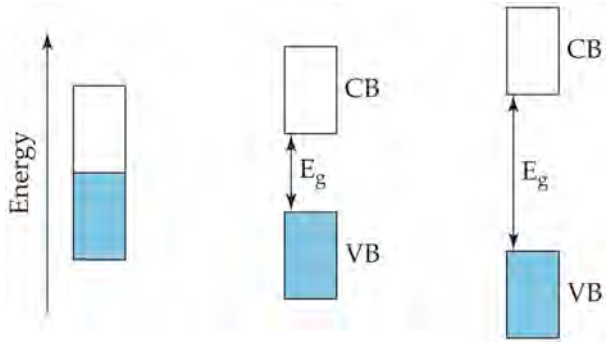


12.1 Metals and semiconductors

Materials may be classified according to their **band structure**.

Metals

Good electrical conductors.

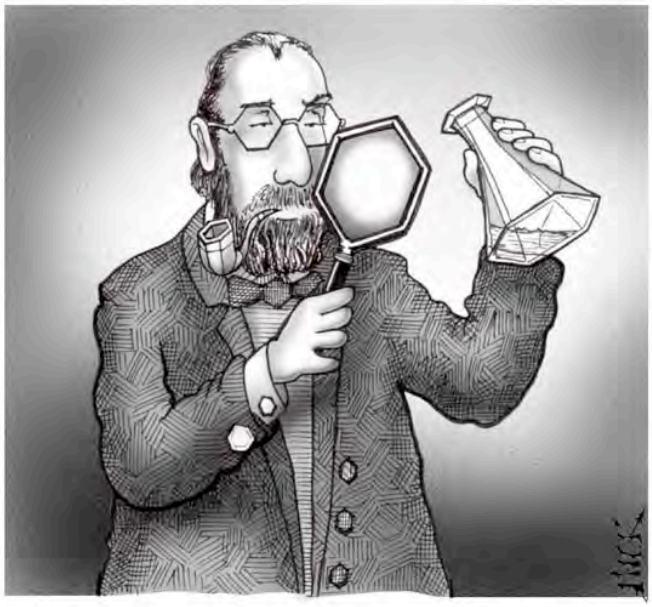


Semiconductors

Band structure has an energy gap separating totally filled bands and empty bands.

Insulators

Great events in Chemistry...



1865: Kekulé, moments before his brilliant insight into the structure of benzene.