Molecular Geometries

- Lewis dot structures are very useful in determining the types of bonds in a molecule, but they may not provide the best insight into the spatial geometry of a molecule, *i.e.*, how the nuclei in a molecule are arranged in space.
- The shape of molecules is very important in determining how they might react with other molecules.

Molecular Geometries

- Remember that covalent bonds are formed when electrons in atomic orbitals are shared between two nuclei.

Methane

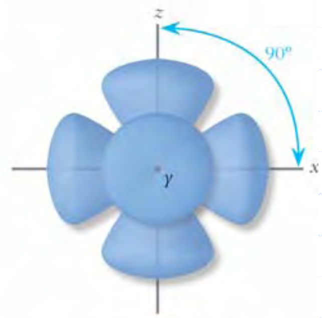
```
     H
     |
H – C – H
     |
     H
```

Molecular Geometries

- The valence orbitals available in carbon are the 2s and three 2p orbitals. Hydrogen only has 1s valence orbitals.
- One approach to forming the bonds would be to overlap the 1s orbitals of H with the 2s and 2p orbitals of C.

  What would be the results?

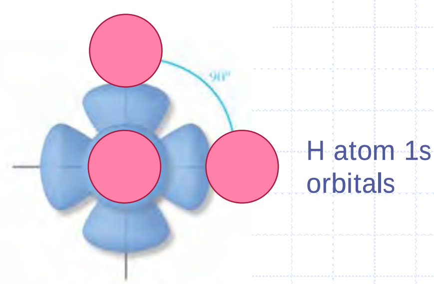
Spherical 2s orbital



The three 2p orbitals

Molecular Geometries

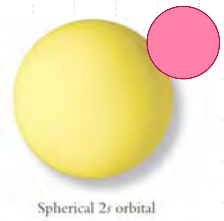
When overlapping the 1s orbitals of H's with the 2p orbitals of carbon, the bonds will be separated by 90º in each direction because the p orbitals are orthogonal.

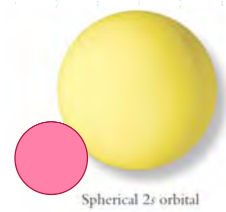


The three 2p orbitals

Molecular Geometries

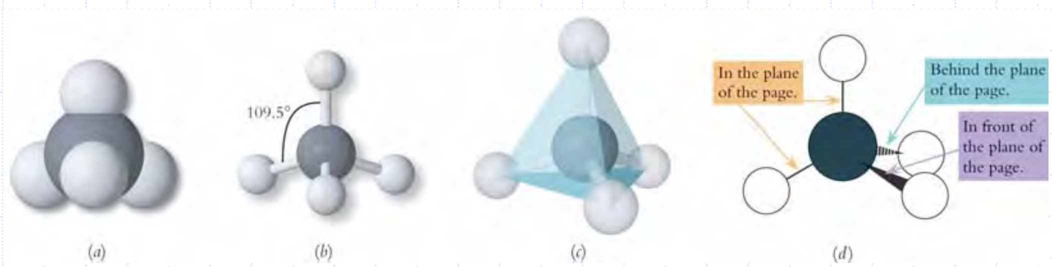
When overlapping the 1s orbital of H with the 2s orbital of carbon, the bond will have no specific orientation in space because both orbitals are spherical in shape.





Molecular Geometries

- The result of this approach for CH_4 would be a molecule in which three of the bonds were orthogonal to each other (separated by 90º) and the fourth bond could point in any direction.
- The true geometry of CH_4 is tetrahedral—each C-H bond is separated by 109.5º from the adjacent bonds.

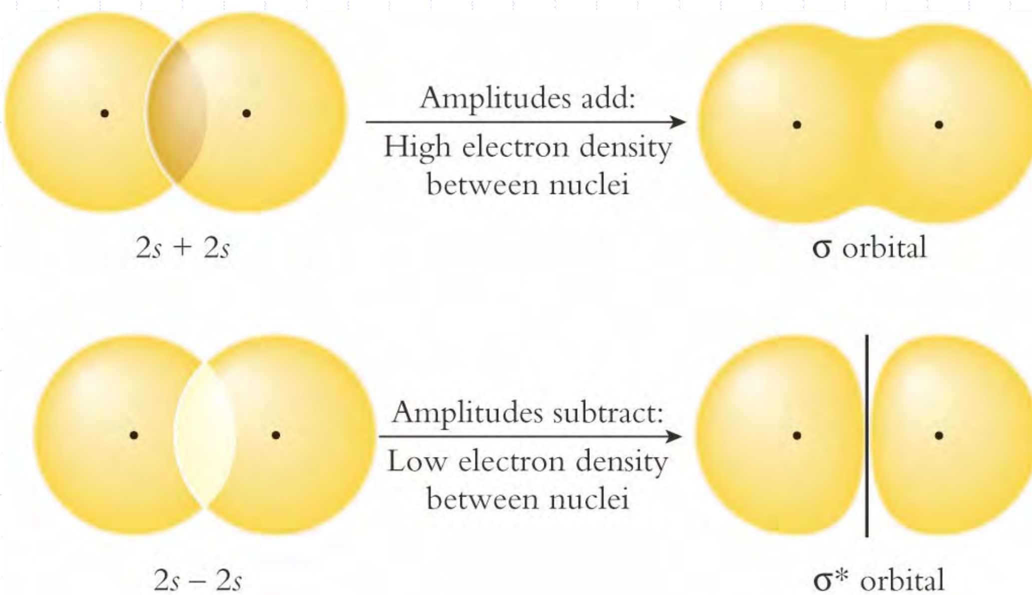


Molecular Orbitals

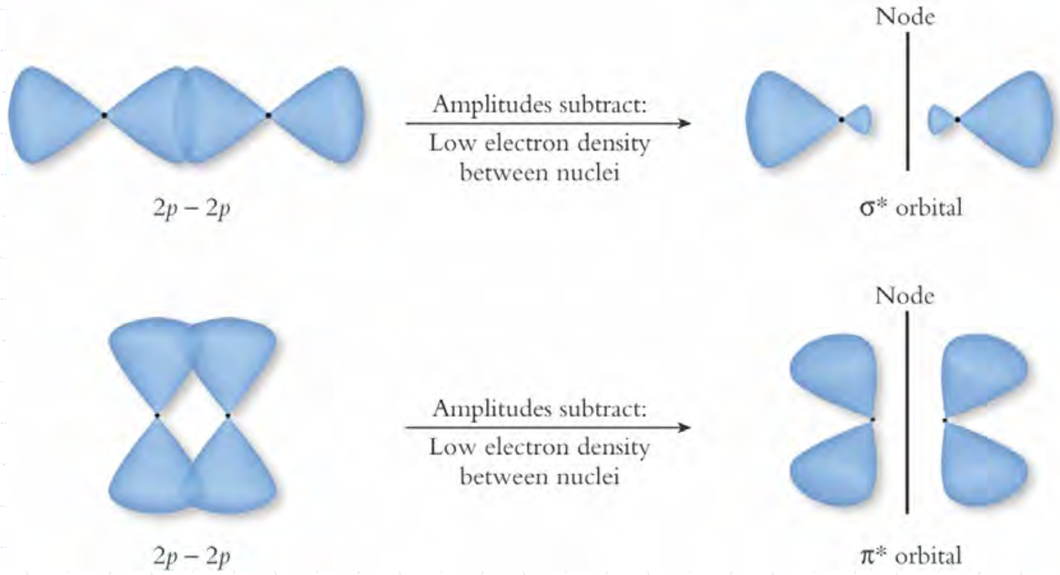
When atomic orbitals overlap to create a covalent bond, the result is the formation of *molecular orbitals*.

Molecular orbitals define the region of space most likely to contain bonding electrons—MO's are drawn as 90% electron density contours just as AO's are drawn 90% electron density contours in atoms.

Molecular Orbitals



Molecular Orbitals

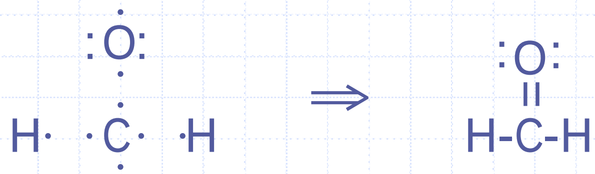


VSEPR Principle

- One way to explain the symmetric geometry of methane is with the VSEPR Principle—valence shell electron pair repulsion.
- VSEPR says that electrons pairs, either in bonds or as unshared electron pairs, want to get as far away from each other as possible because of the electrostatic repulsion of the negative electrical charges.
- The tetrahedral structure of methane optimizes to distant between electron pairs.

VSEPR Principle

Example: Formaldehyde, CH_2O

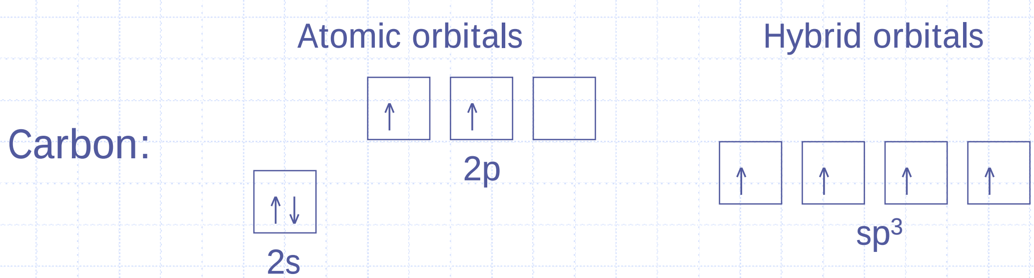


The central carbon atom in formaldehyde has three sets of valence shell electron pairs—the two single C-H bonds and the C=O double bond.

VSEPR theory predicts that the angle between these bonds will be 120º because that will maximize the distance between valence electron pairs.

Hybridization

- When atomic orbitals overlap to form covalent bonds, the energy of the system may be lowered by combining different types of atomic orbitals (*i.e.*, s, p, or d) into *hybrid* orbitals, in which the characteristics of the atomic orbitals are mixed to form the hybrid orbitals.

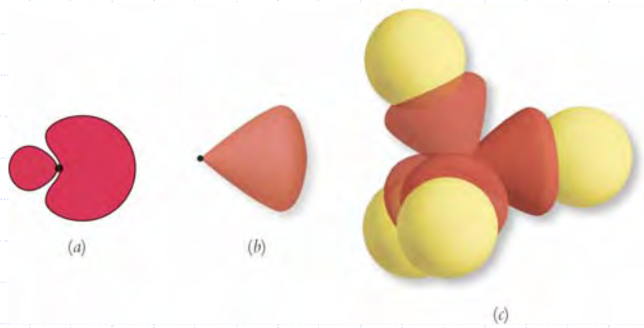


sp^3 Hybridization

- There are different type of hybrid orbitals:

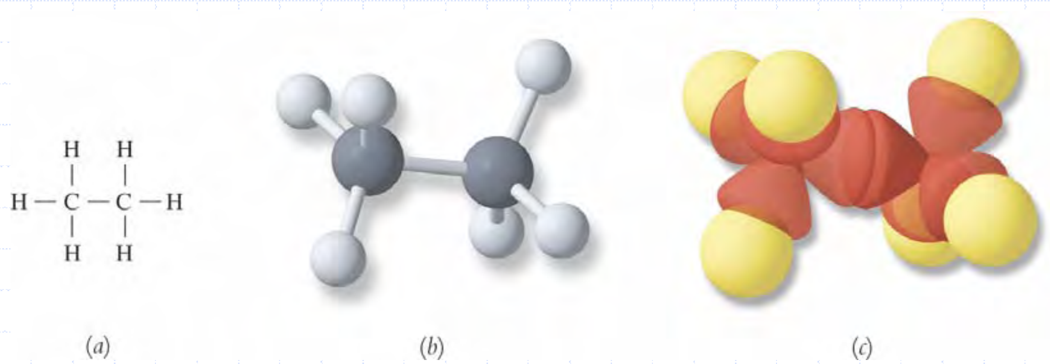
  sp^3: combination of one s orbital with three p orbitals—results in a tetrahedral geometry.

  This is the type of hybrid orbital found in methane, ethane, and other alkanes, water, etc.



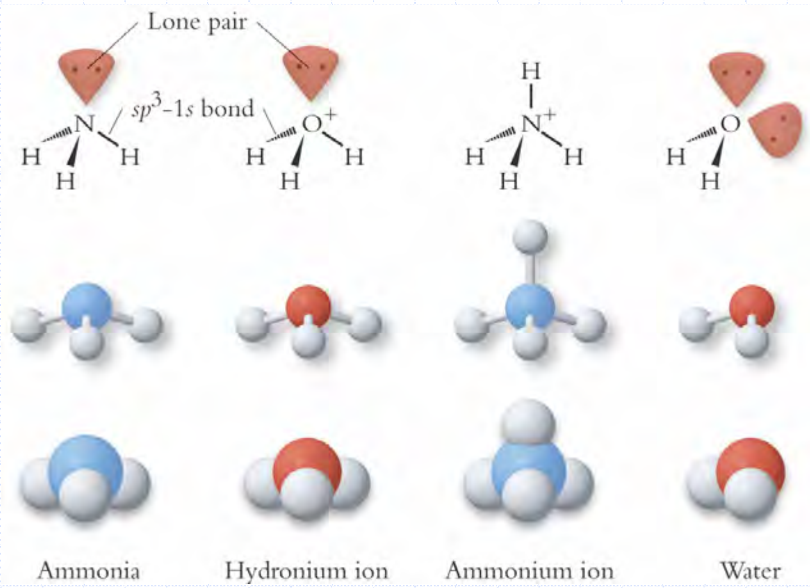
sp^3 Hybridization

Alkanes—all C-C bonds are single bonds



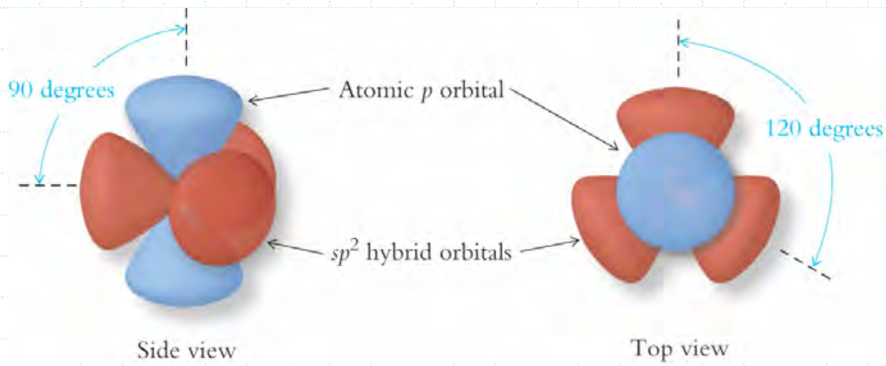
sp^3 Hybridization

Other molecules with sp^3 hybridization



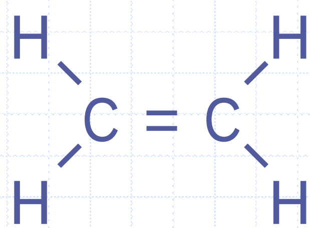
sp^2 Hybridization

- sp^2 hybridization: combination of one s orbital and two p orbitals—results in trigonal planar geometry in which each bond is in a plane separated by an angle of 120^o.
- Atoms with sp^2 hybridization maintain one regular p orbital sticking out of the plane of the hybrid orbitals.



sp^2 Hybridization

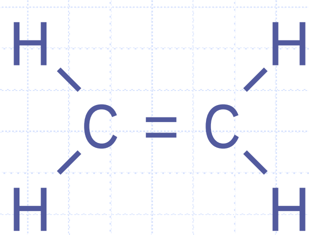
- This type of hybridization is found in molecules such as alkenes and many aluminum containing compounds. Alkenes are hydrocarbons containing at least one C=C double bond.



ethylene (ethene)

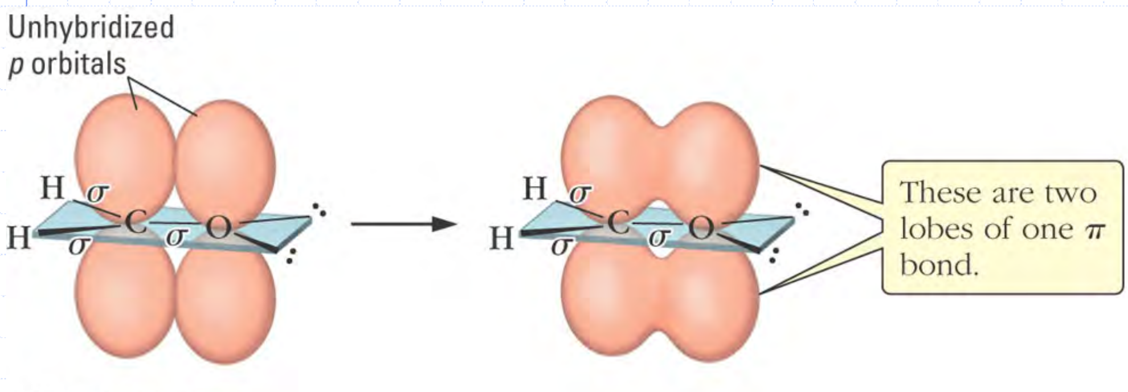
sp^2 Hybridization

- In ethylene, a σ bond along the internuclear axis is formed by the overlap of one sp^2 hybrid orbital from each C atom. The atomic p orbitals from each C atom (each containing one electron) overlap to form a π bond above and below the internuclear axis. The result is a double bond.



ethylene (ethene)

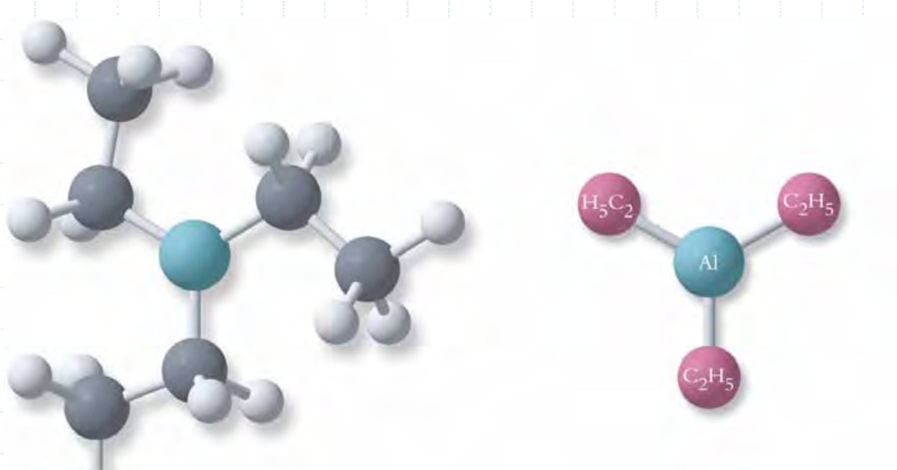
sp^2 Hybridization



formaldehyde

sp^2 Hybridization

Al containing compounds

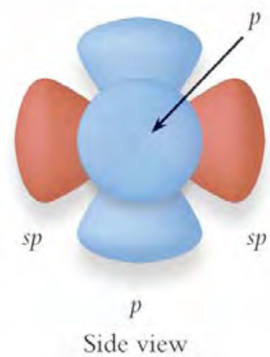


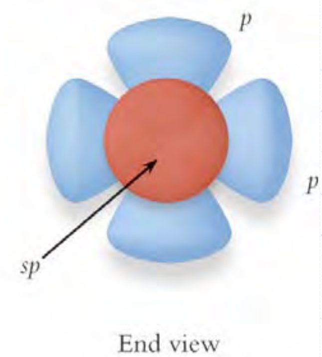
(a) Ball-and-stick model of $Al(C_2H_5)_3$

(b) Top view of simplified ball-and stick model

sp Hybridization

- sp hybridization: combination of one s orbital and one p orbital—results in a linear geometry with a bond angle of 180º.
- Atoms with sp hybridization maintain two regular p orbitals that are perpendicular to both the bond axis and the other p orbital.





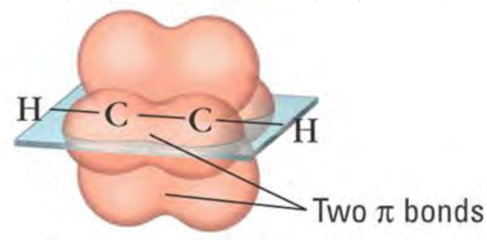
sp Hybridization

Alkynes—hydrocarbons with one or more C≡C triple bonds.

H – C ≡ C – H acetylene

sp Hybridization

In acetylene, a σ bond is formed along the internuclear axis by the overlap of sp hybrid orbitals from each C atom. One p orbital containing one e^- from each C atom overlap to form one π bond. The other p orbital from each C atom also overlap to form a second π bond. The overall result is a triple bond connecting the C atoms.



(b) Pi bonds in acetylene

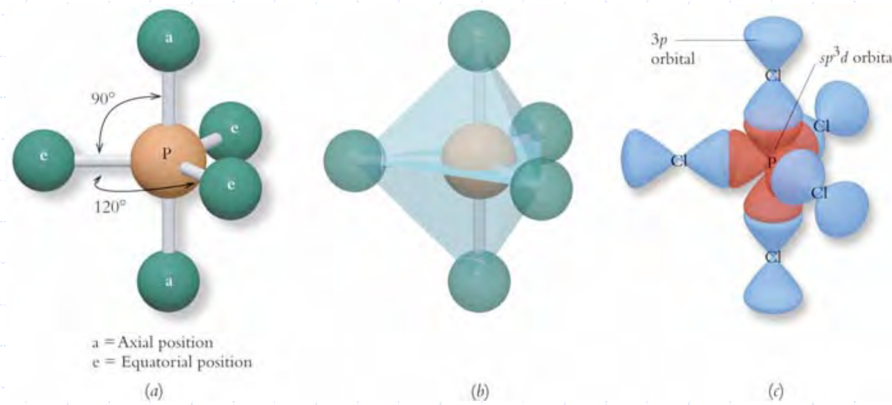
Hybridization involving d orbitals

- Once we get to the third row of the Periodic Table, the elements now have available d orbitals that may participate in bonding. Hybrid orbitals may be formed that involve these d orbitals and result in an overall lowering of the energy of the molecule.

Hybridization involving d orbitals

- sp^3d hybridization—trigonal bipyramidal geometry

PCl_5



Hybridization involving d orbitals

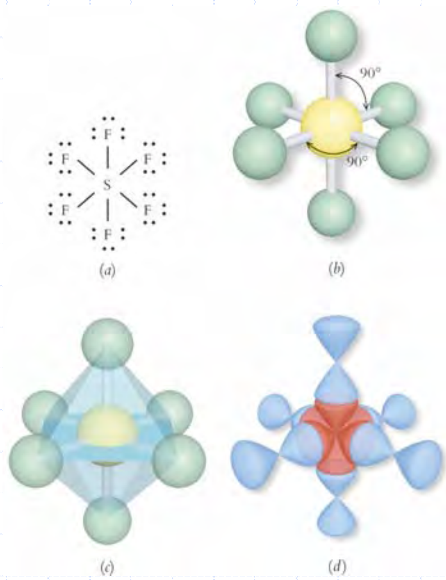
- sp^3d hybridization—trigonal bipyramidal geometry

Coord. #	lone pairs	Shape	Example	Picture
5	0	trig. bipyr.	PCl_5	
4	1	seesaw	SF_4	
3	2	T-shaped	ClF_3	
2	3	linear	I_3^-	

Hybridization involving d orbitals

- sp^3d^2 hybridization—octahedral geometry

SF_6



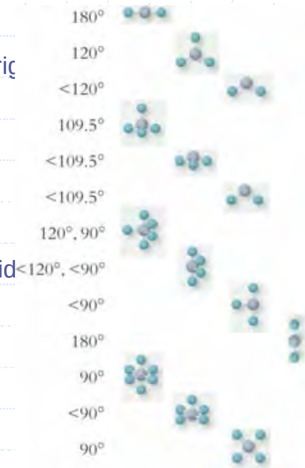
Hybridization involving d orbitals

- sp^3d^2 hybridization—octahedral geometry

Coord. #	Lone pairs	Shape	Example	Picture
6	0	octahedral	SF_6	
5	1	square pyr.	ClF_5	
4	2	square plane	XeF_4	

Summary of Hybridization

Steric #	Geometry	Hybrid.	Lone pairs	Shape
2	linear	sp	0	linear
3	trig. planar	sp^2	0	trig planar
			1	bent
4	tetrahedron	sp^3	0	tetrahedral
			1	trig. pyramid
			2	bent
5	trig. bipyramid	sp^3d	0	trig. bipyramid
			1	seesaw
			2	T-shape
			3	linear
6	octahedron	sp^3d^2	0	octahedral
			1	square pyramid
			2	square planar



Intermolecular Forces

Compound	Boiling point	Molar mass
He	4.2 K	4.0 g mol^{-1}
N_2	77.4 K	28.0 g mol^{-1}
Ar	87.5 K	39.9 g mol^{-1}
CH_4	109.0 K	16.0 g mol^{-1}
Xe	166.1 K	131.3 g mol^{-1}
Br_2	331.9 K	159.8 g mol^{-1}
CCl_4	349.7 K	153.8 g mol^{-1}
H_2O	373.2 K	18.0 g mol^{-1}

Intermolecular Forces

- Why are the boiling points of Ar, CH_4, and H_2O so different?
- Boiling (vaporization) is the transition from the liquid phase to the gas phase. For a liquid to boil, the molecules within the liquid must get enough energy to escape the forces holding the molecules in the liquid phase.
- The boiling point of a liquid can be seen as a metric for the strength of the forces holding molecules together.

Intermolecular Forces

- One of the forces holding molecules in liquid form is gravity. The force of gravity depends on the mass of the object—the heavier the object, the harder it is to overcome the pull of gravity.
- Considering only this argument for Ar, CH_4, and H_2O, CH_4 should have the lowest boiling point and Ar the highest, with the boiling point of H_2O closer to that of CH_4 since they have similar masses.

Ar	87.5 K	39.9 g mol^{-1}
CH_4	109.0 K	16.0 g mol^{-1}
H_2O	373.2 K	18.0 g mol^{-1}

Intermolecular Forces

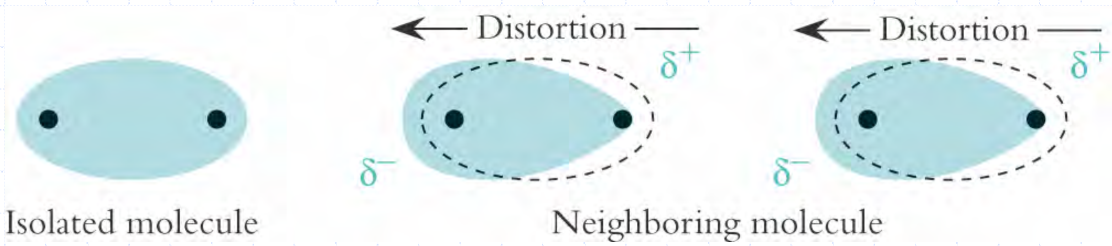
- The observed trend is very different—Ar has the lowest T_b (=87.5 K) followed by CH_4 (T_b=109 K) and then H_2O (T_b=373 K).
- Additionally, the boiling points of CH_4 and H_2O are very different—109 K *vs* 373 K, respectively.
- The explanation stems from the intermolecular attractive forces acting between molecules when they are in close proximity.

Types of Intermolecular Forces

- Dispersion forces: attraction between the electron cloud of one molecule and the positively charged nucleus of another molecule.
- Dipolar forces: attraction between positively and negatively charge sides of polar molecules
- Hydrogen bonding: attraction between lone pair electrons on electronegative atom of one molecule and hydrogen atoms in polar bonds of second molecule. H bonding is limited to molecules containing N, O, and F atoms.

Dispersion Forces

- Dispersion forces: attraction between the electron cloud of one molecule and the positively charged nucleus of another molecule. This results in the creation of a *transient* dipole moment on both molecules, and the dipole-dipole interaction helps pull the molecules together.

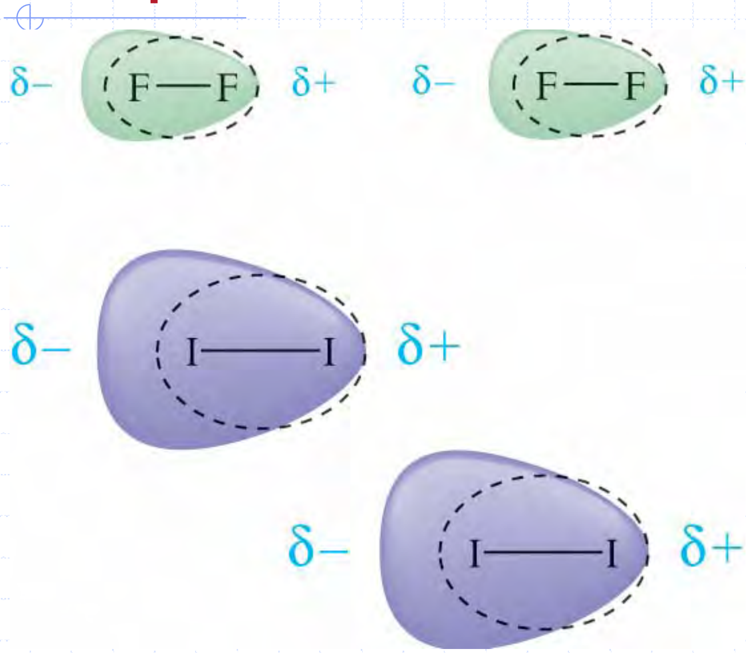


Dispersion Forces

- The larger the electron cloud on an atom or molecule, the larger the dispersion forces.
- The van der Waals *a* constant for Nobel gases:

Gas	*a* (L^2 atm mol^{-2})	radius (pm)
He	0.03412	31
Ne	0.2107	71
Ar	1.345	98
Kr	2.318	112
Xe	4.194	131

Dispersion Forces



It is much easier to distort the electron cloud of I_2 relatively to F_2 because the valence electrons in I_2 are farther from the nuclei and more easily attracted to a neighboring molecule.

F_2 is a gas; I_2 is a solid.

Dipolar Forces

- The electrostatic interaction between permanent dipole moments in polar molecules results in more attraction between neighboring molecules.

Dipolar Forces

Example: N_2 *vs* CO

Both species have ~ same molar mass: 28 g mol^{-1}

N_2 is non-polar; CO has an electronegativity difference of 1.0 resulting in a polar covalent molecule.

melting point (N_2) = 63.3 K

melting point (CO) = 74.2 K

The difference is due to the polar nature of the CO bond.

Dipolar Forces

Example

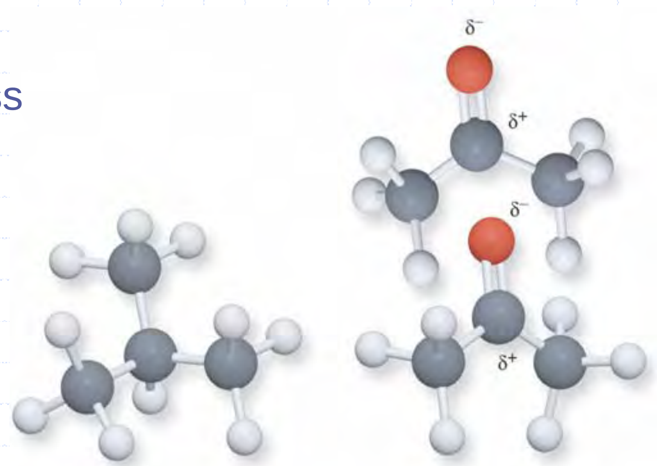
Acetone *vs* t-butane: both have molar mass of 58 g mol^{-1}.

b.p.(acetone)

= 329.4 K

b.p.(isobutane)

= 261.5 K



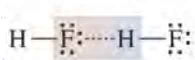
Hydrogen Bonding

- Hydrogen bonding occurs when the lone pair electrons on an O, N, or F atom interact with a hydrogen atom that is part of a polar bond.

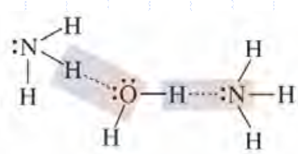
  The non-bonding pair on the O, N, or F atom acts as electron donors.

  The electron-deficient H atom acts as an electron acceptor.

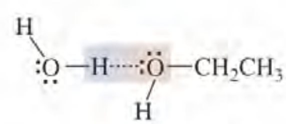
Hydrogen Bonding



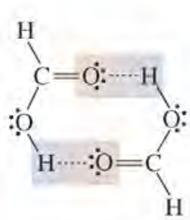
Hydrogen fluoride



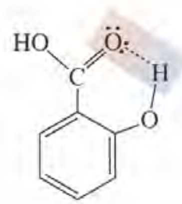
Ammonia-water



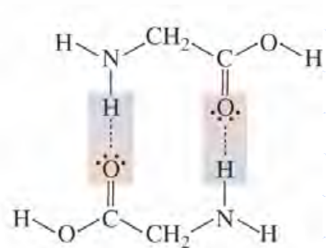
Water-ethanol



Formic acid



Salicylic acid



Glycine
(an amino acid)