

Exercises 9

Exercise 9.1

Among the following pairs, which substance has the highest melting (or boiling) point? Justify your answer.

- | | |
|--------------------|-------------------------------|
| b) HF | HCl |
| c) CH ₄ | C ₂ H ₆ |
| d) NH ₃ | H ₂ O |
| e) NH ₃ | PH ₃ |

Solution:

b) HF HCl

Strong hydrogen bonds occur in HF, so this substance will have a higher melting point. The HCl molecule is larger, but the hydrogen bonds are much stronger than the London forces and are decisive here.

c) CH₄ C₂H₆

Ethane (C₂H₆) has a higher melting point than methane, because it has more electrons and therefore exerts stronger London forces.

d) NH₃ H₂O

Water has a higher melting point than ammonia for 2 reasons.

1) because its dipole is larger than that of ammonia (the electronegativity difference between O and H is higher than between N and H and

2) the main effect is due to the structure of the water molecule: Oxygen has 2 lone pairs and 2 hydrogens. Overall, all hydrogens can therefore find a lone pair with which to interact. Therefore, all molecules are ordered in an extended tetrahedral lattice in the solid state. In the case of ammonia, nitrogen has only one lone pair for every 3 hydrogens. Each of these cannot find a lone pair, and the number of favorable interactions per molecule is less than that of water. This ultimately results in a stronger intermolecular interaction for water than for ammonia.

e) NH₃ PH₃

Ammonia can form hydrogen bonds, but the phosphine lone pair (PH₃) is too diffuse and the difference in electronegativity between P and H too low for hydrogen bonds to form between these molecules. NH₃ therefore has the highest melting point.

Exercise 9.2

For molecules of type AH_x, with A being an element from groups V (15) to VII (17), what distinguishes the second period from the following periods in terms of intermolecular interactions? Why does this distinction not exist for group IV (14)?

Solution:

NH₃, H₂O and HF can make strong hydrogen bonds, which is not the case for the following periods (for example PH₃, H₂S and HCl). Group IV(14) does not have this abrupt change from period to period because neither CH₄ nor molecules composed of elements from later periods form hydrogen bonds.

Exercise 9.3

What interaction(s) can be expected between molecules of:

- a) Benzene
- b) $\text{CH}_3\text{CH}_2\text{OH}$
- c) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

Solution:

- a) Benzene

Due to its great symmetry, this molecule has no dipole. It also contains neither nitrogen, oxygen, nor fluorine and therefore cannot form hydrogen bonds. Only the London forces remain, between two instantaneous dipoles, which can exist for all molecules.

- b) $\text{CH}_3\text{CH}_2\text{OH}$ Ethanol

The forces of London are also present. In addition, this molecule has a permanent dipole (there is a negative partial charge on oxygen), so dipole-dipole interactions are possible. Finally, the presence of a hydrogen atom bonded to oxygen makes it possible to predict the existence of hydrogen bonds.

- c) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ Diethyl ether

In addition to the London forces, there are dipole-dipole interactions. Indeed, the bonds formed by the oxygen atom are not linear but tetrahedral (2 lone pairs on O, VSEPR model AX_2E_2). No hydrogen bonds can form, however, because any hydrogens present are bonded to carbons and not to oxygens.

Exercise 9.4

What interaction(s) can be expected between $\text{C}_2\text{F}_4\text{Br}_2$ molecules? First, draw the two possible Lewis structures for this molecule.

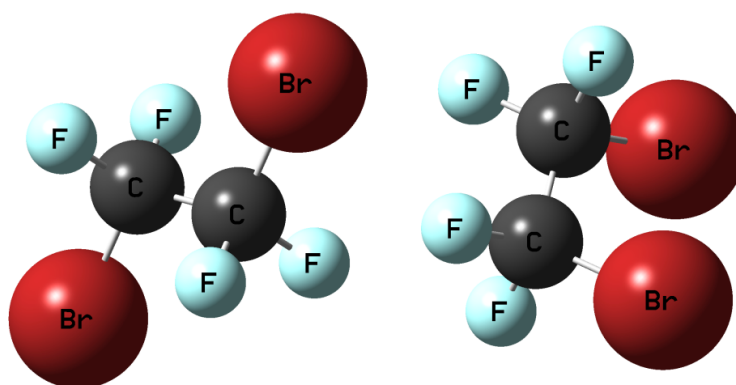
In the same way, predict the interactions between $\text{C}_2\text{F}_2\text{Br}_2$ molecules using the different possible Lewis structures.

Solution:

There are only two possible Lewis structures for the $\text{C}_2\text{F}_4\text{Br}_2$ molecule:



Indeed, we must consider that the groups at the ends of this molecule can rotate freely. The two carbons of the structure on the right are not equivalent, the dipole moments of the bonds do not compensate each other and we obtain a global dipole moment. The possible interactions for CFBr_2CF_3 are therefore dipole-dipole interactions and London forces.



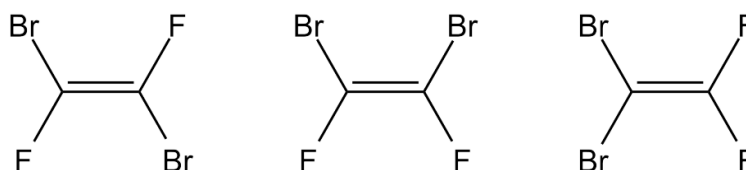
The structure drawn on the left of the figure above has a bromine atom on each carbon. The overall dipole of the molecule will depend on the orientation of the bonds relative to each other. On the left, a conformation of the molecule is shown where the C-Br bonds are in opposite directions.

In this case, their dipole moments cancel each other out. The same is true for the dipole moments resulting from the C-F bonds, and the overall dipole moment is zero.

On the right, the two C-Br bonds are oriented in the same direction and therefore their dipole moments add and an overall dipole moment exists. However, the preferred conformation of the molecule is where the bromine atoms are furthest apart, to avoid unfavorable repulsive interactions. The molecule therefore has no dipole moment.

The possible interactions in a molecule of $\text{C}_2\text{F}_4\text{Br}_2$ are therefore only the London forces. Hydrogen bonds are of course not possible.

Even before considering the structure of $\text{C}_2\text{F}_2\text{Br}_2$, one can predict the existence of London forces and the absence of hydrogen bonding. Then, depending on the structure of the molecule, there can be dipole-dipole interactions: this is the case for the geometries drawn in the middle or on the right of the figure. On the other hand, the structure on the left has no dipole: the vectors of the individual dipoles for each bond exactly compensate each other.

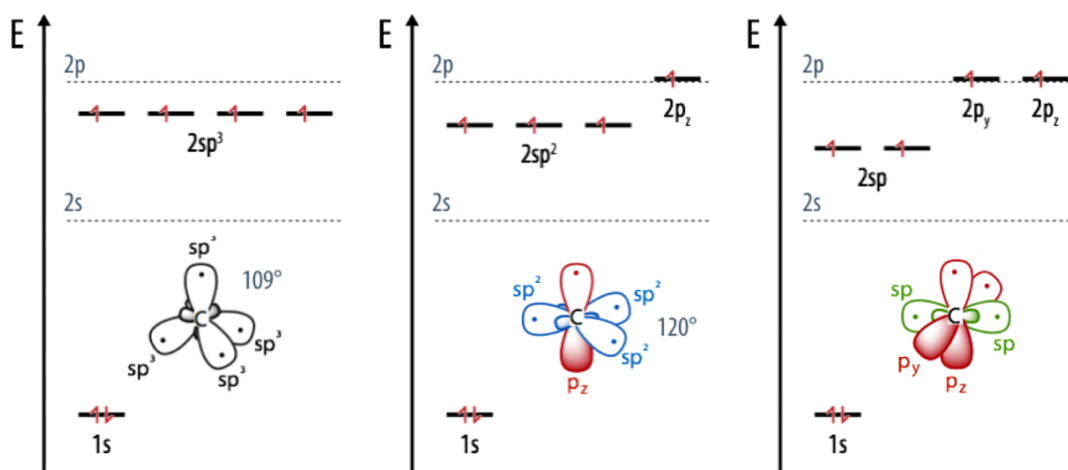


Rotation around the double bond is not possible, so it should not be considered here.

Exercise 9.5

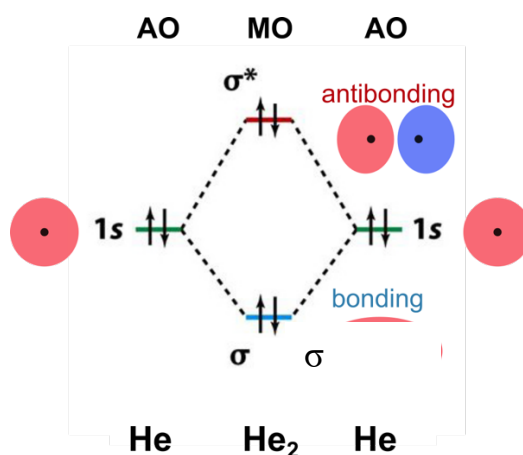
Describe three types of hybrid orbitals that can form in a carbon atom. Include an energy level diagram for each type, and provide illustrations showing the shape and orientation of each resulting hybrid orbital.

The electron configuration of a carbon atom is $1s^2 2s^2 2p^2$. Carbon can exhibit three distinct types of hybrid orbitals: sp^3 , sp^2 , and sp .



Exercise 9.7

Draw a schematic molecular orbital (MO) energy level diagram for the interaction between two helium atoms, including illustrations of the resulting MOs. Label each atomic orbital (AO) and MO, adding electrons to each. Define the terms “bonding” and “antibonding” molecular orbitals, and explain why He_2 is unstable compared to two isolated helium atoms.



Bonding orbitals are formed by constructive overlap, increasing stability, while antibonding orbitals result from destructive overlap, decreasing stability. In He_2 , both bonding and antibonding orbitals are filled, canceling each other out, making He_2 unstable.