

CHAPTER 4. INTERMOLECULAR FORCES AND PHYSICAL PROPERTIES



CHAPTER OVERVIEW

Chapter 4. Intermolecular Forces and Physical Properties



Purdue CHM 26505: Organic Chemistry for Chemistry Majors (1st Semester)

Fall 2014: Prof. Mark Lipton

Template:HideTOC

Topic hierarchy

- 4.1 Bond Polarity and Molecular Dipoles
- 4.2 Intermolecular Forces
- 4.3 Boiling Points
- 4.4 Solubility
- 4.5 Chromatography

Chapter 4. Intermolecular Forces and Physical Properties is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by LibreTexts.

4.1 Bond Polarity and Molecular Dipoles

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor in the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30} \text{ C m}$). The dipole moment of a molecule can be calculated by Equation 1:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \quad (1)$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the i^{th} charge, and
- \vec{r}_i is the vector representing the position of i^{th} charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is H_2O . Because of the lone pair on oxygen, the structure of H_2O is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

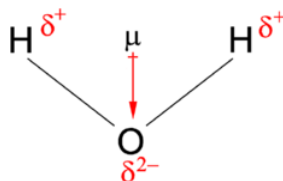


Figure 1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. [Table A2](#) shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments: just place a substance between charged plates (Figure 2); polar molecules increase the charge stored on the plates, and the dipole moment can be obtained (i.e., via the capacitance of the system). Nonpolar CCl_4 is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 2).

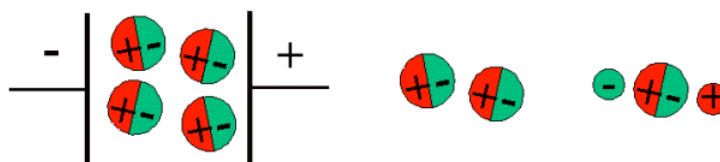


Figure 2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \quad (2)$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fixed distance. When the proton and electron are close together, the dipole moment (degree of polarity) decreases. However, as the proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment is calculated as (via Equation 2):

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19} C)(1.00 \times 10^{-10} m) \\ &= 1.60 \times 10^{-29} C \cdot m \end{aligned}$$

The Debye characterizes the size of the dipole moment. When a proton and electron are 100 pm apart, the dipole moment is 4.80 D :

$$\begin{aligned} \mu &= (1.60 \times 10^{-29} C \cdot m) \left(\frac{1 D}{3.336 \times 10^{-30} C \cdot m} \right) \\ &= 4.80 D \end{aligned}$$

4.80 D is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation is increased then the dipole moment increases (linearly):

- If the proton and electron are separated by 120 pm:

$$\mu = \frac{120}{100}(4.80 D) = 5.76 D \quad (3)$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80 D) = 7.20 D \quad (4)$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80 D) = 9.60 D \quad (5)$$

✓ Example 1: Water

The water molecule in Figure 1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference in electronegativity is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5°).

The bond moment of the O-H bond =1.5 D , so the net dipole moment is

$$\mu = 2(1.5) \cos\left(\frac{104.5^\circ}{2}\right) = 1.84 D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.

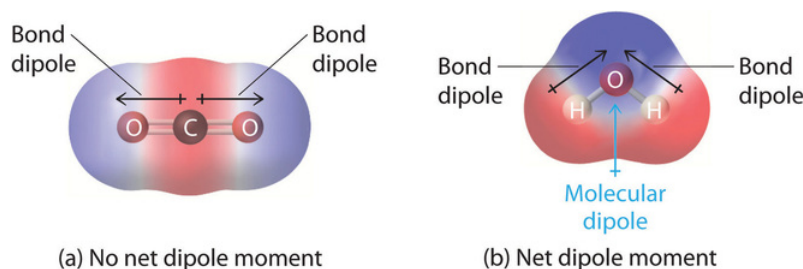


Figure 3: Charge distributions of CO_2 and H_2O . Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure 3a). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

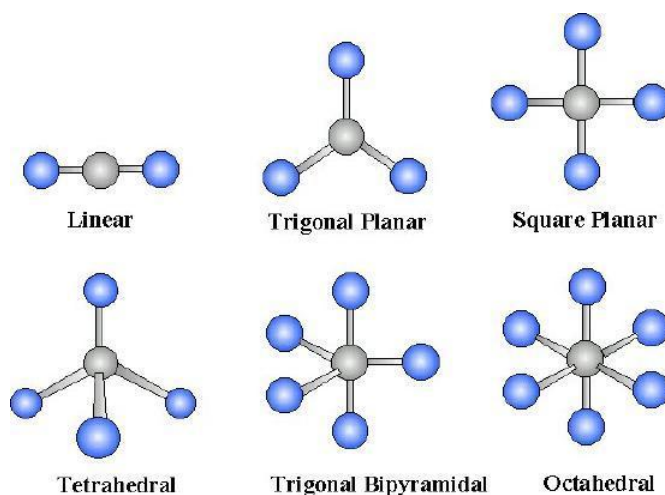
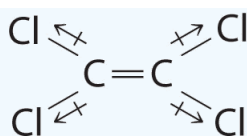


Figure 4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

✓ Example 3: C_2Cl_4

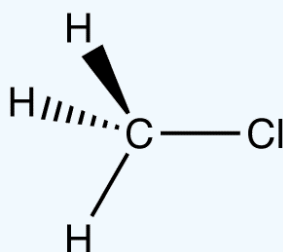
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $\text{Cl}_2\text{C}=\text{CCl}_2$ does not have a net dipole moment.



✓ Example 3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\begin{aligned}\mu &= \frac{178}{100}(4.80 \text{ D}) \\ &= 8.54 \text{ D}\end{aligned}$$



Although the bond length is **increasing**, the dipole is **decreasing** as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the **charge** at the ends of the dipole).

Table 1: Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

References

- Housecroft, Catherine E. and Alan G. Sharpe. *Inorganic Chemistry*. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pages 44-46)
- Tro, Nivaldo J. *Chemistry: A Molecular Approach*. Upper Saddle River: Pearson Education, 2008. Print. (Pages 379-386)

Further Reading

MasterOrganicChemistry

[Partial Charges](#)

[Web Pages](#)

[Electronegativity and Polar Bonds](#)

[Videos](#)

Identifying Polar Covalent Bonds in Organic Molecules

4.1 Bond Polarity and Molecular Dipoles is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [Dipole Moments](#) by Delmar Larsen, Mike Blaber is licensed [CC BY 4.0](#).

4.2 Intermolecular Forces

Skills to Develop

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intramolecular* forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *intermolecular* forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law,.)

In this section, we explicitly consider three kinds of intermolecular interactions: There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure 1a.

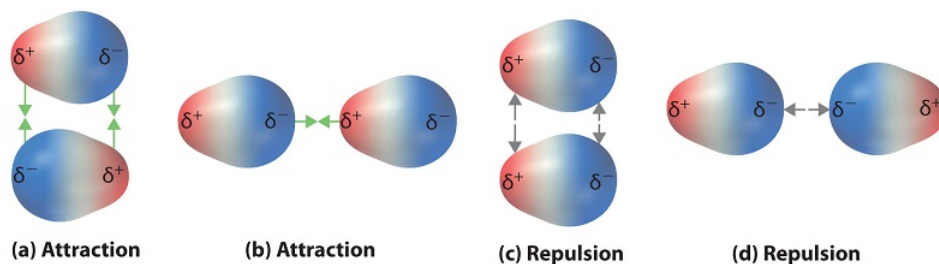


Figure 1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 1c). Hence dipole–dipole interactions, such as those in Figure 1b, are *attractive intermolecular interactions*, whereas those in Figure 1d are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience

both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 2. On average, however, the attractive interactions dominate.

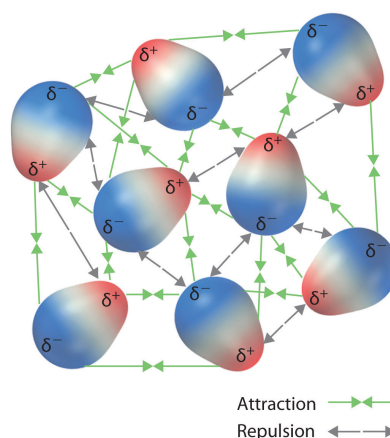


Figure 2: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ± 1 , or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6 , or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 1. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

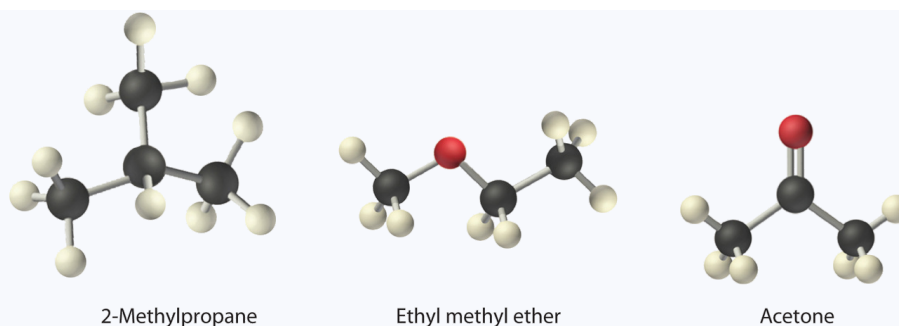
Table 1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C ₃ H ₆ (cyclopropane)	42	0	240
CH ₃ OCH ₃ (dimethyl ether)	46	1.30	248
CH ₃ CN (acetonitrile)	41	3.9	355

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 1

Arrange ethyl methyl ether (CH₃OCH₂CH₃), 2-methylpropane [isobutane, (CH₃)₂CHCH₃], and acetone (CH₃COCH₃) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H₂O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = –11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 1

Arrange carbon tetrafluoride (CF₄), ethyl methyl sulfide (CH₃SC₂H₅), dimethyl sulfoxide [(CH₃)₂S=O], and 2-methylbutane [isopentane, (CH₃)₂CHCH₂CH₃] in order of decreasing boiling points.

Answer: dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = –128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	–189.4	–185.9
Xe	131	–111.8	–108.1

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
N ₂	28	-210	-195.8
O ₂	32	-218.8	-183.0
F ₂	38	-219.7	-188.1
I ₂	254	113.7	184.4
CH ₄	16	-182.5	-161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6 , or 64-fold.

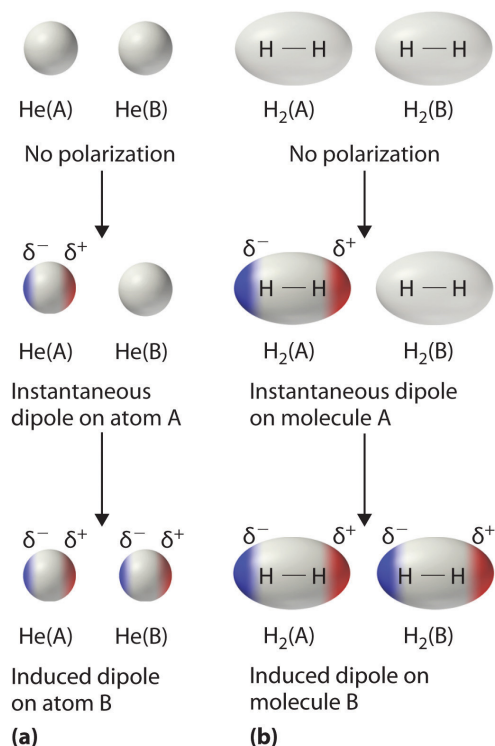


Figure 3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H₂ molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H₂ molecules in part (b) in Figure 3, tends to become more pronounced as atomic and molecular masses increase (Table 2). For example, Xe boils at -108.1°C , whereas He boils at -269°C . The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1s electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because

the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12} . Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

Figure 4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise 2

Arrange GeH_4 , SiCl_4 , SiH_4 , CH_4 , and GeCl_4 in order of decreasing boiling points.

Answer

GeCl_4 (87°C) > SiCl_4 (57.6°C) > GeH_4 (-88.5°C) > SiH_4 (-111.8°C) > CH_4 (-161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of -130°C for water! Imagine the implications for life on Earth if water boiled at -130°C rather than 100°C .

Figure 5: *The Effects of Hydrogen Bonding on Boiling Points.* These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF , NH_3 , and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two $\text{O}\cdots\text{H}$ hydrogen bonds from

adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

Figure 6: *The Hydrogen-Bonded Structure of Ice.*

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Example 3

Considering CH_3OH , C_2H_6 , Xe , and $(\text{CH}_3)_3\text{N}$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

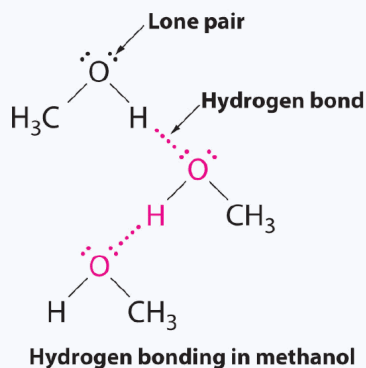
- Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
- Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(\text{CH}_3)_3\text{N}$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can

thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:

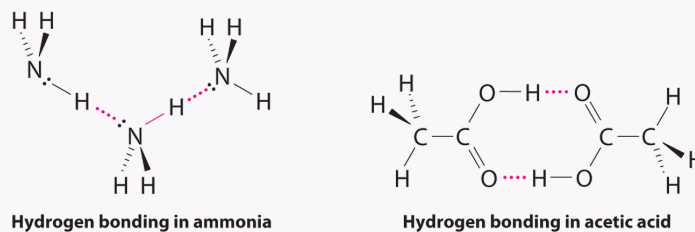


Exercise 3

Considering $\text{CH}_3\text{CO}_2\text{H}$, $(\text{CH}_3)_3\text{N}$, NH_3 , and CH_3F , which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

$\text{CH}_3\text{CO}_2\text{H}$ and NH_3 ;



Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3 . Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl , He , Ar , and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O . Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as

follows, with actual boiling points in parentheses: He (-269°C) < Ar (-185.7°C) < N_2O (-88.5°C) < C_{60} ($>280^{\circ}\text{C}$) < NaCl (1465°C).

Exercise 4

Arrange 2,4-dimethylheptane, Ne, CS_2 , Cl_2 , and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (-34.6°C) > Ne (-246°C)

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong $\text{O}\cdots\text{H}$ hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

Additional Reading

[Links to Different Intermolecular Forces](#)

[List of Intermolecular Forces](#)

[Further Reading on Intermolecular Forces](#)

MasterOrganicChemistry

[The Four Intermolecular Forces and How they Affect Boiling Points](#)

Khan Academy

[Intermolecular Forces in Organic Chemistry](#)

Web Pages

[Description of Intermolecular Forces](#)

[Intermolecular Forces Summary](#)

[Detailed Link on Intermolecular Forces](#)

[Hydrogen Bonding](#)

[van der Waals Forces](#)

Practice Problems

Virtual Text

4.2 Intermolecular Forces is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by LibreTexts.

4.3 Boiling Points

For general purposes it is useful to consider temperature to be a measure of the kinetic energy of all the atoms and molecules in a given system. As temperature is increased, there is a corresponding increase in the vigor of translational and rotation motions of all molecules, as well as the vibrations of atoms and groups of atoms within molecules. Experience shows that many compounds exist normally as liquids and solids; and that even low-density gases, such as hydrogen and helium, can be liquified at sufficiently low temperature and high pressure. A clear conclusion to be drawn from this fact is that intermolecular attractive forces vary considerably, and that the boiling point of a compound is a measure of the strength of these forces. Thus, in order to break the intermolecular attractions that hold the molecules of a compound in the condensed liquid state, it is necessary to increase their kinetic energy by raising the sample temperature to the characteristic boiling point of the compound.

The following table illustrates some of the factors that influence the strength of intermolecular attractions. The formula of each entry is followed by its formula weight in parentheses and the boiling point in degrees Celsius. First there is molecular size. Large molecules have more electrons and nuclei that create [van der Waals](#) attractive forces, so their compounds usually have higher boiling points than [similar](#) compounds made up of smaller molecules. It is very important to apply this rule only to like compounds. The examples given in the first two rows are similar in that the molecules or atoms are spherical in shape and do not have permanent dipoles. Molecular shape is also important, as the second group of compounds illustrate. The upper row consists of roughly spherical molecules, whereas the isomers in the lower row have cylindrical or linear shaped molecules. The attractive forces between the latter group are generally greater. Finally, permanent molecular dipoles generated by polar covalent bonds result in even greater attractive forces between molecules, provided they have the mobility to line up in appropriate orientations. The last entries in the table compare non-polar hydrocarbons with equal-sized compounds having polar bonds to oxygen and nitrogen. Halogens also form polar bonds to carbon, but they also increase the molecular mass, making it difficult to distinguish among these factors.

Table 1: Boiling Points (°C) of Selected Elements and Compounds

Increasing Size				
Atomic	Ar (40) -186	Kr (83) -153	Xe (131) -109	
Molecular	CH ₄ (16) -161	(CH ₃) ₄ C (72) 9.5	(CH ₃) ₄ Si (88) 27	CCl ₄ (154) 77
Molecular Shape				
Spherical:	(CH ₃) ₄ C (72) 9.5	(CH ₃) ₂ CCl ₂ (113) 69	(CH ₃) ₃ CC(CH ₃) ₃ (114) 106	
Linear:	CH ₃ (CH ₂) ₃ CH ₃ (72) 36	Cl(CH ₂) ₃ Cl (113) 121	CH ₃ (CH ₂) ₆ CH ₃ (114) 126	
Molecular Polarity				
Non-polar:	H ₂ C=CH ₂ (28) -104	F ₂ (38) -188	CH ₃ C≡CCH ₃ (54) -32	CF ₄ (88) -130
Polar:	H ₂ C=O (30) -21	CH ₃ CH=O (44) 20	(CH ₃) ₃ N (59) 3.5	(CH ₃) ₂ C=O (58) 56
	HC≡N (27) 26	CH ₃ C≡N (41) 82	(CH ₂) ₃ O (58) 50	CH ₃ NO ₂ (61) 101

The melting points of crystalline solids cannot be categorized in as simple a fashion as boiling points. The distance between molecules in a crystal lattice is small and regular, with intermolecular forces serving to constrain the motion of the molecules more severely than in the liquid state. Molecular size is important, but shape is also critical, since individual molecules need to fit together cooperatively for the attractive lattice forces to be large. Spherically shaped molecules generally have relatively high melting points, which in some cases approach the boiling point. This reflects the fact that spheres can pack together more closely than other shapes. This structure or shape sensitivity is one of the reasons that melting points are widely used to identify specific compounds. The data in the following table serves to illustrate these points.

Compound	Formula	Boiling Point	Melting Point
pentane	CH ₃ (CH ₂) ₃ CH ₃	36°C	-130°C
hexane	CH ₃ (CH ₂) ₄ CH ₃	69°C	-95°C
heptane	CH ₃ (CH ₂) ₅ CH ₃	98°C	-91°C
octane	CH ₃ (CH ₂) ₆ CH ₃	126°C	-57°C

nonane	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	151°C	-54°C
decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	174°C	-30°C
tetramethylbutane	$(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$	106°C	+100°C

Notice that the boiling points of the unbranched alkanes (pentane through decane) increase rather smoothly with molecular weight, but the melting points of the even-carbon chains increase more than those of the odd-carbon chains. Even-membered chains pack together in a uniform fashion more compactly than do odd-membered chains. The last compound, an isomer of octane, is nearly spherical and has an exceptionally high melting point (only 6° below the boiling point).

Contributors

- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

Further Reading

MasterOrganicChemistry

3 Trends That Affect Boiling Points

Websites

Boiling Point Tutorial

Slide Show on Determining Boiling Points

4.3 Boiling Points is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

4.4 Solubility

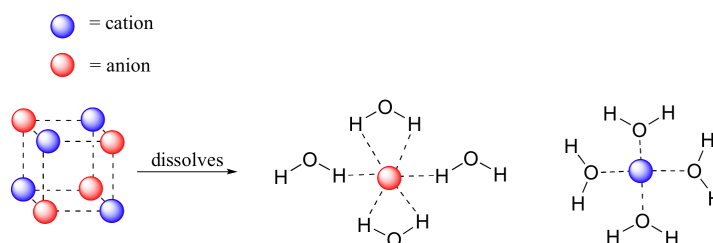
An understanding of bond dipoles and the various types of noncovalent intermolecular forces allows us to explain, on a molecular level, many observable physical properties of organic compounds. In this section, we will concentrate on solubility, melting point, and boiling point.

Solubility

Virtually all of the organic chemistry that you will see in this course takes place in the solution phase. In the organic laboratory, reactions are often run in nonpolar or slightly polar solvents such as toluene (methylbenzene), hexane, dichloromethane, or diethylether. In recent years, much effort has been made to adapt reaction conditions to allow for the use of ‘greener’ (in other words, more environmentally friendly) solvents such as water or ethanol, which are polar and capable of hydrogen bonding. In organic reactions that occur in the cytosolic region of a cell, the solvent is of course water. It is critical for any organic chemist to understand the factors which are involved in the solubility of different molecules in different solvents.

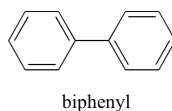
You probably remember the rule you learned in general chemistry regarding solubility: ‘like dissolves like’ (and even before you took any chemistry at all, you probably observed at some point in your life that oil does not mix with water). Let’s revisit this old rule, and put our knowledge of covalent and noncovalent bonding to work.

Imagine that you have a flask filled with water, and a selection of substances that you will test to see how well they dissolve in the water. The first substance is table salt, or sodium chloride. As you would almost certainly predict, especially if you’ve ever inadvertently taken a mouthful of water while swimming in the ocean, this ionic compound dissolves readily in water. Why? Because water, as a very polar molecule, is able to form many ion-dipole interactions with both the sodium cation and the chloride anion, the energy from which is more than enough to make up for energy required to break up the ion-ion interactions in the salt crystal and some water-water hydrogen bonds.



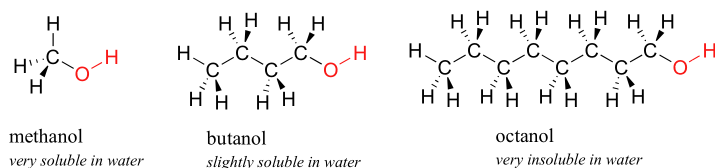
The end result, then, is that in place of sodium chloride crystals, we have individual sodium cations and chloride anions surrounded by water molecules – the salt is now *in solution*. Charged species as a rule dissolve readily in water: in other words, they are very **hydrophilic** (water-loving).

Now, we’ll try a compound called biphenyl, which, like sodium chloride, is a colorless crystalline substance (the two compounds are readily distinguishable by sight, however – the crystals look quite different).



Biphenyl does not dissolve at all in water. Why is this? Because it is a very non-polar molecule, with only carbon-carbon and carbon-hydrogen bonds. It is able to bond to itself very well through nonpolar van der Waals interactions, but it is not able to form significant attractive interactions with the very polar solvent molecules. Thus, the energetic cost of breaking up the biphenyl-to-biphenyl interactions in the solid is high, and very little is gained in terms of new biphenyl-water interactions. Water is a terrible solvent for nonpolar hydrocarbon molecules: they are very **hydrophobic** (water-hating).

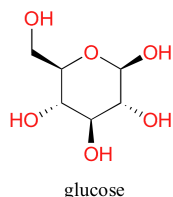
Next, you try a series of increasingly large alcohol compounds, starting with methanol (1 carbon) and ending with octanol (8 carbons).



You find that the smaller alcohols - methanol, ethanol, and propanol - dissolve easily in water. This is because the water is able to form hydrogen bonds with the hydroxyl group in these molecules, and the combined energy of formation of these water-alcohol hydrogen bonds is more than enough to make up for the energy that is lost when the alcohol-alcohol hydrogen bonds are broken up. When you try butanol, however, you begin to notice that, as you add more and more to the water, it starts to form its own layer on top of the water.

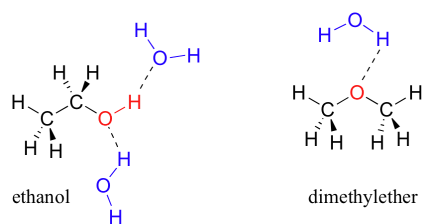
The longer-chain alcohols - pentanol, hexanol, heptanol, and octanol - are increasingly non-soluble. What is happening here? Clearly, the same favorable water-alcohol hydrogen bonds are still possible with these larger alcohols. The difference, of course, is that the larger alcohols have larger nonpolar, hydrophobic regions in addition to their hydrophilic hydroxyl group. At about four or five carbons, the hydrophobic effect begins to overcome the hydrophilic effect, and water solubility is lost.

Now, try dissolving glucose in the water – even though it has six carbons just like hexanol, it also has five hydrogen-bonding, hydrophilic hydroxyl groups in addition to a sixth oxygen that is capable of being a hydrogen bond acceptor.



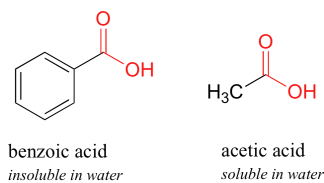
We have tipped the scales to the hydrophilic side, and we find that glucose is quite soluble in water.

We saw that ethanol was very water-soluble (if it were not, drinking beer or vodka would be rather inconvenient!) How about dimethyl ether, which is a constitutional isomer of ethanol but with an ether rather than an alcohol functional group? We find that diethyl ether is much less soluble in water. Is it capable of forming hydrogen bonds with water? Yes, in fact, it is –the ether oxygen can act as a hydrogen-bond acceptor. The difference between the ether group and the alcohol group, however, is that the alcohol group is both a hydrogen bond donor *and* acceptor.



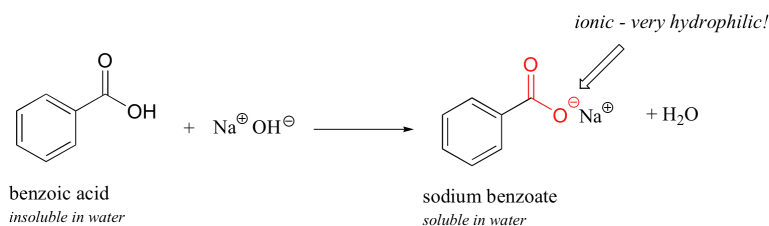
The result is that the alcohol is able to form more energetically favorable interactions with the solvent compared to the ether, and the alcohol is therefore more soluble.

Here is another easy experiment that can be done (with proper supervision) in an organic laboratory. Try dissolving benzoic acid crystals in room temperature water – you'll find that it is not soluble. As we will learn when we study acid-base chemistry in a later chapter, carboxylic acids such as benzoic acid are relatively weak acids, and thus exist mostly in the acidic (protonated) form when added to pure water.



Acetic acid, however, is quite soluble. This is easy to explain using the small alcohol vs large alcohol argument: the hydrogen-bonding, hydrophilic effect of the carboxylic acid group is powerful enough to overcome the hydrophobic effect of a single methyl group on acetic acid, but not the larger hydrophobic effect of the 6-carbon benzene group on benzoic acid.

Now, try slowly adding some aqueous sodium hydroxide to the flask containing undissolved benzoic acid. As the solvent becomes more and more basic, the benzoic acid begins to dissolve, until it is completely in solution.



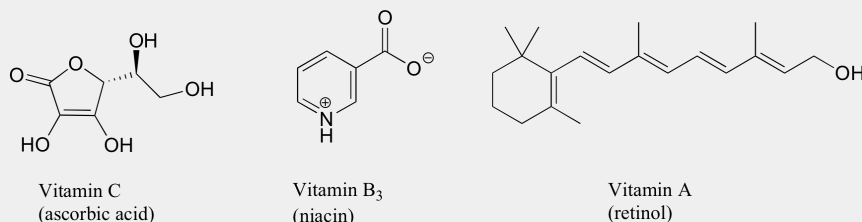
What is happening here is that the benzoic acid is being converted to its conjugate base, benzoate. The *neutral* carboxylic acid group was not hydrophilic enough to make up for the hydrophobic benzene ring, but the carboxylate group, with its *full negative charge*, is much more hydrophilic. Now, the balance is tipped in favor of water solubility, as the powerfully hydrophilic anion part of the molecule drags the hydrophobic part, kicking and screaming, (if a benzene ring can kick and scream) into solution. If you want to precipitate the benzoic acid back out of solution, you can simply add enough hydrochloric acid to neutralize the solution and reprotonate the carboxylate.

If you are taking a lab component of your organic chemistry course, you will probably do at least one experiment in which you will use this phenomenon to separate an organic acid like benzoic acid from a hydrocarbon compound like biphenyl.

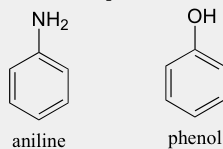
Similar arguments can be made to rationalize the solubility of different organic compounds in nonpolar or slightly polar solvents. In general, the greater the content of charged and polar groups in a molecule, the less soluble it tends to be in solvents such as hexane. The ionic and very hydrophilic sodium chloride, for example, is not at all soluble in hexane solvent, while the hydrophobic biphenyl is very soluble in hexane.

Example

Exercise 2.12: Vitamins can be classified as water-soluble or fat-soluble (consider fat to be a very non-polar, hydrophobic 'solvent'. Decide on a classification for each of the vitamins shown below.



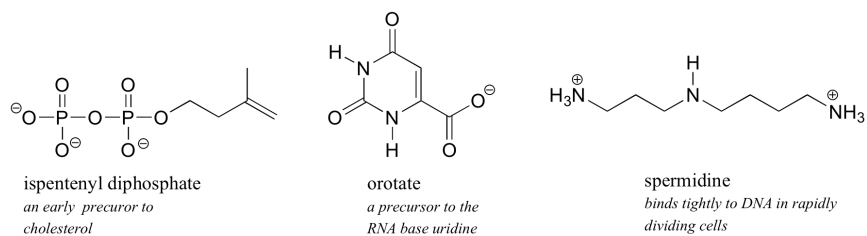
Exercise 2.13: Both aniline and phenol are insoluble in pure water. Predict the solubility of these two compounds in 10% aqueous hydrochloric acid, and explain your reasoning. Hint – in this context, aniline is basic, phenol is not!



Solutions

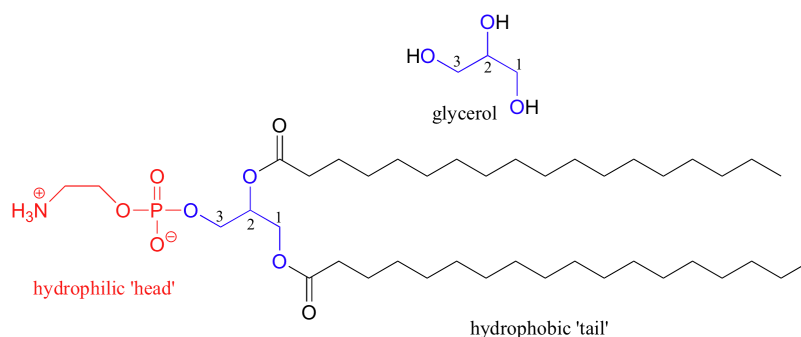
Illustrations of solubility concepts: metabolic intermediates, lipid bilayer membranes, soaps and detergents

Because water is the biological solvent, most biological organic molecules, in order to maintain water-solubility, contain one or more charged functional groups. These are most often phosphate, ammonium or carboxylate, all of which are charged when dissolved in an aqueous solution buffered to pH 7.



Sugars often lack charged groups, but as we discussed in our ‘thought experiment’ with glucose, they are quite water-soluble due to the presence of multiple hydroxyl groups.

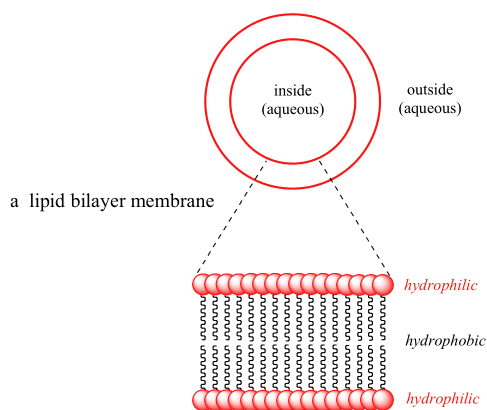
Some biomolecules, in contrast, contain distinctly hydrophobic components. The ‘lipid bilayer’ membranes of cells and subcellular organelles serve to enclose volumes of water and myriad biomolecules in solution. The lipid (fat) molecules that make up membranes are **amphipathic**: they have a charged, hydrophilic ‘head’ and a hydrophobic hydrocarbon ‘tail’.



cartoon drawing of a membrane lipid

[interactive 3D image of a membrane phospholipid \(BioTopics\)](#)

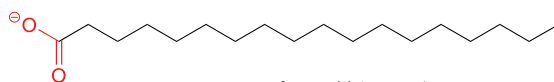
Notice that the entire molecule is built on a ‘backbone’ of glycerol, a simple 3-carbon molecule with three alcohol groups. In a biological membrane structure, lipid molecules are arranged in a spherical bilayer: hydrophobic tails point inward and bind together by van der Waals forces, while the hydrophilic head groups form the inner and outer surfaces in contact with water.



[Interactive 3D Image of a lipid bilayer \(BioTopics\)](#)

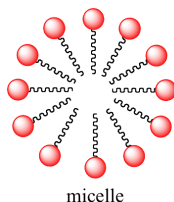
Because the interior of the bilayer is extremely hydrophobic, biomolecules (which as we know are generally charged species) are not able to diffuse through the membrane— they are simply not soluble in the hydrophobic interior. The transport of molecules across the membrane of a cell or organelle can therefore be accomplished in a controlled and specific manner by special transmembrane transport proteins, a fascinating topic that you will learn more about if you take a class in biochemistry.

A similar principle is the basis for the action of soaps and detergents. Soaps are composed of fatty acids, which are long (typically 18-carbon), hydrophobic hydrocarbon chains with a (charged) carboxylate group on one end,



a common fatty acid (stearate)

Fatty acids are derived from animal and vegetable fats and oils. In aqueous solution, the fatty acid molecules in soaps will spontaneously form **micelles**, a spherical structure that allows the hydrophobic tails to avoid contact with water and simultaneously form favorable van der Waals contacts.

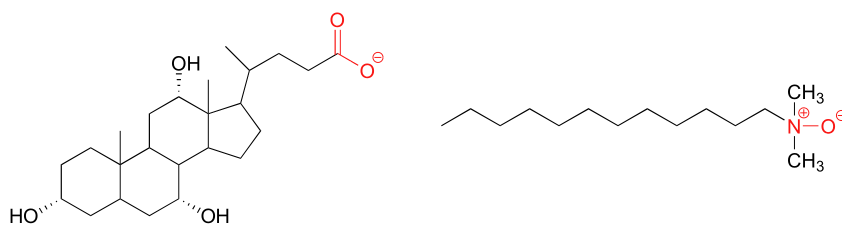


micelle

[Interactive 3D images of a fatty acid soap molecule and a soap micelle](#) (Edutopics)

Because the outside of the micelle is charged and hydrophilic, the structure as a whole is soluble in water. Micelles will form spontaneously around small particles of oil that normally would not dissolve in water (like that greasy spot on your shirt from the pepperoni slice that fell off your pizza), and will carry the particle away with it into solution. We will learn more about the chemistry of soap-making in a later chapter ([section 12.4B](#)).

Synthetic detergents are non-natural amphipathic molecules that work by the same principle as that described for soaps.

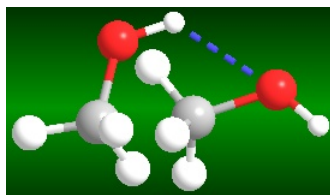


synthetic detergents

[Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

Hydrogen Bonding and Solubility

The physical properties of alcohols are influenced by the hydrogen bonding ability of the -OH group. The -OH groups can hydrogen bond with one another and with other molecules.



Hydrogen Bonding of Methanol

Hydrogen bonding raises the boiling point of alcohols. This is due to the combined strength of so many hydrogen bonds forming between oxygen atoms of one alcohol molecule and the hydroxy H atoms of another. The longer the carbon chain in an alcohol is, the lower the solubility in polar solvents and the higher the solubility in nonpolar solvents.

Physical Properties of Alcohols and Selected Analogous Haloalkanes and Alkanes

Compound	IUPAC Name	Common Name	Melting Point (°C)	Boiling Point (°C)	Solubility in H ₂ O at 23°C
CH ₃ OH	Methanol	Methyl alcohol	-97.8	65.0	Infinite
CH ₃ Cl	Chloromethane	Methyl chloride	-97.7	-24.2	0.74 g/100 mL
CH ₄	Methane		-182.5	-161.7	3.5 mL (gas)/ 100 mL

$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	Ethyl alcohol	-114.7	78.5	Infinite
$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane	Ethyl chloride	-136.4	12.3	0.447 g/100 mL
CH_3CH_3	Ethane		-183.3	-88.6	4.7 mL (gas)/ 100 mL
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1-Propanol	Propyl alcohol	-126.5	97.4	Infinite
$\text{CH}_3\text{CH}_2\text{CH}_3$	Propane		-187.7	-42.1	6.5 mL (gas)/ 100 mL
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1-Butanol	Butyl alcohol	-89.5	117.3	8.0 g/100 mL
$\text{CH}_3(\text{CH}_2)_4\text{OH}$	1-Pentanol	Pentyl alcohol	-79	138	2.2 g/100 mL

This table shows that alcohols (in red) have higher boiling points and greater solubility in H_2O than haloalkanes and alkanes with the same number of carbons. It also shows that the boiling point of alcohols increase with the number of carbon atoms.

References

- Schore, Neil E. and Vollhardt, K. Peter C. Organic Chemistry: Structure and Function. New York: Bleyer, Brennan, 2007.
- Allen, Frank; Kennard, Olga; Watson, David G.; Brammer, Lee; Orpen, Guy; Taylor, Robin, *J. Chem Soc. Perkin Trans II*, 1987, S1-S19.

Outside Links

- http://en.wikipedia.org/wiki/Alcohol#Physical_and_chemical_properties
- <http://www.chemguide.co.uk/organicprops/alcohols/background.html>

Problems

Arrange according to increasing boiling point. (start with lowest boiling point)

- CH_4 , CH_3OH , CH_3CH_3
- $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_3$
- $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{Cl}$, CH_4

Arrange according to increasing solubility (start with lowest solubility)

- CH_4 , CH_3OH , CH_3CH_3
- CH_4 , $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{OH}$,
- $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_3$

Answers

- CH_4 , CH_3CH_3 , CH_3OH
- $\text{CH}_3\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- $\text{CH}_3\text{CH}_2\text{Cl}$, CH_4 , $\text{CH}_3\text{CH}_2\text{OH}$
- CH_3CH_3 , CH_4 , CH_3OH
- $\text{CH}_3\text{CH}_2\text{Cl}$, CH_4 , $\text{CH}_3\text{CH}_2\text{OH}$,
- $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

Contributors

- Jaspreet Dheri

4.4 Solubility is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by LibreTexts.

4.5 Chromatography

The main chromatographic techniques (thin layer chromatography, column chromatography, and gas chromatography) follow the same general principles in terms of how they are able to separate mixtures.

In all chromatographic methods, a sample is first applied onto a stationary material that either **absorbs** or **adsorbs** the sample: adsorption is when molecules or ions in a sample adhere to a surface, while absorption is when the sample particles penetrate into the interior of another material. A paper towel absorbs water because the water molecules form intermolecular forces (in this case hydrogen bonds) with the cellulose in the paper towel. In chromatography, a sample is typically adsorbed onto a surface, and can form a variety of intermolecular forces with this surface.

After adsorption, the sample is then exposed to a liquid or gas traveling in one direction. The sample may overcome its intermolecular forces with the stationary surface and transfer into the moving material, due to some attraction or sufficient thermal energy. The sample will later re-adsorb to the stationary material, and transition between the two materials in a constant equilibrium (Equation 1). If there is to be any separation between components in a mixture, it is crucial that there are many equilibrium "steps" in the process (summarized in Figure 2.3).



The material the sample adsorbs onto is referred to as the "**stationary phase**" because it retains the sample's position. The moving material is called the "**mobile phase**" because it can cause the sample to move from its original position.

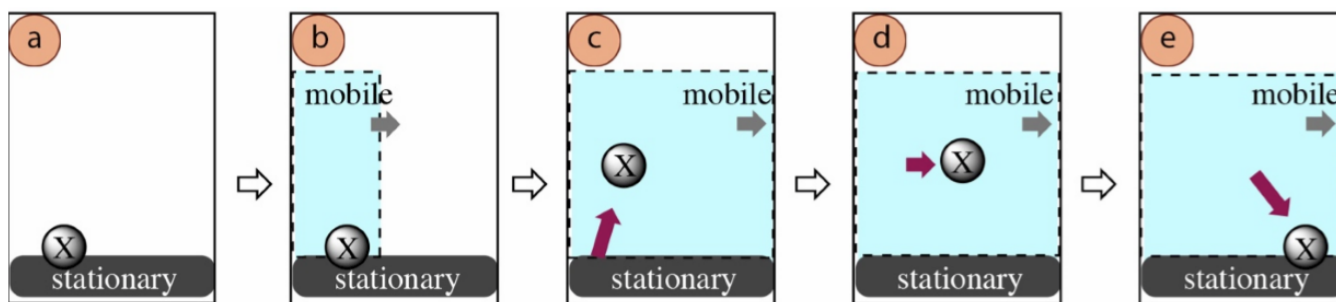


Figure 2.3: Generic chromatography sequence for compound X: a) Adsorption, b) Exposure to a mobile phase, c) Sample X breaks its attachment to the stationary phase, d) Movement with the mobile phase, e) Reattachment to the stationary phase. Steps c-e are equilibrium steps and constantly repeated.

The main principle that allows chromatography to separate components of a mixture is that components will spend different amounts of time interacting with the stationary and mobile phases. A compound that spends a large amount of time mobile will move quickly away from its original location, and will separate from a compound that spends a larger amount of time stationary. The main principle that determines the amount of time spent in the phases is the **strength of intermolecular forces** experienced in each phase. If a compound has strong intermolecular forces with the stationary phase it will remain adsorbed for a longer amount of time than a compound that has weaker intermolecular forces. This causes compounds with different strengths of intermolecular forces to move at different rates.

How these general ideas apply to each chromatographic technique (thin layer chromatography, column chromatography, and gas chromatography) will be explained in greater detail in each section.

Contributor

- [Lisa Nichols](#) (Butte Community College). *Organic Chemistry Laboratory Techniques* is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License. Complete text is available [online](#).

4.5 Chromatography is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.