

FUNCTIONAL GROUP

Structural features of organic molecules

Most organic molecules have C–C and C–H bonds. These bonds are strong, non-polar, and not readily broken. Organic molecules may have the following structural features as well:

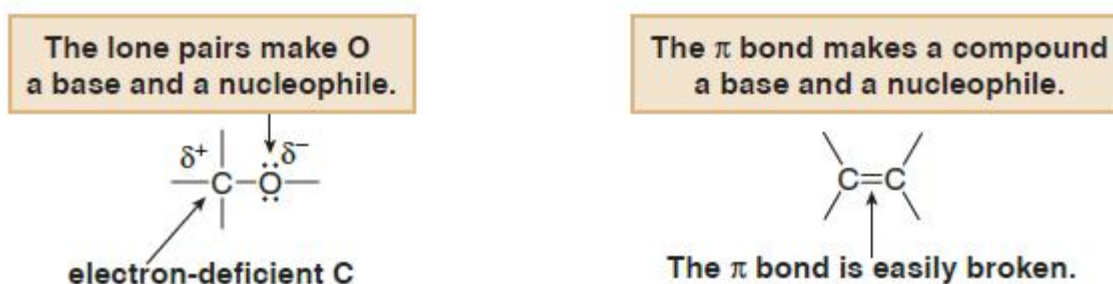
- **Heteroatoms**—atoms other than carbon or hydrogen (or atoms that are more electronegative than carbon). Common heteroatoms are nitrogen, oxygen, sulfur, phosphorus, and the halogens.
- **π Bonds**. The most common π bonds occur in C–C and C–O double bonds.

These structural features distinguish one organic molecule from another. They determine a molecule's geometry, physical properties, and reactivity, and comprise what is called a **functional group**.

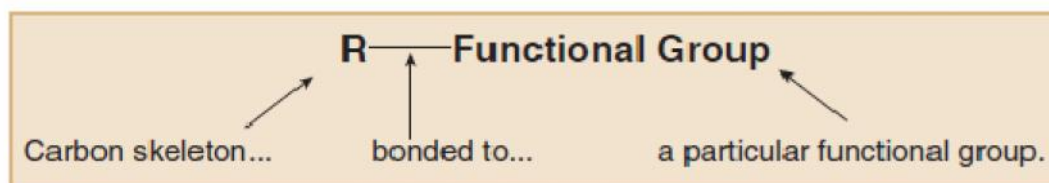
A **functional group** is an atom or a group of atoms with characteristic chemical and physical properties. It is the *reactive part* of the molecule.

Why do heteroatoms and π bonds confer reactivity on a particular molecule?

- **Heteroatoms** have lone pairs and create electron-deficient sites on carbon.
- **π Bonds** are easily broken in chemical reactions. A π bond makes a molecule a base and a nucleophile.



The C–C and C–H σ bonds form the **carbon backbone** or **skeleton** to which the functional groups are bonded. A functional group usually behaves the same whether it is bonded to a carbon skeleton having as few as two or as many as 20 carbons. For this reason, we often abbreviate the carbon and hydrogen portion of the molecule by a capital letter **R**, and draw the **R** bonded to a particular functional group.



Ethane, for example, has only C–C and C–H σ bonds, so it has *no* functional group. Ethane has no polar bonds, no lone pairs, and no π bonds, so it has **no reactive sites**. Because of this, ethane and molecules like it are very unreactive.

Ethanol, on the other hand, has two carbons and five hydrogens in its carbon backbone, as well as an OH group, a functional group called a **hydroxy** group. Ethanol has lone pairs and polar bonds that make it reactive with a variety of reagents, including the acids and bases.

Classifications of functional group

Functional group can be classified into three classes:

- Hydrocarbons
- Compounds containing a C – Z σ bond where Z = an electronegative element
- Compounds containing a C=O group

Hydrocarbons

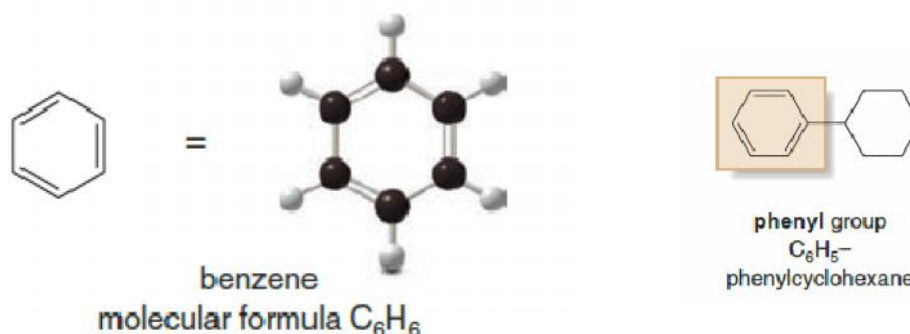
Hydrocarbons are compounds made up of only the elements carbon and hydrogen. They may be aliphatic or aromatic.

[1] Aliphatic hydrocarbons. Aliphatic hydrocarbons can be divided into three subgroups.

- **Alkanes** have only C – C σ bonds and no functional group. Ethane, CH_3CH_3 , is a simple alkane.
- **Alkenes** have a C – C double bond as a functional group. Ethylene, $\text{CH}_2=\text{CH}_2$, is a simple alkene.
- **Alkynes** have a C – C triple bond as a functional group. Acetylene, $\text{HC}\equiv\text{CH}$, is a simple alkyne.


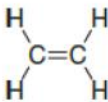


[2] Aromatic hydrocarbons. This class of hydrocarbons was so named because many of the earliest known aromatic compounds had strong, characteristic odours.

The simplest aromatic hydrocarbon is **benzene**. The six-membered ring and three π bonds of benzene comprise a *single* functional group. Benzene is a component of the **BTX** mixture (**B** for **benzene**) added to gasoline to boost octane ratings.

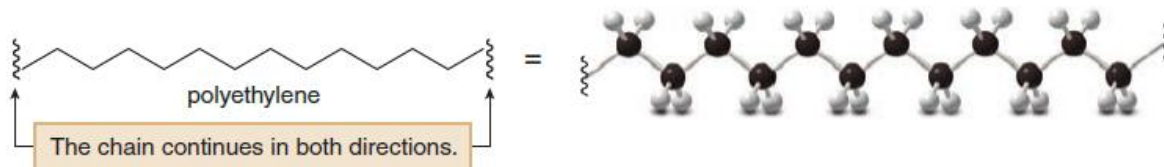


When a benzene ring is bonded to another group, it is called a **phenyl group**. In phenylcyclohexane, for example, a phenyl group is bonded to the six-membered cyclohexane ring. Table 1 summarizes the four different types of hydrocarbons.

Table 1: Hydrocarbon

Type of compound	General structure	Example	Functional group
Alkane	$\text{R}-\text{H}$	CH_3CH_3	—
Alkene			double bond
Alkyne	$-\text{C}\equiv\text{C}-$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	triple bond
Aromatic compound			phenyl group

Alkanes, which have no functional groups, are notoriously unreactive except under very drastic conditions. For example, **polyethylene** is a synthetic plastic and high molecular weight alkane, consisting of chains of $-\text{CH}_2-$ groups bonded together, hundreds or even thousands of atoms long. Because it is an alkane with no reactive sites, it is a very stable compound that does not readily degrade and thus persists for years in landfills.



Compounds Containing C–Z σ Bonds

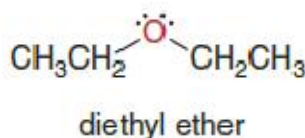
Several types of functional groups that contain C – Z σ bonds are listed in Table 2. The electronegative heteroatom Z creates a polar bond, making carbon electron deficient. The lone pairs on Z are available for reaction with protons and other electrophiles, especially when Z = N or O.



Several simple compounds in this category are widely used. As an example, Molecules containing these functional groups may be simple or very complex.

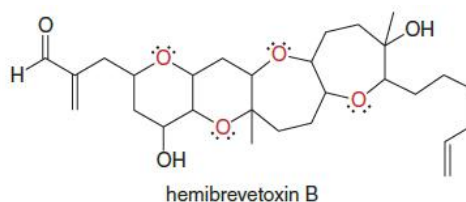
Examples of simple molecules include:

- chloroethane ($\text{CH}_3\text{CH}_2\text{Cl}$, commonly called ethyl chloride) is an alkyl halide used as a local anesthetic. Chloroethane quickly evaporates when sprayed on a wound, causing a cooling sensation that numbs the site of an injury.
- Diethyl ether, the first common general anesthetic, is a simple ether because it contains a single O atom bonded to two C atoms.



Example of complex molecule include:

- Hemibrevetoxin B, on the other hand, contains four ether groups, in addition to other functional groups.

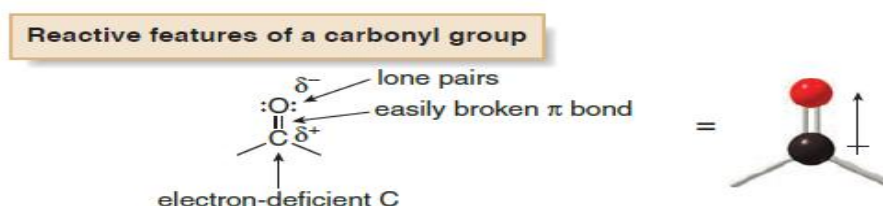


Type of compound	General structure	Example	3-D structure	Functional group
Alkyl halide	$R-\ddot{X}:$ (X = F, Cl, Br, I)	$CH_3-\ddot{Br}:$		-X halo group
Alcohol	$R-\ddot{O}H$	$CH_3-\ddot{O}H$		-OH hydroxy group
Ether	$R-\ddot{O}-R$	$CH_3-\ddot{O}-CH_3$		-OR alkoxy group
Amine	$R-\ddot{N}H_2$ or $R_2\ddot{N}H$ or $R_3\ddot{N}$	$CH_3-\ddot{N}H_2$		-NH ₂ amino group
Thiol	$R-\ddot{S}H$	$CH_3-\ddot{S}H$		-SH mercapto group
Sulfide	$R-\ddot{S}-R$	$CH_3-\ddot{S}-CH_3$		-SR alkylthio group

Table 2: Compounds Containing C—Z r Bonds.

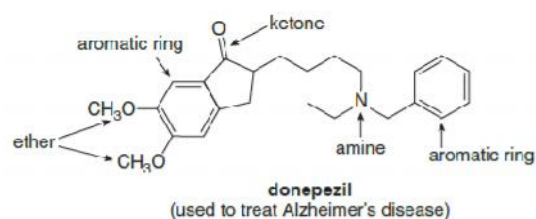
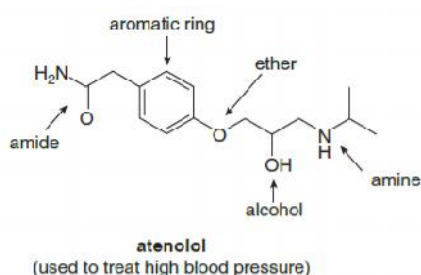
Compounds Containing a C=O Group

Many different types of functional groups possess a C – O double bond (a **carbonyl group**), as shown in Table 3. The polar C – O bond makes the carbonyl carbon an electrophile, while the lone pairs on O allow it to react as a nucleophile and base. The carbonyl group also contains a π bond that is more easily broken than a C – O σ bond.



Atenolol and donepezil are examples of useful drugs that contain a variety of functional groups.

Atenolol is a β -blocker, a group of drugs used to treat hypertension. Donepezil, sold under the trade name Aricept, is used to treat mild to moderate dementia associated with Alzheimer's disease.



Type of compound	General structure	Example	3-D structure	Functional group
Aldehyde	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\text{H} \end{array}$		C=O carbonyl group
Ketone	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}_3 \end{array}$		C=O carbonyl group
Carboxylic acid	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}\text{H} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}\text{H} \end{array}$		—COOH carboxy group
Ester	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}\text{R} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}\text{CH}_3 \end{array}$		—COOR
Amide	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{N}}\text{H (or R)} \\ \text{H (or R)} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{N}}\text{H}_2 \end{array}$		—CONH ₂ , —CONHR, or —CONR ₂
Acid chloride	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}\text{Cl} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}\text{Cl} \end{array}$		—COCl

Table 3: Compounds Containing a C=O Group

APPLICATIONS OF FUNCTIONAL GROUPS

The importance of a functional group cannot be overstated. A functional group determines all the following properties of a molecule:

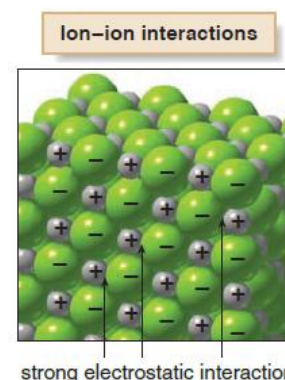
- bonding and shape
- type and strength of intermolecular forces
- physical properties
- nomenclature
- chemical reactivity

Intermolecular Forces

Intermolecular forces are the interactions that exist *between* molecules. A functional group determines the type and strength of these interactions.

Ionic Compounds

Ionic compounds contain oppositely charged particles held together by **extremely strong electrostatic interactions**. These ionic interactions are much stronger than the intermolecular forces present between covalent molecules, so it takes a great deal of energy to separate oppositely charged ions from each other.



Covalent Compounds

Covalent compounds are composed of discrete molecules. The nature of the forces between the molecules depends on the *functional group* present.

TYPES OF INTERMOLECULAR INTERACTION

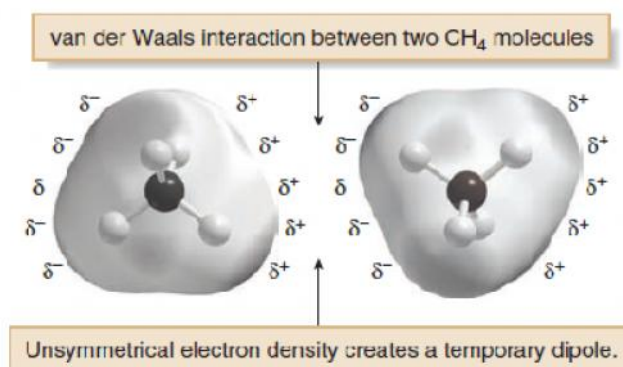
There are three different types of interactions, presented here in order of *increasing strength*:

- I. van der Waals forces
- II. dipole–dipole interactions
- III. hydrogen bonding

I. van der Waals Forces

van der Waals forces, also called **London forces**, are very weak interactions caused by the **momentary changes in electron density in a molecule**. van der Waals forces are the only attractive forces present in nonpolar compounds.

For example, although a nonpolar CH_4 molecule has no net dipole, at any one instant its electron density may not be completely symmetrical, creating a *temporary* dipole. This can induce a temporary dipole in another CH_4 molecule, with the partial positive and negative charges arranged close to each other. **The weak interaction of these temporary dipoles constitutes van der Waals forces.** All compounds exhibit van der Waals forces.



Factors affecting the strength of van der Waals forces/interactions

i. Surface area of a molecule

The surface area of a molecule determines the strength of the van der Waals interactions. **The larger the surface area, the larger the attractive force between two molecules, and the stronger the intermolecular forces.** Long, sausage-shaped molecules such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (pentane) have stronger van der Waals interactions than compact spherical ones like $\text{C}(\text{CH}_3)_4$ (neopentane), as shown in Figure 1

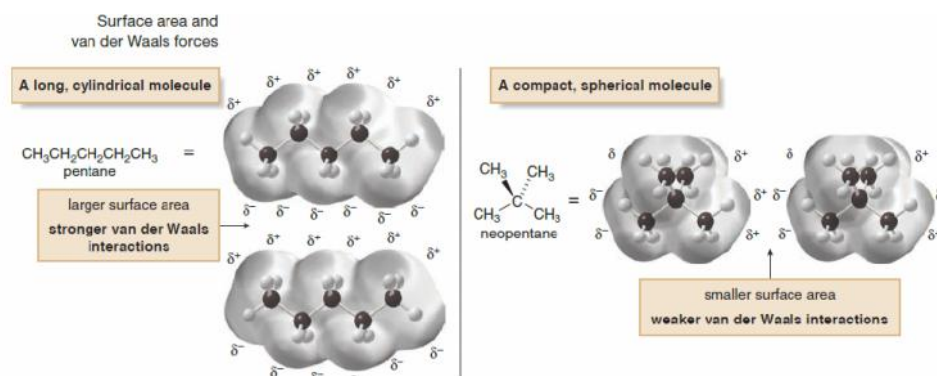
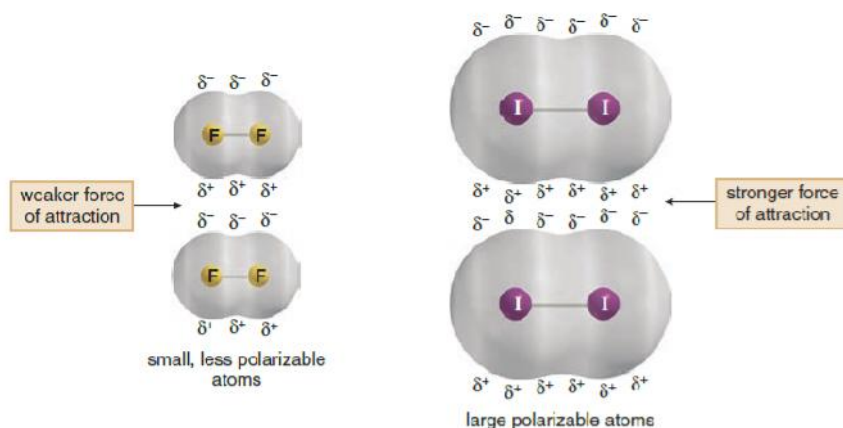


figure 1. surface area and van der Waals forces

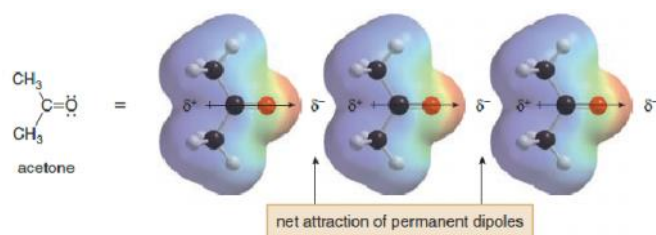
ii. **Polarizability.** Another factor affecting the strength of van der Waals forces is **polarizability** which is a measure of how the electron cloud around an atom responds to changes in its electronic environment. Larger atoms like iodine, which have more loosely held valence electrons, are more polarisable than smaller atoms like fluorine, which have more tightly held electrons. Because larger atoms have more easily induced dipoles, compounds containing them possess stronger intermolecular interactions.

Thus, two F_2 molecules have little force of attraction between them, because the electrons are held very tightly and temporary dipoles are difficult to induce. On the other hand, two I_2 molecules exhibit a much stronger force of attraction because the electrons are held much more loosely and temporary dipoles are easily induced.



ii. Dipole–Dipole Interactions

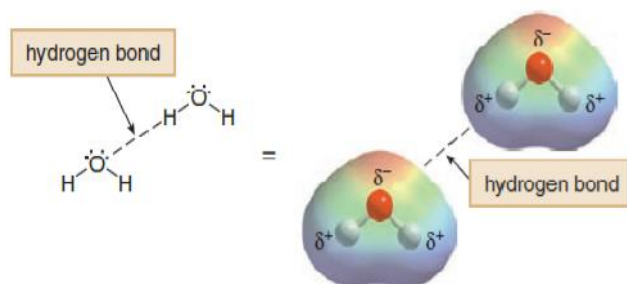
Dipole–dipole interactions are the attractive forces between the permanent dipoles of two polar molecules. In acetone, $(CH_3)_2C=O$, for example, the dipoles in adjacent molecules align so that the partial positive and partial negative charges are in close proximity. These attractive forces caused by permanent dipoles are much stronger than weak van der Waals forces.



Hydrogen Bonding

Hydrogen bonding typically occurs when a hydrogen atom bonded to O, N, or F, is electrostatically attracted to a lone pair of electrons on an O, N, or F atom in another molecule.

Thus, H_2O molecules can form hydrogen bond to each other. When they do, an H atom covalently bonded to O in one water molecule is attracted to a lone pair of electrons on the O in another water molecule. Hydrogen bonds are the strongest of the three types of intermolecular forces, though they are still much weaker than any covalent bond.



Summary of types of intermolecular forces

Type of force	Relative strength	Exhibited by	Example
van der Waals	weak	all molecules	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃ CH ₃ CH ₂ CH ₂ CHO CH ₃ CH ₂ CH ₂ CH ₂ OH
dipole–dipole	moderate	molecules with a net dipole	CH ₃ CH ₂ CH ₂ CHO CH ₃ CH ₂ CH ₂ CH ₂ OH
hydrogen bonding	strong	molecules with an O–H, N–H, or H–F bond	CH ₃ CH ₂ CH ₂ CH ₂ OH
ion–ion	very strong	ionic compounds	NaCl, LiF

Physical Properties

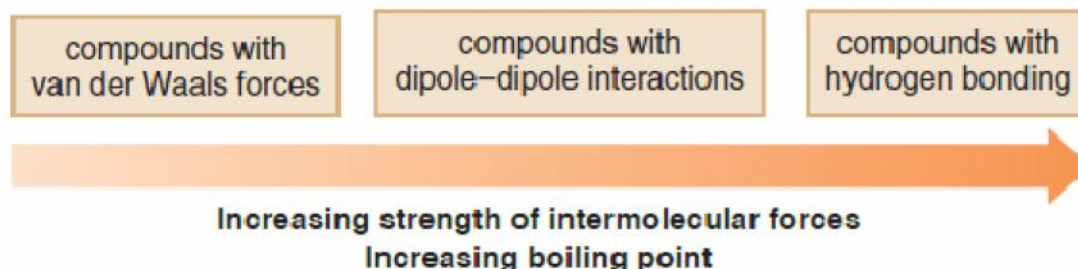
The strength of a compound's intermolecular forces determines many of its physical properties, including its boiling point, melting point, and solubility.

❖ Boiling Point (bp)

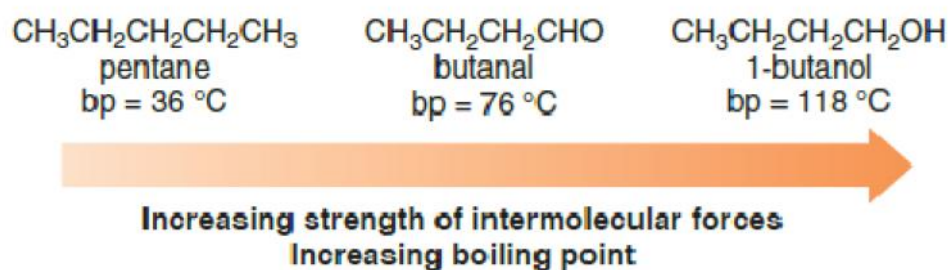
The *boiling point* of a compound is the temperature at which a liquid is converted to a gas. In boiling, energy is needed to overcome the attractive forces in the more ordered liquid state.

• The stronger the intermolecular forces, the higher the boiling point.

Because ionic compounds are held together by extremely strong interactions, they have very high boiling points. The boiling point of NaCl, for example, is 1413°C. With covalent molecules, the boiling point depends on the identity of the functional group. For compounds of approximately the same molecular weight:



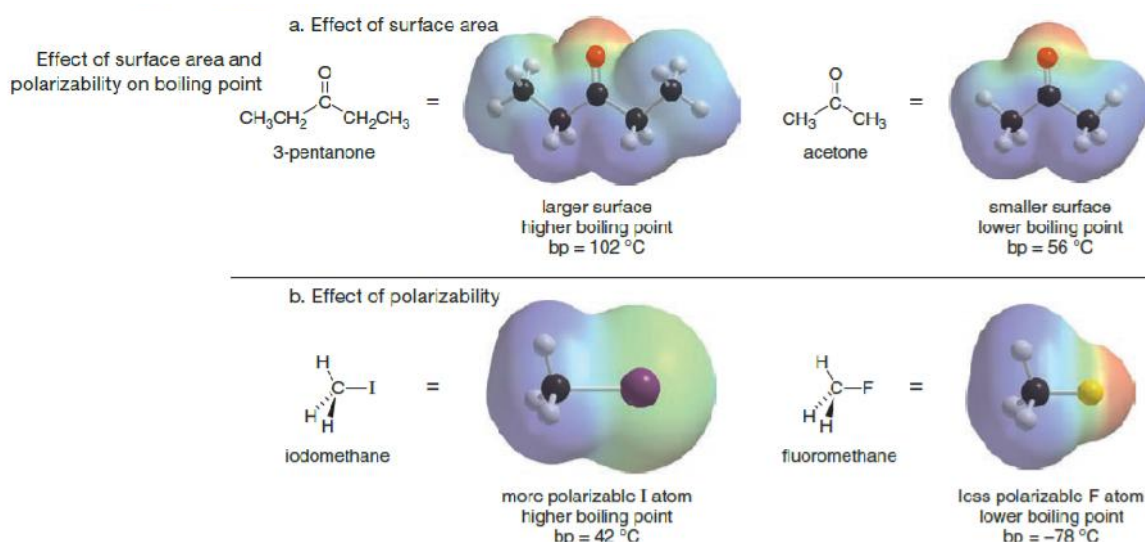
For example, the relative strength of the intermolecular forces increases from pentane to butanal to 1-butanol. The boiling points of these compounds increase in the same order.



Because surface area and polarizability affect the strength of intermolecular forces, they also affect the boiling point. For two compounds with similar functional groups:

- The larger the surface area, the higher the boiling point.
- The more polarizable the atoms, the higher the boiling point.

Examples of each phenomenon are illustrated in the scheme below. In comparing two ketones that differ in size, 3-pentanone has a higher boiling point than acetone because it has a greater molecular weight and larger surface area. In comparing two alkyl halides having the same number of carbon atoms, CH_3I has a higher boiling point than CH_3F because I is more polarizable than F.



Liquids having different boiling points can be separated in the laboratory using a **distillation apparatus** (Figure 3.3). When a mixture of two liquids is heated in the distilling flask, the lower boiling compound, the **more volatile component**, distills first, followed by the **less volatile, higher boiling component**. By collecting the distillate in a series of receiver flasks, the two liquids can usually be separated from each other. The best separations are generally achieved when the liquids in the mixture have widely different boiling points.

❖ Melting Point (mp)

The **melting point** is the temperature at which a solid is converted to its liquid phase. In melting, energy is needed to overcome the attractive forces in the more ordered crystalline solid.

Factors determining the melting point of a compound

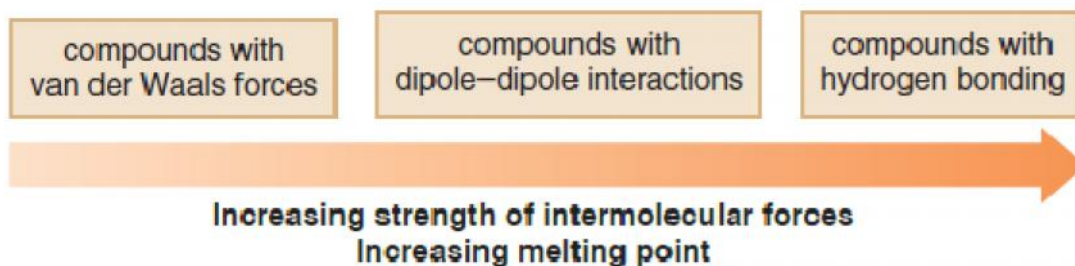
There are two factors that determine the melting point of a compound.

- strong intermolecular forces and
- symmetry of compound

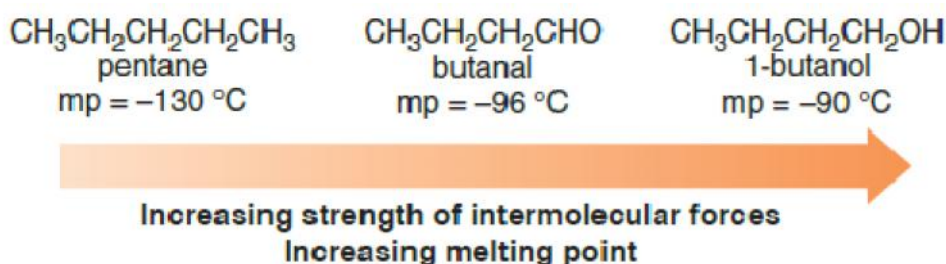
note:

- The stronger the intermolecular forces, the higher the melting point.
- Given the same functional group, the more symmetrical the compound, the higher the melting point.

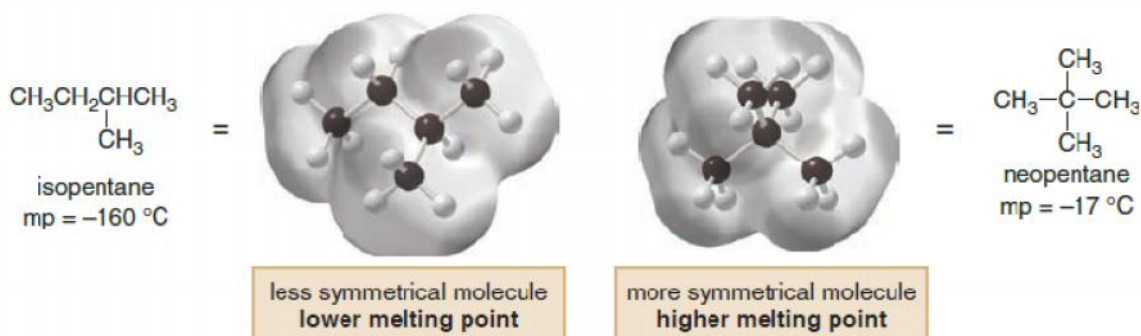
Because ionic compounds are held together by extremely strong interactions, they have very high melting points. For example, the melting point of NaCl is 801 °C. With covalent molecules, the melting point once again depends on the identity of the functional group. For compounds of approximately the same molecular weight:



The trend in the melting points of pentane, butanal, and 1-butanol parallels the trend observed in their boiling points.

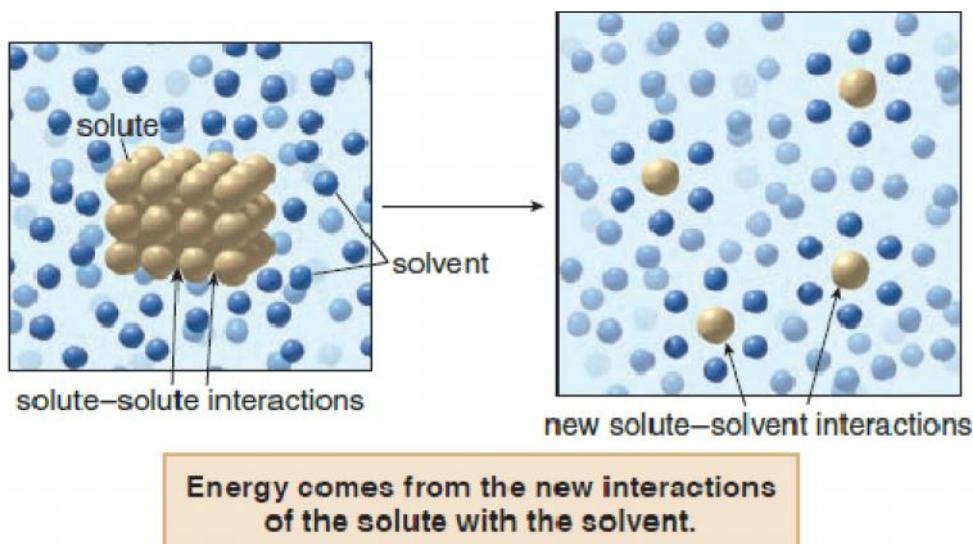


ii. **Symmetry** also plays a role in determining the melting points of compounds having the same functional group and similar molecular weights, but very different shapes. A compact symmetrical molecule like neopentane packs well into a crystalline lattice whereas isopentane, which has a CH_3 group dangling from a four-carbon chain, does not. Thus, neopentane has a much higher melting point.



❖ Solubility

Solubility is the extent to which a compound, called the *solute*, dissolves in a liquid, called the *solvent*. In dissolving a compound, the energy needed to break up the interactions between the molecules or ions of the solute comes from new interactions between the solute and the solvent.



Compounds dissolve in solvents having similar kinds of intermolecular forces.

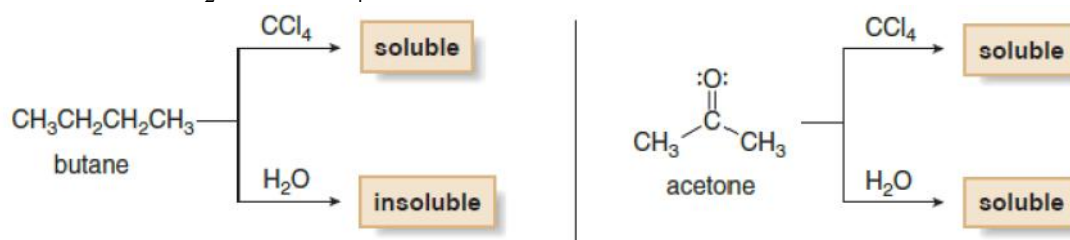
- “Like dissolves like.”

- **Polar compounds dissolve in polar solvents. Nonpolar or weakly polar compounds dissolve in nonpolar or weakly polar solvents.**

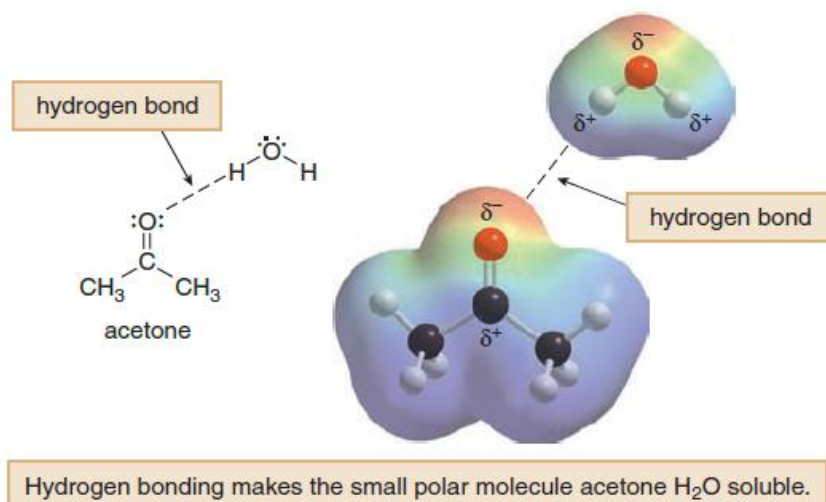
Water and organic liquids are two different kinds of solvents. Water is very polar because it is capable of forming hydrogen bond with a solute. Many organic solvents are either nonpolar, like carbon tetrachloride (CCl_4) and hexane [$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$], or weakly polar like diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$).

Ionic compounds are held together by strong electrostatic forces, so they need very polar solvents to dissolve. **Most ionic compounds are soluble in water, but are insoluble in organic solvents.** To dissolve an ionic compound, the strong ion-ion interactions must be replaced by many weaker **ion-dipole interactions**.

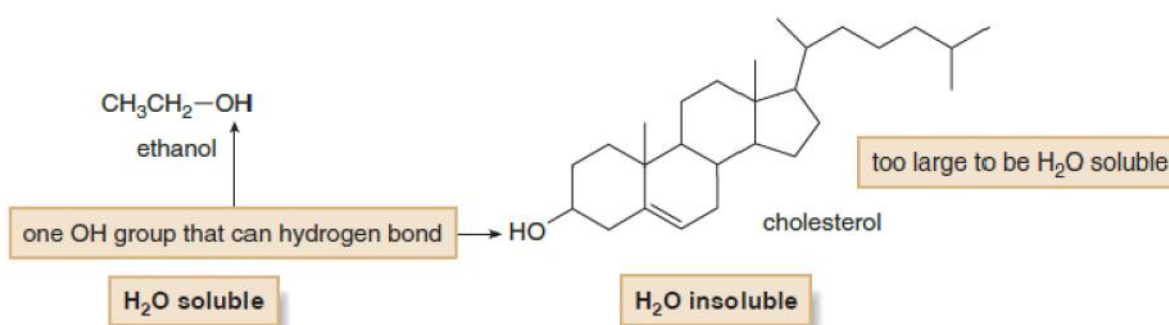
Most organic compounds are soluble in organic solvents (remember, *like dissolves like*). **An organic compound is water soluble only if it contains one polar functional group capable of forming hydrogen bond with the solvent for every five C atoms it contains.** In other words, a water-soluble organic compound has an O- or N-containing functional group that solubilizes its nonpolar carbon backbone. Compare, for example, the solubility of butane and acetone in H_2O and CCl_4 .



Because butane and acetone are both organic compounds having a C-C and C-H backbone, they are soluble in the organic solvent CCl_4 . Butane, a nonpolar molecule, is insoluble in the polar solvent H_2O . Acetone, however, is H_2O soluble because it contains only three C atoms and its O atom can hydrogen bond with one H atom of H_2O . In fact, acetone is so soluble in water that acetone and water are **miscible**—they form solutions in all proportions with each other.



The size of an organic molecule with a polar functional group determines its water solubility. A low molecular weight alcohol like **ethanol is water soluble** because it has a small carbon skeleton (\leq five C atoms) compared to the size of its polar OH group. Cholesterol, on the other hand, has 27 carbon atoms and only one OH group. Its carbon skeleton is too large for the OH group to solubilize by hydrogen bonding, so **cholesterol is insoluble in water**.



- ❖ The nonpolar part of a molecule that is not attracted to H₂O is said to be *hydrophobic*.
- ❖ The polar part of a molecule that can hydrogen bond to H₂O is said to be *hydrophilic*.

In cholesterol, for example, the **hydroxy group is hydrophilic**, whereas the **carbon skeleton is hydrophobic**.