Chapter 2

Representative Carbon Compounds:

Functional Groups
Intermolecular Forces

Bonding in Organic Compunds

Ability of carbon to form 4 covalent bonds leads to an infinite number of possible compounds

- Chains of carbon atoms bonded to each other
- Can incorporate O, N, Cl, S and other atoms

Functional groups – the reactions of organic compounds will be focused at key parts of a molecule

- A *functional group* is a specific grouping of atoms (*e.g.* carbon- carbon double bonds are in the family of alkenes)
- Makes properties and reactions predictable

Hydrocarbons – contain only Carbon and Hydrogen

Simplest hydrocarbon
Methane CH_4

Methane

Boiling point -161°C

A component of the atmosphere of many planets
Major component of natural gas
Produced by primitive organisms called methanogens found in mud, sewage and cows' stomachs

Alkanes = saturated hydrocarbons

Methane is first in a series of saturated hydrocarbons

Alkanes contain only C and H and no multiple bonds

Ethane C_2H_6 CH_3-CH_3

Alkanes are combustible, but otherwise resistant to most reactions

Unsaturated Hydrocarbons

With two or more carbons, multiple bonds are possible

- Alkenes contain one or more carbon-carbon double bonds
- Alkynes contain one or more carbon-carbon triple bonds
- Aromatic hydrocarbons contain benzene-like stable structures

♦ Saturated hydrocarbons: contain only carbon-carbon single bonds e.g. alkanes

♦ Unsaturated hydrocarbons: contain double or triple carbon-carbon bonds e.g. alkene, alkynes, aromatics

- Contain fewer than maximum number of hydrogens per carbon
- Capable of reacting with H_2 to become saturated

Examples of alkenes

Ethene (ethylene) is a major industrial feedstock (30 B lbs/yr)

- Used for production of ethanol, ethylene oxide and polyethylene

$H_2C{=}CH_2$

Ethene

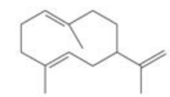
Propene (propylene) is also very important in industry

- Molecular formula C_3H_6

  $CH_3CH{=}CH_2$

Many alkenes occur naturally

β-Pinene (a component of turpentine)



An aphid alarm pheromone

Alkynes

Ethyne (acetylene) is used in welding torches because it burns at high temperature

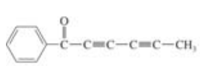
$HC{\equiv}CH$

ethyne

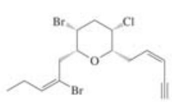
Ethyne

Many alkynes are of biological interest

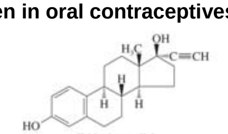
- Capillin is an antifungal agent found naturally
- Dactylyne is a marine natural product
- Ethinyl estradiol is a synthetic estrogen in oral contraceptives



Capillin



Dactylyne



Ethinyl estradiol [17α-ethynyl-1,3,5(10)-estratriene-3,17*β*-diol]

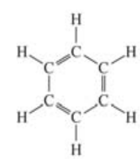
Benzene and Aromatic Hydrocarbons

Benzene is a remarkable compound

With formula C_6H_6, should be unsaturated and very reactive

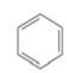
But it is unusually stable!

The Kekulé structure (named after August Kekulé who formulated it) is a six-membered ring with alternating double and single bonds



Kekulé structure for benzene

or



Bond-line representation of Kekulé structure

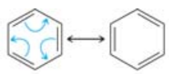
Benzene: An Extraordinary Hydrocarbon

Benzene does not actually have discreet single and double carbon-carbon bonds

- **All carbon-carbon bonds are exactly equal in length (1.38 Å)**
- **This is between the length of a carbon-carbon single bond and a carbon-carbon double bond**

Resonance theory explains this with two resonance hybrids that contribute equally to the real structure

- **The real structure is often depicted as a hexagon with a circle in the middle**

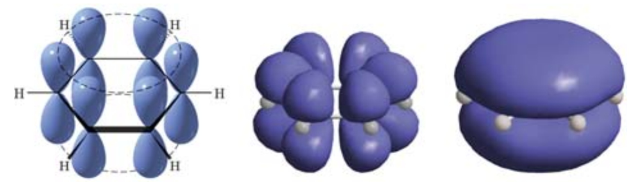


Two contributing Kekulé structures for benzene

Molecular Orbital Theory explains benzene even better

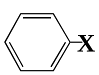
Continuous overlap of *p* orbitals over the entire ring

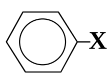
- **All carbons in benzene are *sp*^{2} hybridized**
  - **→Each carbon also has a *p* orbital**
- **Each *p* orbital overlaps with *p* orbitals on either side to give a continuous bonding molecular orbital that encompasses all 6 carbons**
- **All 6 π electrons are therefore *delocalized* over the entire ring, producing equivalency of all carbon-carbon bonds**



Benzene and Aromatic Hydrocarbons

All of the following representations are used for benzene. When the benzene ring is attached to other groups, it is called a phenyl group.





C_6H_5-X   Ph-X

Substituted benzenes and other compounds with benzene-like stability is called aromatic

Polar Covalent Bonds

- **When a covalent bond is formed between two atoms of differing electronegativities, it will be polar**
  - **The more electronegative atom draws electron density closer to itself**
  - **The more electronegative atom develops a partial negative charge (δ-) and the less electronegative atom develops a partial positive charge (δ+)**
  - **A bond which is polarized is a dipole and has a dipole moment**
  - **The direction of the dipole can be indicated by a dipole arrow**

$$\text{(positive end)} \;\overset{\delta^{+}\qquad\delta^{-}}{\longrightarrow}\; \text{(negative end)}$$

Example: the molecule HCl

The more electronegative chlorine draws electron density away from the hydrogen

- Chlorine develops a partial negative charge

The dipole moment of a molecule can be measured

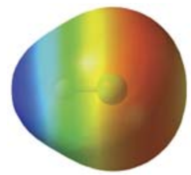
- A product of the magnitude of the charges (in electrostatic units: esu) and the distance between the charges (in cm)
- The actual unit of measurement is a Debye (D) which is equivalent to 1 x 10^{-18} esu cm

$$\text{Dipole moment} = \text{charge (in esu)} \times \text{distance (in cm)}$$
$$\mu = e \times d$$

Visualization of charge distribution

Computer-generated map of electrostatic potential (MEP)

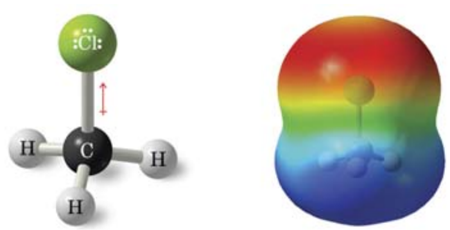
- Red = regions of highest electron density
- Blue = regions of lowest electron density
- The MEP is plotted at the van Der Waals surface of a molecule
  - This is the farthest extent of a molecule's electron cloud
- The MEP of hydrogen chlorine shows the negative charge is concentrated near the chlorine
  - The overall shape of the molecule is also represented



Example: Chloromethane CH_3Cl

In larger complicated molecules the molecular dipole is the vector sum of the individual bond dipoles.

In chloromethane the C-H bonds have only small dipoles but the C-Cl bond has a large dipole, making molecule quite polar

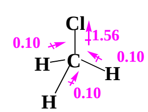


μ = 1.87 D (*a*)

Chloromethane (*b*)

Chloromethane – a closer look

The analysis assumes a tetrahedral geometry.



The net dipole moment in the +Z direction is

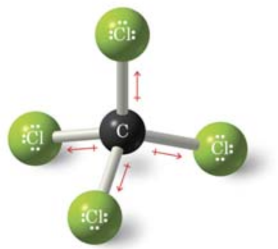
1.56	(C-Cl)
0.10	3 x (C-H)
1.66 D	

Note: The direction of the C-H bond moment is determined from this and similar analyses to be H-C.

Example: Carbon tetrachloride

Some molecules with polar bonds will have no net molecular dipole because the bond dipoles cancel out.

In carbon tetrachloride the bond dipoles cancel and the overall molecular dipole is 0 Debye.

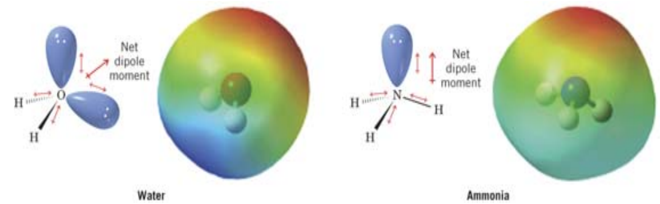


$\mu = 0$ D

Lone pairs can contribute to dipoles

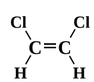
An unshared pair of electrons on atoms such as oxygen and nitrogen contribute a great deal to a dipole

Water and ammonia have very large net dipoles

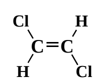


Geometric isomers may be identified by dipole moments

- **In trans 1,2-dichloroethene the two carbon-chlorine dipoles cancel out and the molecular dipole is 0 Debye**
- **In the cis isomer the carbon-chlorine dipoles reinforce and there is a large molecular dipole**



cis-1,2-dichloroethene



trans-1,2-dichloroethene

Compound	Melting Point (°C)	Boiling Point (°C)	Dipole Moment (D)
cis-1,2-Dichloroethene	−80	60	1.90
trans-1,2-Dichloroethene	−50	48	0
cis-1,2-Dibromoethene	−53	112.5	1.35
trans-1,2-Dibromoethene	−6	108	0

Functional Groups

Certain arrangements of atoms are called a *functional group* because this is the site of most chemical reactivity of a molecule

- **The functional group is also responsible for many of the physical properties of a molecule**

Alkanes do not have a functional groups

Alkenes have the C=C as a functional group

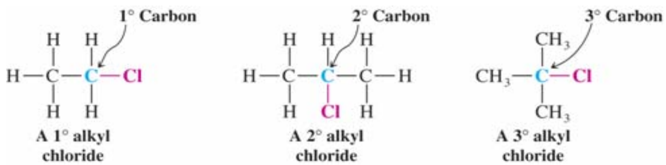
Alkynes have a triple bond as a functional group

Haloalkanes or Alkyl Halides

- Compounds that contain one or more halogen atoms

examples CH_3Br CH_3CH_2Cl

Alkyl halides are classified by how many other carbons are attached to the carbon bearing the halogen



Identifying Alkyl groups

Alkyl groups are identified by removing 1 H from an alkane

ALKANE	ALKYL GROUP	ABBREVIATION
CH_4 **Methane**	CH_3— **Methyl group**	Me—
CH_3CH_3 **Ethane**	CH_3CH_2— or C_2H_5— **Ethyl group**	Et—
$CH_3CH_2CH_3$ **Propane**	$CH_3CH_2CH_2$— **Propyl group**	Pr—
$CH_3CH_2CH_3$ **Propane**	CH_3CHCH_3 or $CH_3CH(CH_3)$— **Isopropyl group**	*i*-Pr—

Note the two groups that can be obtained from propane

Alkyl Groups and the Symbol R

- Since we will refer to alkyl groups so often, we use the letter R to symbolize any alkyl group

CH_3—	Methyl	**These and others can be designated by R.**
CH_3CH_2—	Ethyl	
$CH_3CH_2CH_2$—	Propyl	
CH_3CHCH_3	Isopropyl	

Example of an equation using the general symbol "R"

$$R{-}\ddot{O}{-}H + Na^+ :H^- \longrightarrow R{-}\ddot{O}:^- Na^+ + H{-}H$$

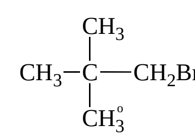
Example of an equation using a specific alkyl group:

$$CH_3{-}\ddot{O}{-}H + Na^+ :H^- \longrightarrow CH_3{-}\ddot{O}:^- Na^+ + H{-}H$$

Classification of Alkyl Halides

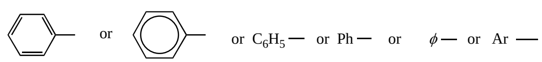
	methyl	primary	secondary	tertiary
	$H{-}C(H)(H){-}$	$R{-}C(H)(H){-}$	$R{-}C(R)(H){-}$	$R{-}C(R)(R){-}$
number of alkyl or aryl groups	0	1	2	3

What type of alkyl halide is this?



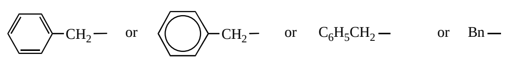
Aromatic groups are generalized differently from alkyl groups

➔ A benzene ring with a hydrogen removed is called a *phenyl group* and can be represented in various ways



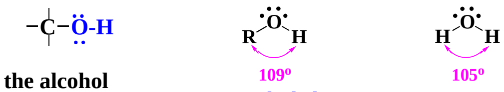
Ways of Representing a Phenyl Group

Another common aromatic group is called a *benzyl group* and can be represented in various way



Ways of Representing a Benzyl Group

Functional Group: Alcohols: R-OH



the alcohol functional group — *an alcohol* — *water*

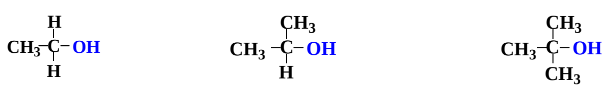
Simple alcohols often are named by using the alkyl group name followed by "alcohol."

CH_4	CH_3^-	CH_3-OH
methane	methyl	methyl alcohol
CH_3CH_3	$CH_3CH_2^-$	CH_3CH_2-OH
ethane	ethyl	ethyl alcohol

Classification of alcohols

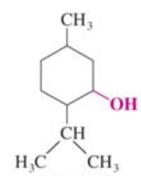
Alcohols are classified as primary, secondary or tertiary according to the structure around the carbon to which the hydroxyl group is attached.

ethyl alcohol	isopropyl alcohol	*tertiary*-butyl alcohol
CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$

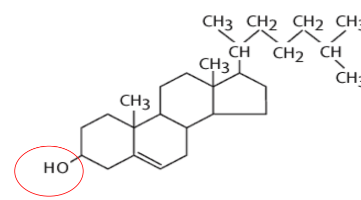


a 1º alcohol — a 2º alcohol — a 3º alcohol

Some typical alcohols



Menthol
(a 2° alcohol found in peppermint oil)



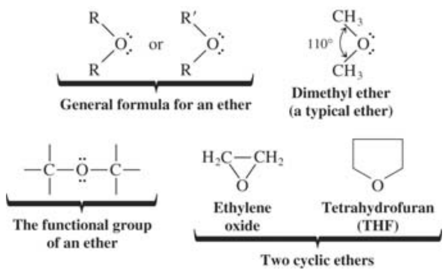
cholesterol

Ethers

Contain oxygen bonded to two alkyl groups

R-O-R (a symmetrical ether)

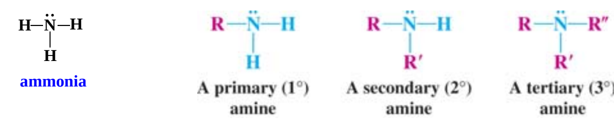
R-O-R' (unsymmetrical ether)



Ethers are less polar and less reactive than alcohols

Amines – the Bases of Organic Chemistry

- **Amines are organic derivatives of ammonia**



Classified as 1°, 2°, or 3° depending on number of R groups (not the type of R group)

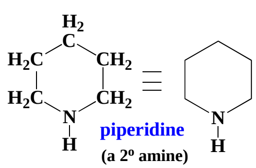
Some Typical Amines

$CH_3CH_2NH_2$ — **ethylamine** (a 1° amine)

$CH_3CH(NH_2)CH_3$ — **isopropylamine** (a 1° amine)

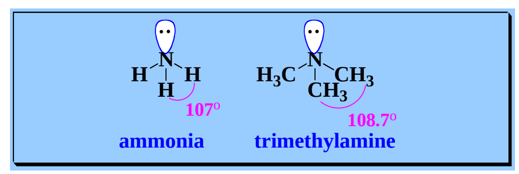
$CH_3C(CH_3)(NH_2)CH_3$ — **tertiary-butylamine** (a 1° amine)

$(CH_3)_2CHNHCH(CH_3)_2$ — **diisopropylamine** (a 2° amine)

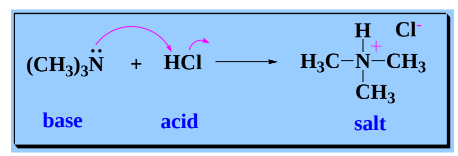


$CH_3CH_2N(CH_2CH_3)CH_2CH_3$ — **triethylamine** (a 3° amine)

$CH_3CH_2N(CH_2CH_3)CH_3$ — **diethylmethylamine** (a 3° amine)



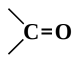
Amines are bases.



Aldehydes and Ketones

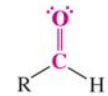
Aldehydes and ketones both contain the very important **carbonyl group**.

The Carbonyl Group



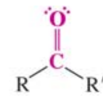
Aldehydes differ from ketones by having a H on C=O

aldehyde



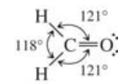
or RCHO

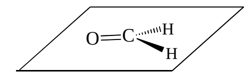
Ketones have two alkyl groups attached to the carbonyl group



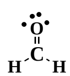
or RCOR′

The carbonyl carbon is trigonal planar with bond angles about 120º

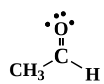




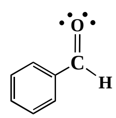
Examples of aldehydes and ketones



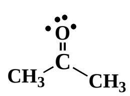
formaldehyde



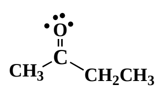
acetaldehyde



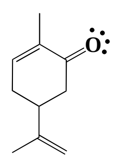
benzaldehyde



acetone



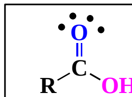
ethyl methyl ketone



carvone

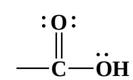
Carboxylic acids: The Acids of Organic Chemistry

Carboxylic acids have a general structure that incorporates the **carbonyl** and **hydroxyl** groups:

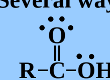


R may be H, alkyl or aryl

The characteristic functional group of a carboxylic acid is called the **carboxyl group**.



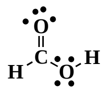
Several ways of representing carboxylic acids:



RCO_2H RCOOH

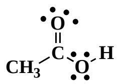
Examples of Carboxylic Acids

formic acid (R = H)



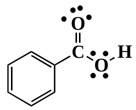
HCO_2H $HCOOH$

acetic acid (R = methyl)



$CH_3CH_2CO_2H$ CH_3CH_2COOH

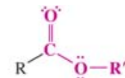
benzoic acid (R = phenyl)



$C_6H_5CO_2H$ C_6H_5COOH

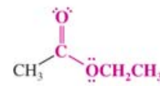
Esters & Amides: Members of the Carboxylic Acid Family
(sometimes referred to as Carboxylic Acid Derivatives)

Esters: carbonyl group is bonded to an alkoxyl (OR') group



or RCO_2R' or $RCOOR'$

General formula for an ester

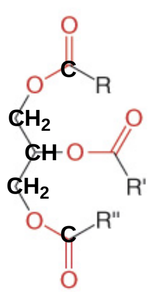


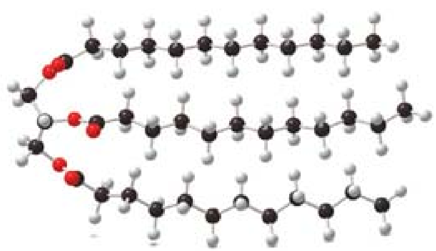
or $CH_3CO_2CH_2CH_3$ or $CH_3COOCH_2CH_3$

A specific ester called ethyl acetate

Example of Ester Groups

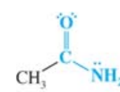
Most common lipids (fats and oils) are esters of the trihydroxy alcohol, glycerol, plus carboxylic acids of 10 to 20 carbon atoms.



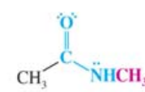


Amides: Another Carboxylic Acid Derivative

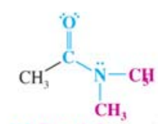
Amides have a nitrogen attached directly to the C=O



Acetamide



N-Methylacetamide

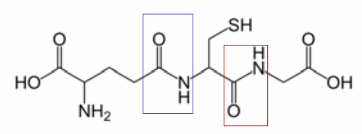


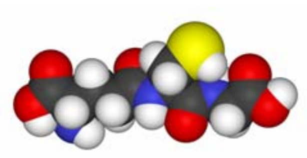
N,*N*-Dimethylacetamide

Amides are called carboxylic acid derivatives because they are usually made from carboxylic acids.

We'll learn later that amides, unlike amines, are <u>not</u> bases.

Amide bonds are the backbone of peptides and proteins





Glutathione:
an antioxidant

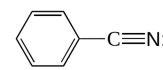
Tripeptide (cysteine, glutamate, and glycine) with two amide links

Nitriles: R-CN

Alkyl group attached to a carbon triply bonded to a nitrogen

- **This functional group is called a nitrile.**

The —C≡N: is called a cyano group.



Benzonitrile

The CN triple bond is structurally similar to the triple bond of an alkyne.

Summary of Major Families of Organic Compounds

	Family						
	Alkane	Alkene	Alkyne	Aromatic	Haloalkane	Alcohol	Ether
Functional group	C—H and C—C bonds	>C=C<	—C≡C—	Aromatic ring	$-\overset{\vert}{\underset{\vert}{C}}-\ddot{\underset{..}{X}}:$	$-\overset{\vert}{\underset{\vert}{C}}-\ddot{\underset{..}{O}}H$	$-\overset{\vert}{\underset{\vert}{C}}-\ddot{\underset{..}{O}}-\overset{\vert}{\underset{\vert}{C}}-$
General formula	RH	$RCH{=}CH_2$ $RCH{=}CHR$ $R_2C{=}CHR$ $R_2C{=}CR_2$	RC≡CH RC≡CR	ArH	RX	ROH	ROR
Specific example	CH_3CH_3	$CH_2{=}CH_2$	HC≡CH		CH_3CH_2Cl	CH_3CH_2OH	CH_3OCH_3
IUPAC name	Ethane	Ethene	Ethyne	Benzene	Chloroethane	Ethanol	Methoxymethane
Common name[a]	Ethane	Ethylene	Acetylene	Benzene	Ethyl chloride	Ethyl alcohol	Dimethyl ether

[a]These names are also accepted by the IUPAC.

Summary (cont.)

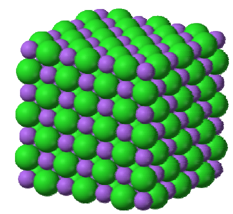
Family						
Amine	Aldehyde	Ketone	Carboxylic Acid	Ester	Amide	Nitrile
$-\overset{\vert}{\underset{\vert}{C}}-\ddot{N}<$	$\ddot{O}{=}C(-)H$	$-\overset{\vert}{\underset{\vert}{C}}-C(=\ddot{O})-\overset{\vert}{\underset{\vert}{C}}-$	$-C(=\ddot{O})-\ddot{O}H$	$-C(=\ddot{O})-\ddot{O}-\overset{\vert}{\underset{\vert}{C}}-$	$-C(=\ddot{O})-\ddot{N}<$	—C≡N
RNH_2 R_2NH R_3N	RCH(=O)	RCR′(=O)	RCOH(=O)	RCOR′(=O)	$RCNH_2$(=O) RCNHR′(=O) RCNR′R″(=O)	RCN
CH_3NH_2	CH_3CH(=O)	CH_3CCH_3(=O)	CH_3COH(=O)	CH_3COCH_3(=O)	CH_3CNH_2(=O)	$CH_3C{\equiv}N$
Methanamine	Ethanal	Propanone	Ethanoic acid	Methyl ethanoate	Ethanamide	Ethanenitrile
Methylamine	Acetaldehyde	Acetone	Acetic acid	Methyl acetate	Acetamide	Acetonitrile

Structure and Physical Properties

- What makes atoms and molecules stick to one another?
- **Intermolecular Attractive Forces**
- If there were no intermolecular attractive forces, everything would be a gas!
  - Helium - a gas down to 4º K
- In order to exist as solids or liquids, molecules must have some attractive forces, which are overcome in melting, boiling, and solubility
- Higher melting points and boiling points will be a measure of the strength of the intermolecular attractive forces
- Intermolecular attractive forces are based on electrostatic attractions, either permanent or temporarily-induced

Greatest intermolecular forces are between ions

- Ions of opposite charge attract each other strongly
- They forms a solid consisting of ions held together in a crystalline lattice
- Ionically bonded compounds are usually well ordered crystals with high melting points



NaCl

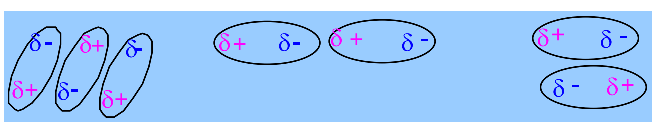
mp 801˚C

Dipole-Dipole Forces

(a second type of Intermolecular Attractive Force)

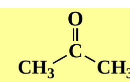
Forces are between molecules with permanent dipoles

- There is an attraction between δ+ and δ- areas in each molecule
- Much weaker than ion-ion forces
- Molecules align to maximize attraction of δ+ and δ- parts of molecules

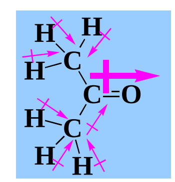


These interactions are felt in the close distances of condensed phases (liquids and solids)

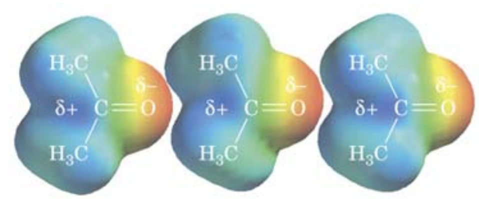
An Example of a Polar Molecule: Acetone



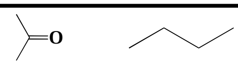
The carbonyl is a highly polarized bond because of the electronegative oxygen atom and the highly polarizable π electrons.



Net dipole moment = 2.72 D



Comparing Acetone and Butane



	Acetone	Butane
MW	58	58
MP	-95 ºC	-138 ºC
BP	56 ºC	-0.5 ºC
solubility in water	miscible	insoluble

More thermal energy (higher temp) is need to overcome intermolecular forces in more polar molecules. Therefore, higher melting point and boiling point

Also, solubility reflects interaction of dipole with water molecules

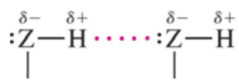
(we'll discuss this later)

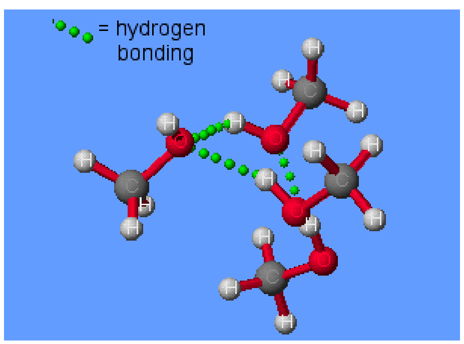
Hydrogen bonding
(a third type of Intermolecular Attractive Force)

- **Hydrogen Bonds**
  - ➔**There is an interaction between hydrogens bonded to strongly electronegative atoms (O, N or F) and nonbonding electron pairs on other strongly electronegative atoms (O, N or F)**

Hydrogen bonding

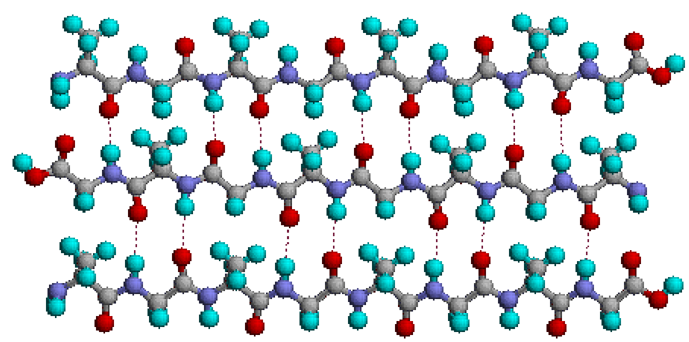
- ♦ **H is electron-deficient in these bonds with small electronegative elements (O, N, and F)**
- ♦ **Links to the lone pairs on the X atom**
- ♦ **About 10% the strength of a covalent bond**





H-bonding in Methyl alcohol CH_3OH

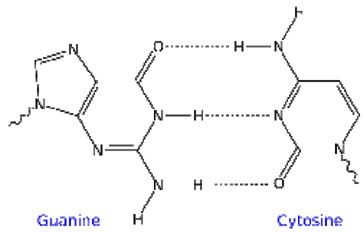
HYDROGEN BONDING IN PROTEINS
Model of H-bonding in a β-sheet protein



red=oxygen purple=nitrogen

H-bonding in DNA bases

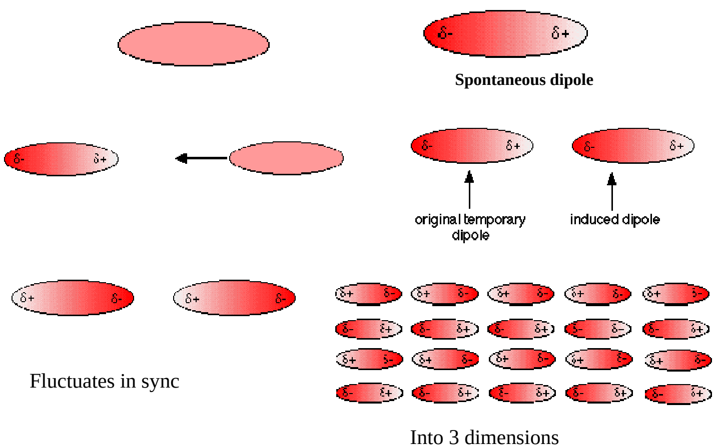
- The replication mechanism in DNA and RNA is dependent on the “perfect fit” between specific bases



Van der Waals Forces
(the fourth Intermolecular Attractive Force)

- Why does Methane (m.p. -182°C, b.p. - 162°C) condense at all
- These are the weakest of the Intermolecular Attractive Forces
- Caused by Induced dipoles
  - At one instant, electrons may be more on one side than another
  - Electrons on adjacent molecule tend to align with that temporary dipole
  - These temporary opposite dipoles cause a weak attraction between the two molecules
- Also known as London Forces or London dispersion forces

Consider an oval molecule like ethane or N_2

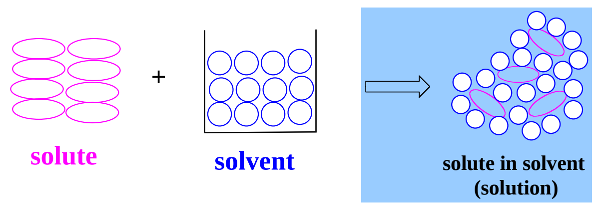


van der Waals Forces are small, but…

- Molecules which rely only on van der Waals forces generally have low melting points and boiling points

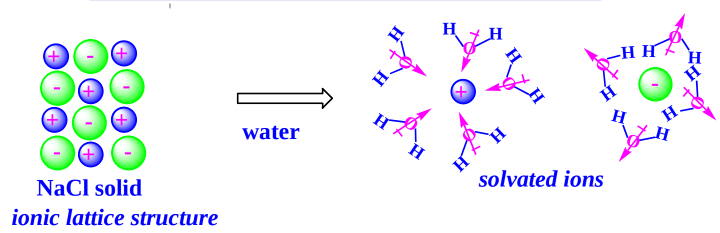
A Gecko can hang from 1 pad, with no known stickum

Solubilities are a Result of Intermolecular Attractive Forces



Solution occurs because IAF's between solvent and solute molecules are stronger than between solute molecules with one another.

Why ionic compounds tend to dissolve in water



Ion-dipole interactions are strong

The solvation energy of the solvated ions is greater than the lattice energy of the ionic solid

"Like Dissolves Like"

- **Polar compounds tend to dissolve in polar solvents**
  - **Polar liquids are miscible with other polar liquids**
- **Hydrogen-bonding of oxygen or nitrogen facilitates solubility in protic solvents such as water or alcohol**
- **Non-polar compounds are more soluble in non-polar solvents**
  - **Non-polar liquids and polar liquids are usually immiscible**

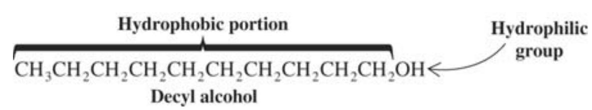
➔Generally the presence of one hydrophilic group *(e.g.*, hydroxyl) can make a compound with 3 carbons completely soluble in water.

- **One hydrophilic group can make a 5 carbon compound at least partially soluble in water.**
- **A compound is said to be "water soluble" if at least 3g of it will dissolve in 100 mL of water**

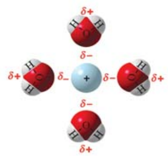
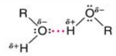
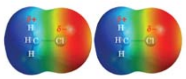
➔A large alkyl group can overwhelm the ability of a polar group which is also in a molecule to solubilize that molecule in water.

For example

- **Decyl alcohol is only slightly soluble in water**
- **The large alkyl portion is hydrophobic ("water hating") and overwhelms the capacity of the hydrophilic ("water loving") hydroxyl**



Summary of attractive forces

Electric Force	Relative Strength	Type	Example
Cation–anion (in a crystal)	Very strong		Sodium chloride crystal lattice
Covalent bonds	Strong (140–523 kJ mol^{-1})	Shared electron pairs	H—H (436 kJ mol^{-1}) CH_3—CH_3 (378 kJ mol^{-1}) I—I (151 kJ mol^{-1})
Ion–dipole	Moderate		Na^+ in water (see Fig. 2.9)
Hydrogen bonds	Moderate to weak (4–38 kJ mol^{-1})	$-\overset{\delta-}{Z}:\cdots\overset{\delta+}{H}-$	
Dipole–dipole	Weak	$\delta+\cdots\delta-$	
van der Waals	Variable	Transient dipole	Interactions between methane molecules