

# **Chemical concepts: Functional Groups, Polarity, Solubility**

**NU FS 372+373**

# Key concepts

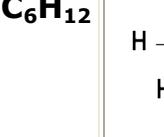
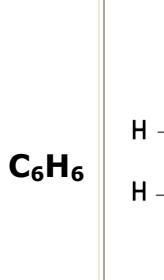
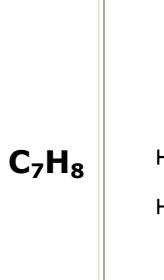
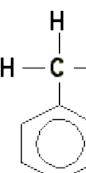
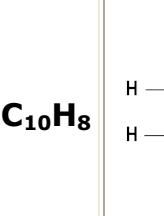
1. *Remember common functional groups and be able to recognise them in complex organic molecules (slides 3-12)*
2. *Understand the concepts of electronegativity and polarity*
3. *Understand the principles governing solubility and miscibility*
4. *Be able to define  $\log P_{ow}$  and understand the significance of  $\log P_{ow}$  values*

# Alkanes:

**C<sub>n</sub>H<sub>2n+2</sub>**

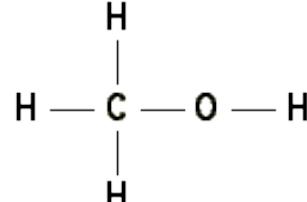
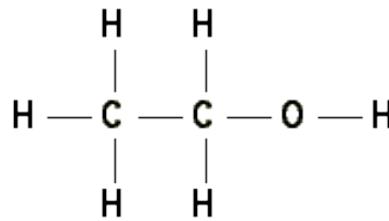
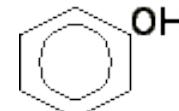
Formula	Structure	Name / Uses
<b>CH<sub>4</sub></b>	<pre>       H               H — C — H               H     </pre>	<b>Methane</b> - gas used for cooking.
<b>C<sub>2</sub>H<sub>6</sub></b>	<pre>       H   H                   H — C — C — H                   H   H     </pre>	<b>Ethane</b>
<b>C<sub>3</sub>H<sub>8</sub></b>	<pre>       H   H   H                       H — C — C — C — H                       H   H   H     </pre>	<b>Propane</b> - heating fuel.
<b>C<sub>4</sub>H<sub>10</sub></b>	<pre>       H   H   H   H                           H — C — C — C — C — H                           H   H   H   H     </pre>	<b>Butane</b> - lighter / camping fuel.
<b>C<sub>5</sub>H<sub>12</sub></b>	<pre>       H   H   H   H   H                           H — C — C — C — C — C — H                           H   H   H   H   H     </pre>	<b>Pentane</b>
<b>C<sub>6</sub>H<sub>14</sub></b>	<pre>       H   H   H   H   H   H                           H — C — C — C — C — C — C — H                           H   H   H   H   H   H     </pre>	<b>Hexane</b>

# Hydrocarbon Rings:

Formula	Structure	Name / Uses
$C_6H_{12}$		<b>Cyclohexane</b> - a saturated hydrocarbon with the atoms arranged in a hexagonal ring. In organic chemistry, the presence of Hydrogen atoms is often assumed and this compound can be represented by a hexagonal ring: 
$C_6H_6$		<b>Benzene</b> - an industrial solvent. The Benzene Ring is one of the most important structures in organic chemistry. In reality, its alternate double and single bonds are "spread around" the ring so that the molecule is symmetrical. This structure is represented by a hexagon with a circle: 
$C_7H_8$		<b>Toluene</b> - an important solvent and starter chemical. Using the Benzene Ring, this molecule can also be depicted as: 
$C_{10}H_8$		<b>Naphthalene</b> - used in moth balls. This can be depicted as two fused Benzene Rings: 

# Alcohols:

$$C_nH_{2n+1}OH$$

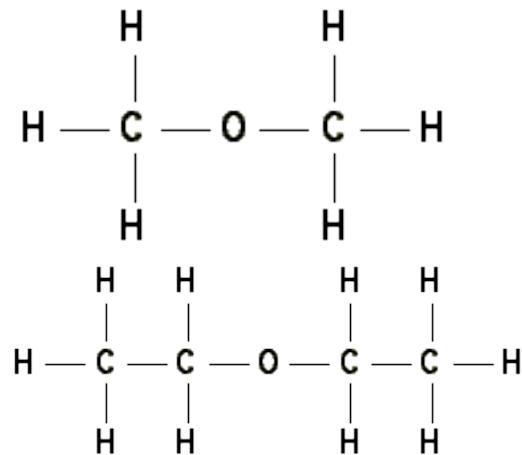
General Formula	Series Name	Details	Examples	Structures
$C_nH_{2n+1}OH$	Alcohols	Alcohols have the OH (hydroxyl) group in the molecule.	<p><math>CH_3OH</math>  <b>Methanol</b>          wood alcohol</p> <p><math>C_2H_5OH</math>  <b>Ethanol</b>          drinking alcohol</p> <p><math>C_6H_5OH</math>  <b>Phenol</b>          carbolic acid - used as disinfectant</p>	  

# Ethers: $(C_nH_{2n+1})_2O$

$(C_nH_{2n+1})_2O$  **Ethers**

Ethers have an O atom attached to two hydrocarbon chains (or rings).

$(CH_3)_2O$   
**Dimethyl Ether**  
a gas  
 $(C_2H_5)_2O$   
**Diethyl Ether**  
a liquid used as an anaesthetic)



# Aldehydes - $C_nH_{2n+1}CHO$

$C_nH_{2n+1}CHO$

Aldehydes have a CHO group attached to a hydrocarbon chain (or ring).

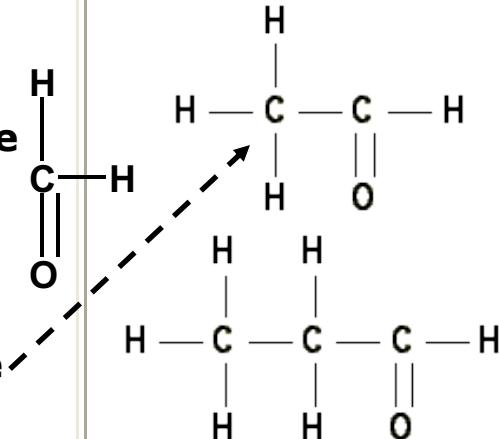
HCHO

**Formaldehyde**

preservative in labs

CH<sub>3</sub>CHO

**Acetaldehyde**



# Ketones - $(C_nH_{2n+1})_2CO$

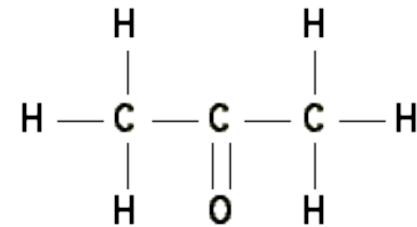
$(C_nH_{2n+1})_2CO$

Ketones have a CO group attached to two hydrocarbon chains (or rings).

CH<sub>3</sub>COCH<sub>3</sub>

**Dimethyl Ketone**

Also known as **acetone**: nail-varnish remover



# Carboxylic Acids

(fatty acids for high n):

$$C_nH_{2n+1}CO_2H$$

$C_nH_{2n+1}CO_2H$	Fatty Acids contain the $CO_2H$ (or $COOH$ ) group attached to a hydrocarbon chain or ring.	$HCO_2H$ <b>Formic Acid</b> in ant bites and stinging nettles $CH_3CO_2H$ <b>Acetic Acid</b> vinegar $C_3H_7CO_2H$ <b>Butyric Acid</b> the rancid butter smell	$\begin{array}{c} H-C-O-H \\    \\ O \\   \\ H-C-C-O-H \\   \quad   \\ H \quad O \\   \quad   \\ H \quad H \\   \quad   \\ H_3C-C-C-O-H \\   \quad   \\ H \quad H \end{array}$
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# Esters:

## $\text{RCO}_2\text{R}'$

$\text{RCO}_2\text{R}'$  <b>(R, R' are Hydrocarbon chains or rings).</b>	<p>Esters are similar to Fatty Acids except that the H in the COOH group is another hydrocarbon chain. They are usually very sweet smelling liquids used in perfumes.</p>	$\text{CH}_3\text{CO}_2\text{CH}_3$ <b>Methyl Methoate</b> essence of pear drops	$\begin{array}{ccccc} & \text{H} & & \text{H} & \\ &   & &   & \\ \text{H} & - \text{C} & - \text{C} & - \text{O} & - \text{C} - \text{H} \\ &   & &    & \\ & \text{H} & & \text{O} & \\ & & & & \text{H} \end{array}$
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# Amines:

## $\text{RCH}_{2n+1}\text{NH}_2$



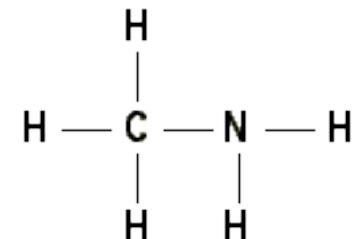
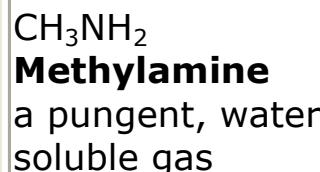
Amines have one or more of the Hydrogen atoms in Ammonia ( $\text{NH}_3$ ) replaced by a Hydrocarbon chain or ring.

**Primary Amines** have the formula  $\text{RNH}_2$

**Secondary Amines** have the formula  $\text{RR}'\text{NH}$

**Tertiary Amines** have the formula  $\text{RR}'\text{R}''\text{N}$ .

( $\text{R}$ ,  $\text{R}'$ ,  $\text{R}''$  are Hydrocarbon chains or rings).

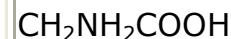


# Amino Acids

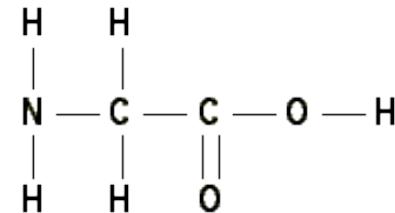


Amino Acids have two functional groups: the amine ( $\text{HN}_2$ ) group and the fatty acid ( $\text{COOH}$ ) group.

Amino Acids combine together to form **proteins** which are an important component of living organisms.



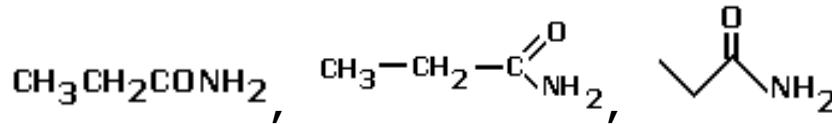
**Glycine**  
the simplest amino acid.



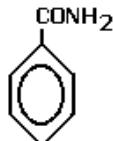
# Amides: $\text{RCONH}_2$

## Primary Amides

propanamide



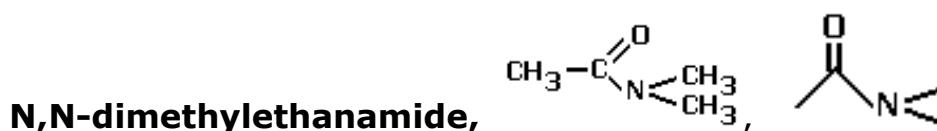
Benzamide



**Secondary Amides** - have one hydrogen and one alkyl or aryl group on the N of the amide group.



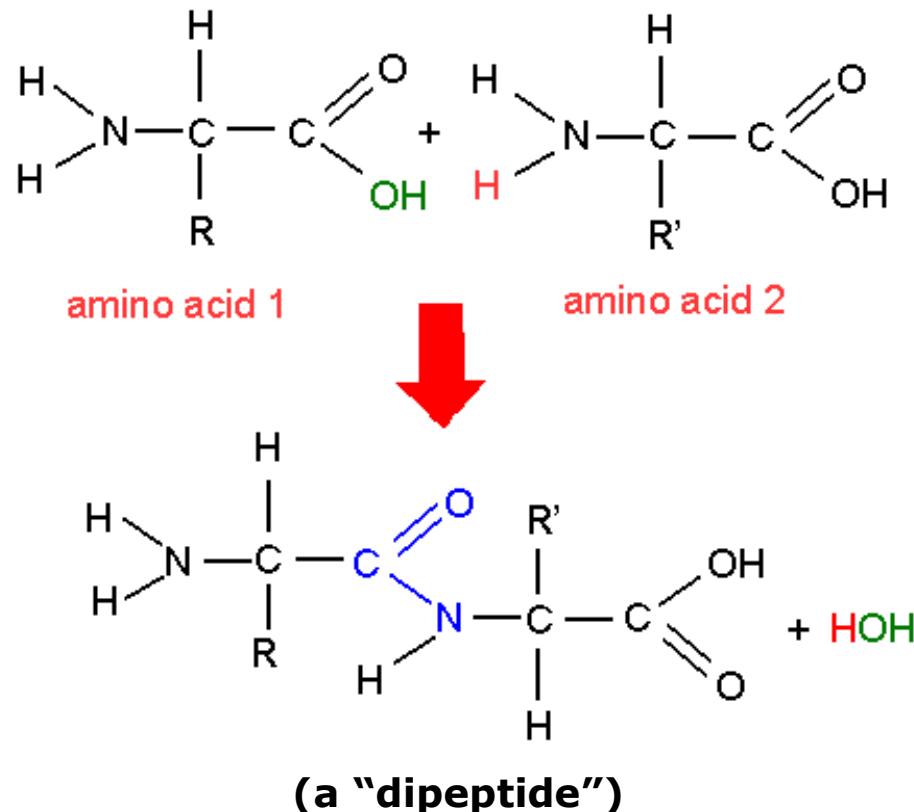
**Tertiary Amides** - have two alkyl or aryl groups attached to the N of the amide group.



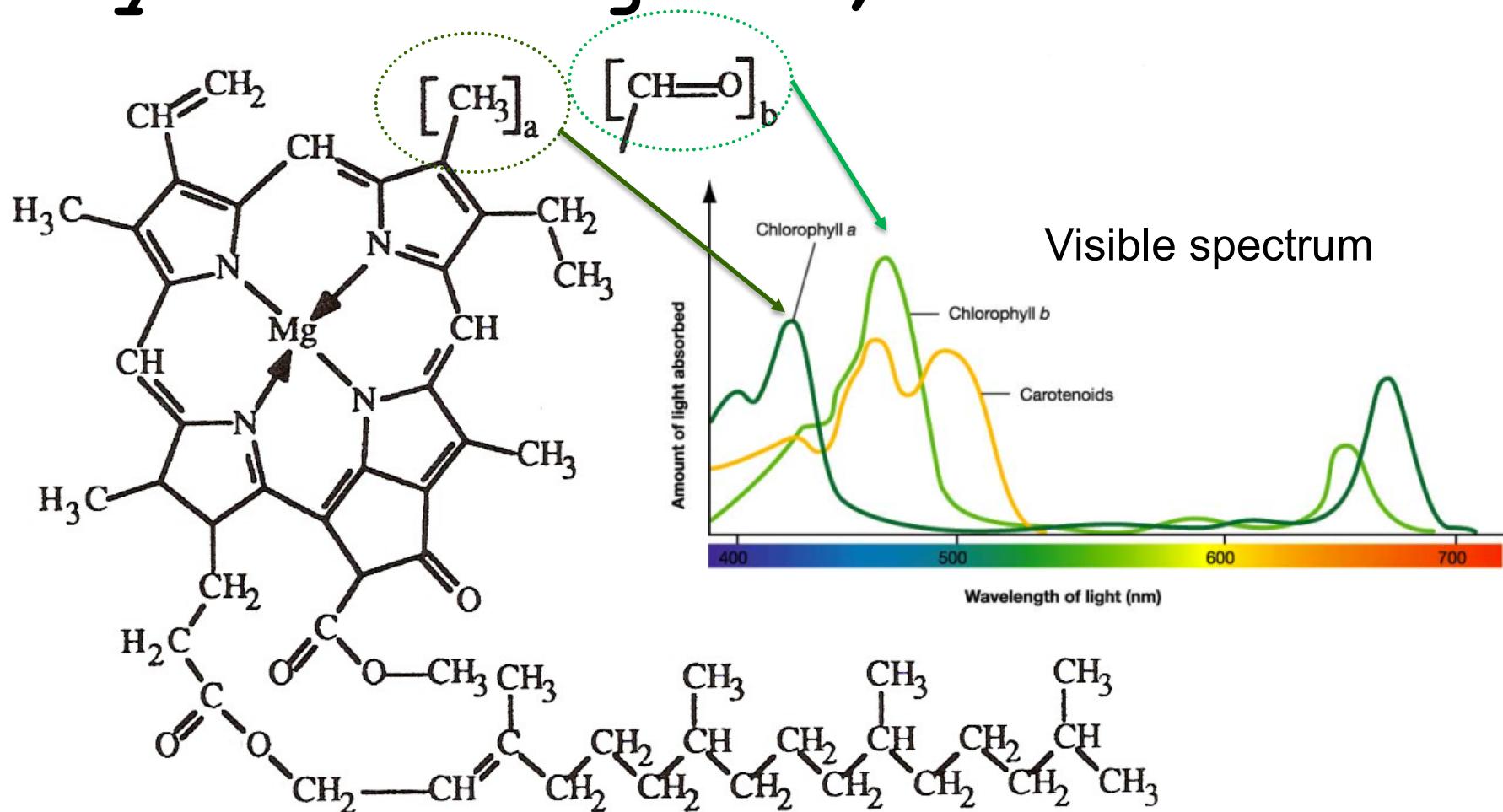
- **POLYAMIDES** are secondary amides formed in a condensation reaction between a carboxylic acid and an amine.



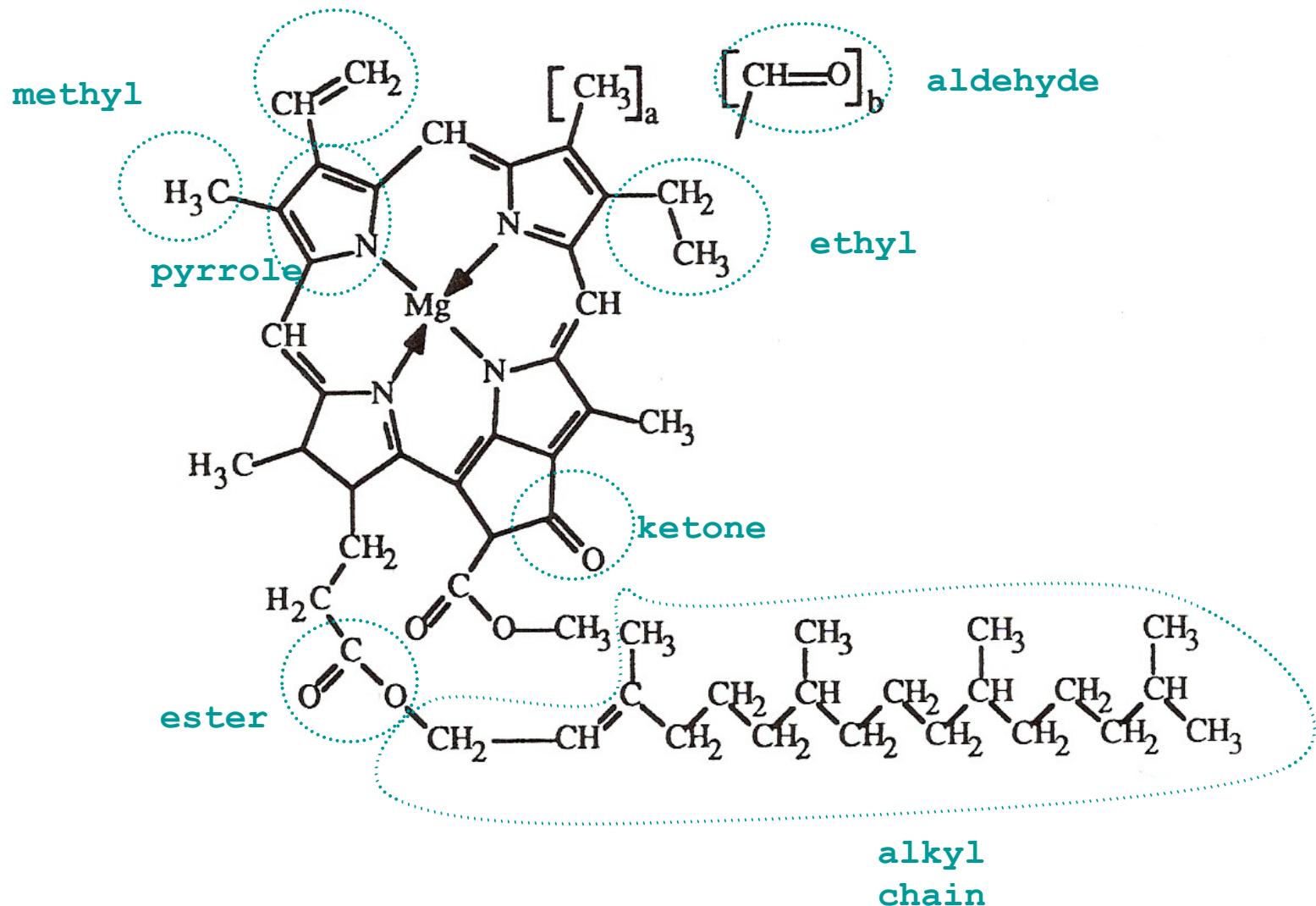
- **POLYPEPTIDES** (proteins) are polyamides formed between amino acids



# Chlorophyll a (bluish-green and b yellowish-green)



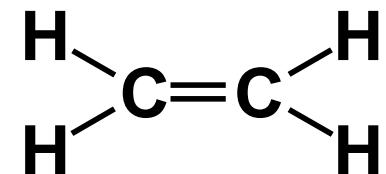
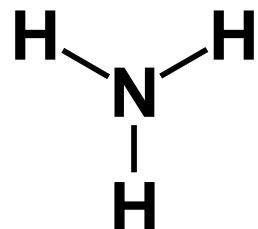
# Chlorophyll a and b



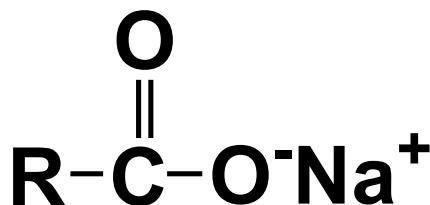
# Intramolecular Bonds

- **Covalent bonds** –

sharing pairs of electrons. Single or multiple. Number of covalent bonds dependent on valency



- **Ionic bonds** – between strongly electronegative and electropositive atoms eg. salts

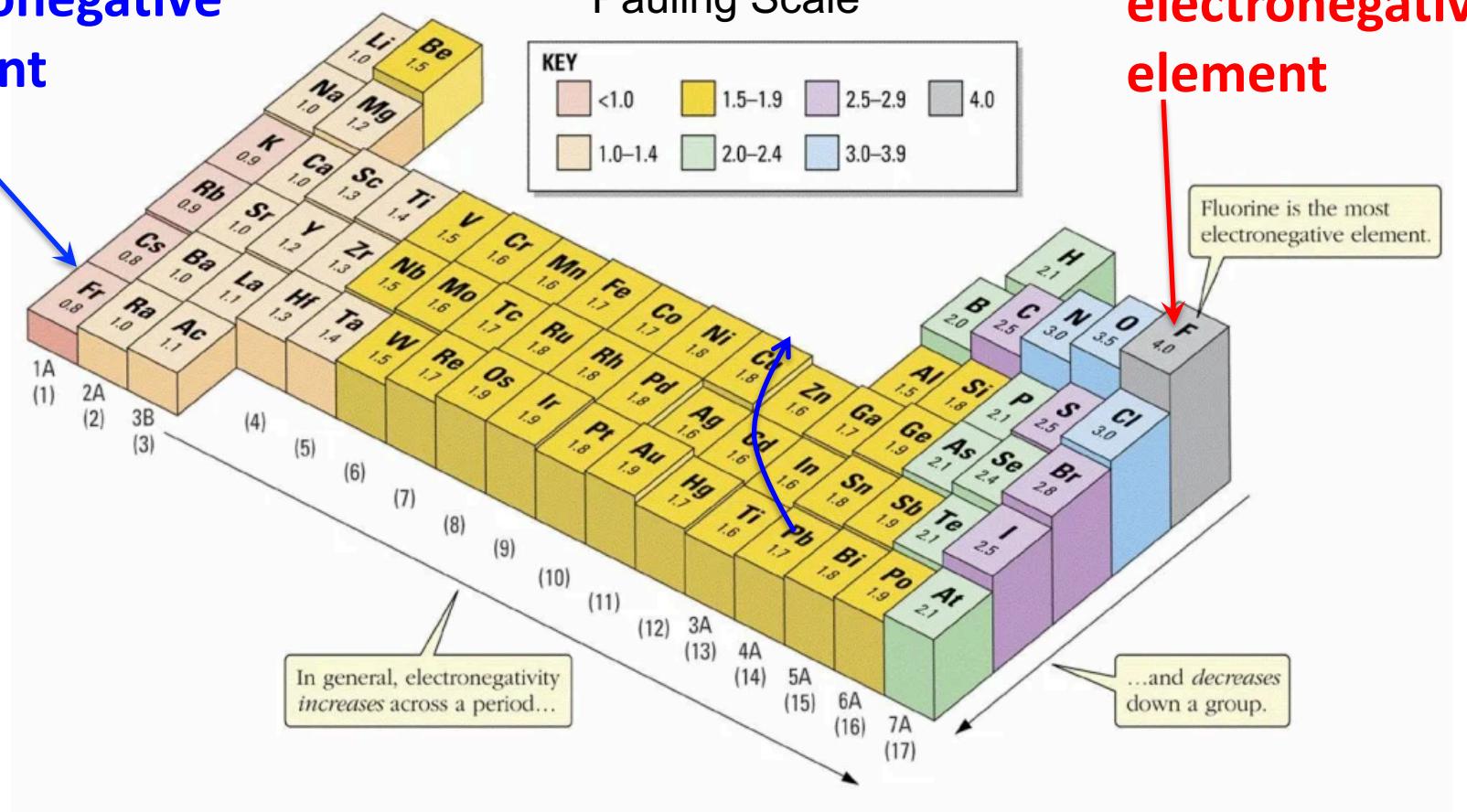


# Electronegativity

Electronegativity is the attraction of an atom for the electron cloud that forms the bond between 2 atoms

Least  
electronegative  
element

Most  
electronegative  
element



# Polarity

*Arises through differences in electronegativity:*



*A and B have equal electronegativities..*

→ nonpolar bond



*B is more electronegative than A..*

→ polar bond

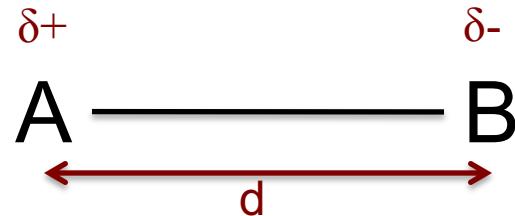


*B is much more electronegative than A..*

→ ionic bond

# Dipole Moment

B is more electronegative than A:

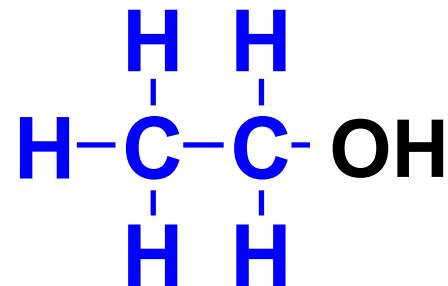
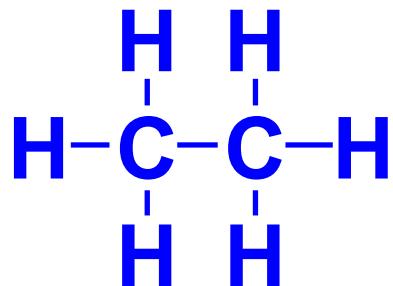


*The product of the magnitude of the charge ( $\delta$ ) either on A or B and the AB bond length (d) is called the dipole moment ( $\mu$ ) of the bond:*

$$\mu (AB) = \delta \times d \quad (\text{SI units are debye (D)})$$

Molecular dipole moments are the vector sum of the dipole moments of all bonds in the molecule

# Polar vs. Nonpolar Molecules



Ethane: Non-polar

Ethanol: Polar

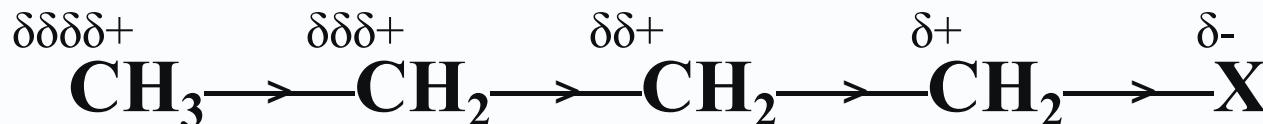
Functional groups can be classified as electron withdrawing ( $-I$ ) or electron donating ( $+I$ ) groups relative to hydrogen

$+I$	$-I$		
O <sup>-</sup>	NR <sub>3</sub> <sup>+</sup>	COOH	OR
COO <sup>-</sup>	SR <sub>2</sub> <sup>+</sup>	F	COR
CR <sub>3</sub>	NH <sub>3</sub> <sup>+</sup>	Cl	SH
CHR <sub>2</sub>	NO <sub>2</sub>	Br	SR
CH <sub>2</sub> R	SO <sub>2</sub> R	I	OH
CH <sub>3</sub>	CN	OAr	C≡CR
D	SO <sub>2</sub> Ar	COOR	Ar
			CH=CR <sub>2</sub>

# Inductive Effects



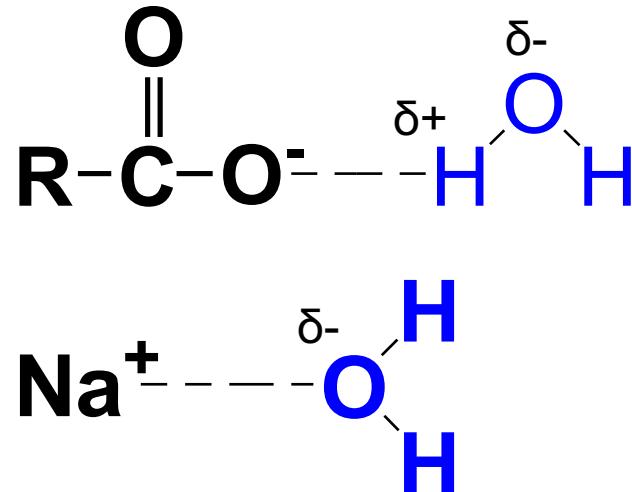
NO<sub>2</sub> is  $-I$  i.e. electron withdrawing; this also draws electrons away from the Ph group in the C-Ph bond



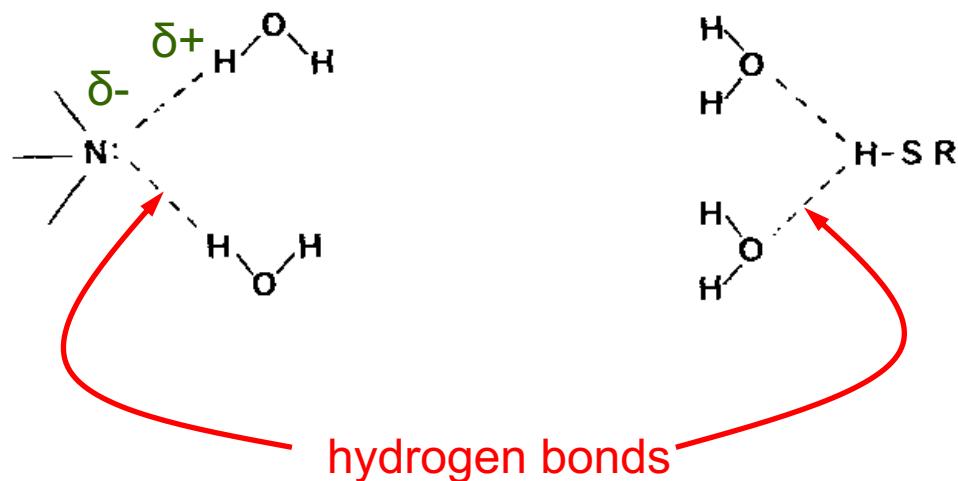
An electronegative (electron withdrawing) element X not only polarizes the C-X bond but also draws electrons away from more distant bonds to a diminishing extent. This is the inductive effect, occurring through  $\sigma$  bonds.

# Intermolecular Bonds

- **Ion-Dipole** – responsible for salts dissolving in water

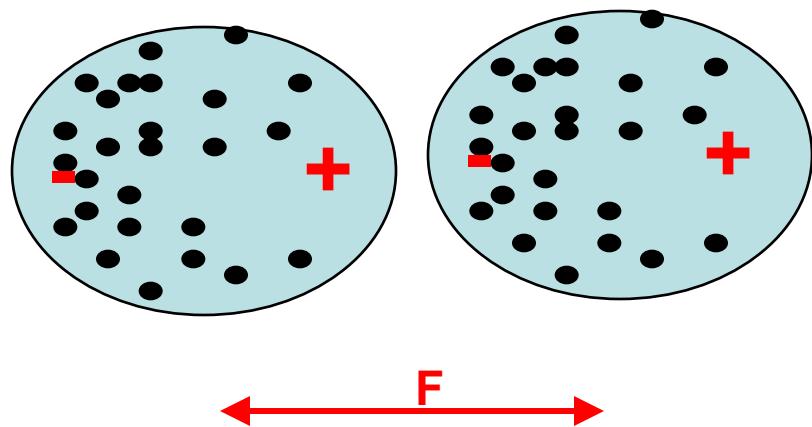


- **Hydrogen Bond (dipole-dipole)** – between two polar molecules



# Intermolecular Bonds

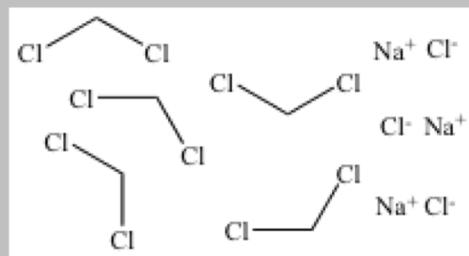
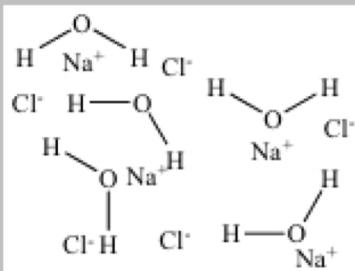
- **Van der Waals Forces** – induced or temporary dipole occurring as non-polar compounds approach each other – a type of dipole-dipole interaction.





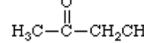
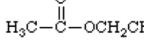
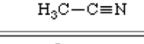
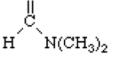
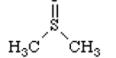
# Dielectric constant

- *Dielectric constant ( $\epsilon$ ): A measure of a substance's ability to insulate opposite charges from each other.*
- ***As a measure of solvent polarity, higher  $\epsilon$  = higher polarity, greater ability to stabilize charges.***
- *(In physics, dielectric constant is also known as permittivity or relative permittivity referring to the ability of a substance to attenuate the transmission of an electrostatic force from one charged body to another, compared to a vacuum for which  $\epsilon = 1$ )*



$\epsilon > 15$  = polar solvent  
 $\epsilon < 15$  = nonpolar solvent

# Polar vs. Nonpolar Solvents

Name	Structure	bp, °C	dipole moment	dielectric constant
water	H-OH	100	1.85	80
methanol	CH <sub>3</sub> -OH	68	1.70	33
ethanol	CH <sub>3</sub> CH <sub>2</sub> -OH	78	1.69	24.3
1-propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	97	1.68	20.1
1-butanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -OH	118	1.66	17.8
acetone		56	2.88	20.7
methyl ethyl ketone		80	2.78	18.5
ethyl acetate		78	1.78	6.02
acetonitrile		81	3.92	36.6
N,N-dimethylformamide (DMF)		153	3.82	38.3
dimethyl sulfoxide (DMSO)		189	3.96	47.2
hexane	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	69	----	2.02
benzene		80	0	2.28
diethyl ether	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	35	1.15	4.34
tetrahydrofuran (THF)		66	1.63	7.52
methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>	40	1.60	9.08
carbon tetrachloride	CCl <sub>4</sub>	76	0	2.24

Longer hydrocarbon chain → less polarity

# Miscibility of Solvents with Water

## Water

Miscible

Immiscible

Acetic acid	<input type="checkbox"/>	Dimethylformamide
** Acetone	<input type="checkbox"/>	Dimethyl sulfoxide
Acetonitrile	<input type="checkbox"/>	1,4-Dioxane
Benzene	<input type="checkbox"/>	Ethanol
1-Butanol	<input type="checkbox"/>	Ethyl acetate
2-Butanone	<input type="checkbox"/>	Heptane
Butyl acetate	<input type="checkbox"/>	Hexane
tert-Butyl methyl ether	<input type="checkbox"/>	Methanol
Carbon tetrachloride	<input type="checkbox"/>	Pentane
Chloroform	<input type="checkbox"/>	1-Propanol
Cyclohexane	<input type="checkbox"/>	2-Propanol **
1,2-Dichloroethane	<input type="checkbox"/>	Tetrahydrofuran **
Dichloromethane	<input type="checkbox"/>	Toluene
Diethyl ether	<input type="checkbox"/>	Trichloroethylene
Diisopropyl ether	<input type="checkbox"/>	2,2,4-Trimethylpentane
	<input type="checkbox"/>	Xylene

# Miscibility of Solvents with Hexane

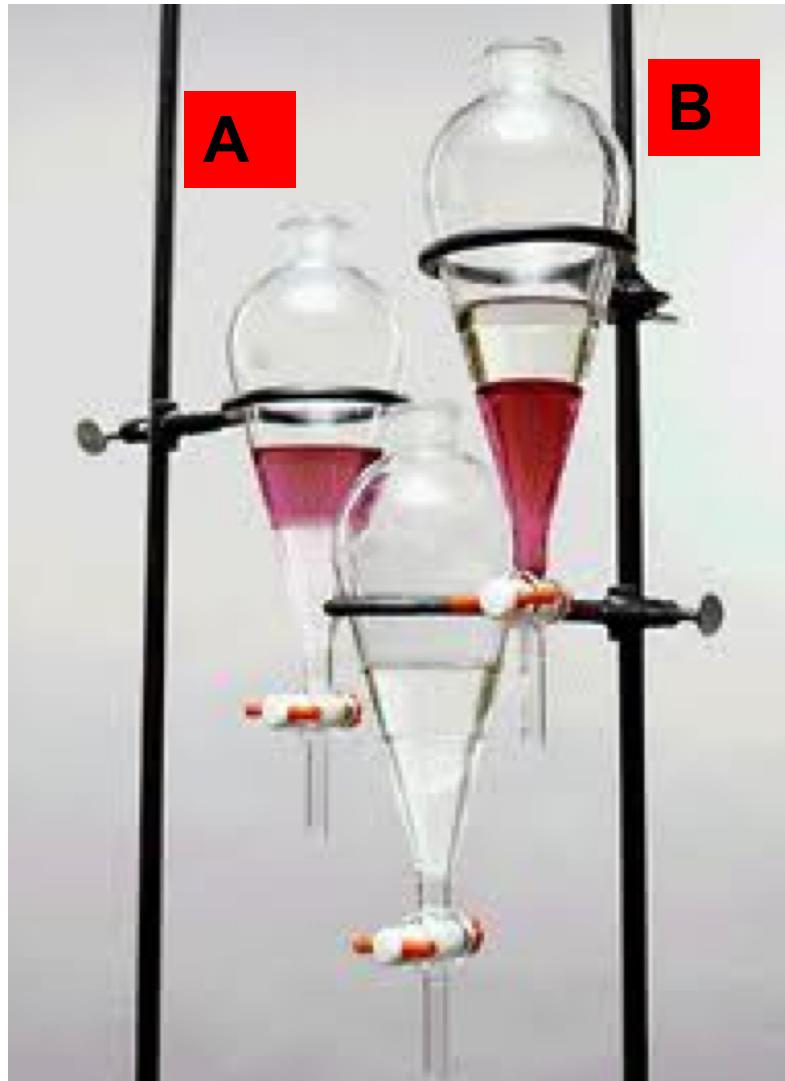
Hexane	
Miscible	Immiscible
	Acetic acid
** Acetone	
	Acetonitrile
	Benzene
	1-Butanol
	2-Butanone
	Butyl acetate
	<i>tert</i> -Butyl methyl ether
	Carbon tetrachloride
	Chloroform
	Cyclohexane
	1,2-Dichloroethane
	Dichloromethane
	Diethyl ether
	Diisopropyl ether
	Dimethylformamide
	Dimethyl sulfoxide
	1,4-Dioxane
	Ethanol
	Ethyl acetate
	Heptane
	Methanol
	Pentane
	1-Propanol
	2-Propanol **
	Tetrahydrofuran **
	Toluene
	Trichloroethylene
	2,2,4-Trimethylpentane
	Water
	Xylene

# **Solubility of Alcohols[ C<sub>n</sub>H<sub>2n+1</sub>OH ]**

<b>R-OH</b>	<b>Boiling Point °C</b>	<b>Solubility g/100g Water</b>
Methanol	65.5	∞
Ethanol	78.3	∞
1-Propanol	97.0	∞
2-Propanol	82.4	∞
1-Butanol	117.2	7.9
1-Pentanol	137.3	2.3

# Solubility of Carboxylic Acids

R=	O R-C-OH	Boiling Point °C	Solubility g/100g Water	Solubility g/100g Ethanol
H	101	∞	∞	∞
CH <sub>3</sub>	118	∞	∞	∞
CH <sub>3</sub> -CH <sub>2</sub> -	141	∞	∞	∞
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -	164	∞	∞	∞
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -	187	3.7	Soluble	
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>4</sub> -	205	1.0	Soluble	
C <sub>6</sub> H <sub>5</sub> -	250	0.34	Soluble	
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>10</sub> -		Insoluble	100	
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>16</sub> -		Insoluble	5.0	



**Solvents are  $\text{H}_2\text{O}$  and  $\text{CCl}_4$**

**Density of  $\text{CCl}_4$  is  $1.59 \text{ g/cm}^3$**

**Solutes are  $\text{I}_2$  and  $\text{KMnO}_4$**

**Which solvent is  
the upper layer?**

**Which flask has  
 $\text{I}_2$  added ?**

# *How will the (coloured) compounds partition?*



Herb infused oils



Oil/vinegar mixture

# Partition Coefficient

- The partition (or distribution) coefficient is the ratio of the concentrations of a compound in two immiscible solvents at equilibrium
  - *ie. it is a measure of the difference in solubility of the compound between these two solvents.*
- Often the hydrophobic solvent **octanol** and **water** are used.
- $\log P_{ow}$  is a measure of hydrophobicity (or lipophilicity):

$$\log P_{\text{octanol/water}} = \log \left( \frac{[\text{solute}]_{\text{octanol}}}{[\text{solute}]_{\text{un-ionized water}}} \right)$$

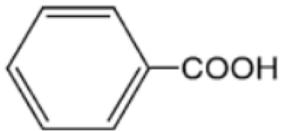
# **log P<sub>ow</sub> Values**

(note:  $\log_{10}(10)=1$ ;  $\log_{10}(1)=0$ ;  $\log_{10}(0.1)=-1$ ; etc)

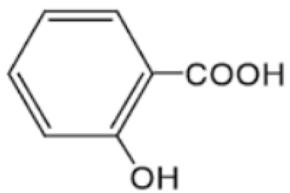


Compound	log P <sub>ow</sub>
Methanol	-0.77
2-Propanol	0.5
1-Hexanol	2.03
Benzene	2.13
Limonene	4.57
PCDD/PCDF (polychlorodibenzo-dioxin/furan)	6.5-8.8

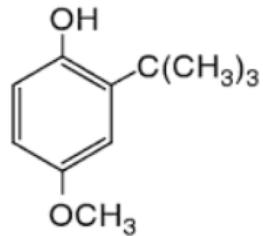
# $\log P_{ow}$ Values of mostly lipophilic food components



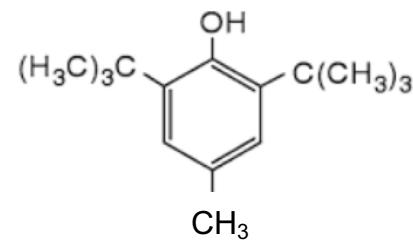
Benzoic Acid



Salicylic Acid



BHA



BHT

**1.87**

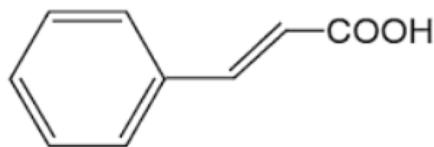
**2.26**

**3.5**

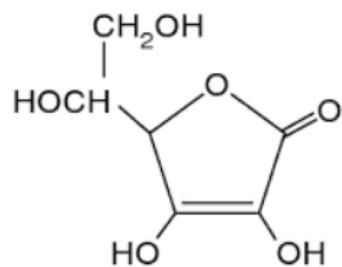
**5.1**

**INCREASING experimental log P values >>>>>**

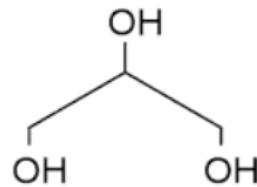
# $\log P_{ow}$ Values of mostly hydrophilic food components



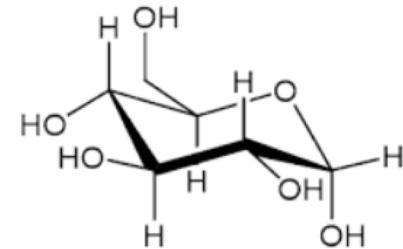
Cinnamic Acid



Ascorbic Acid



Glycerol



Glucose

**2.13**

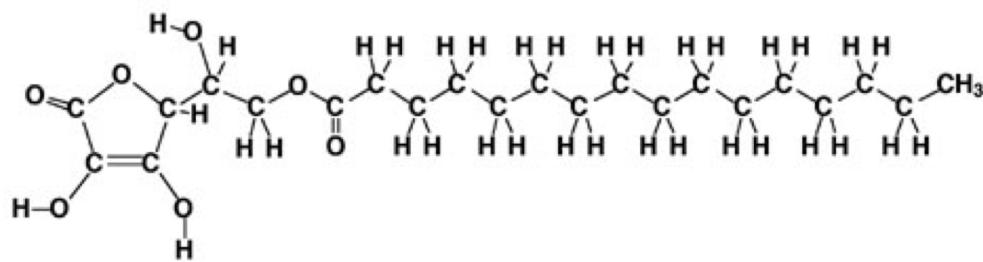
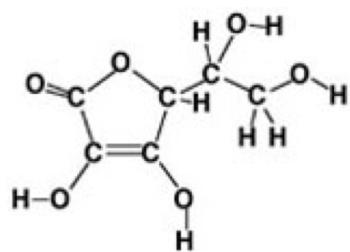
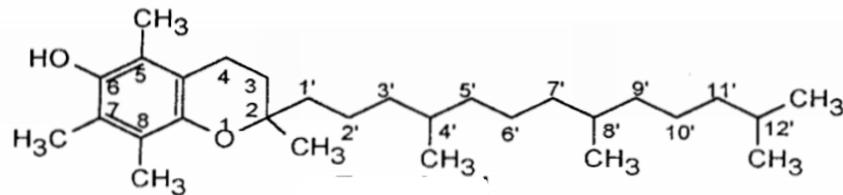
**-1.85**

**-1.76**

**-3.24**

**DECREASING experimental  $\log P$  values >>>>**

# Soluble in what ??



# Solubility of CO<sub>2</sub> in water

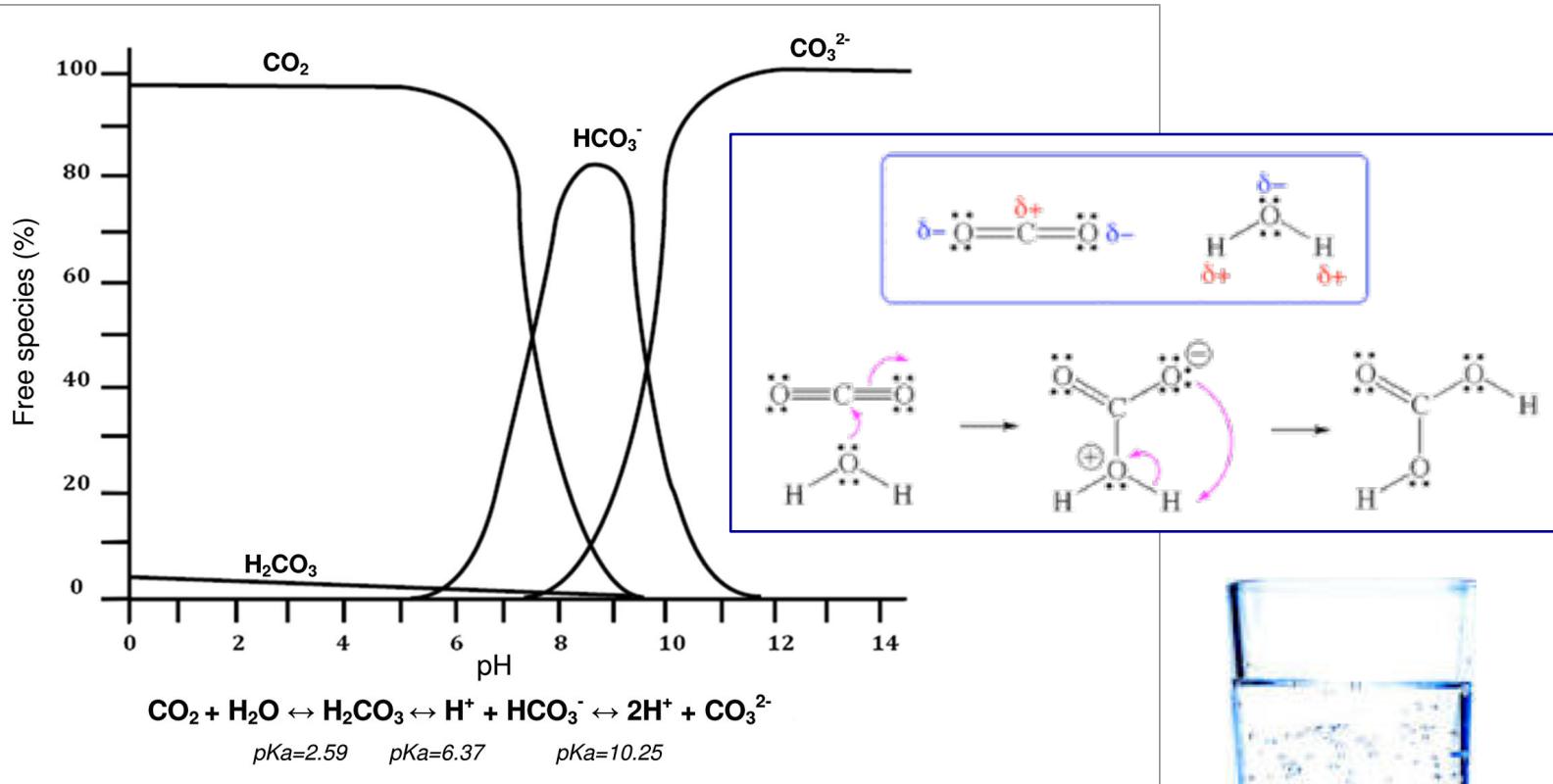
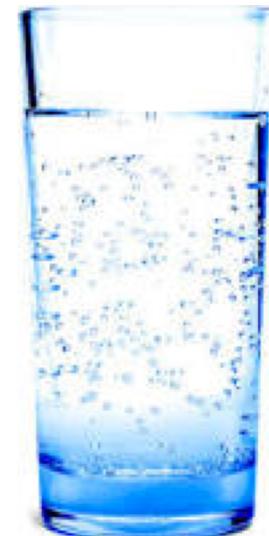


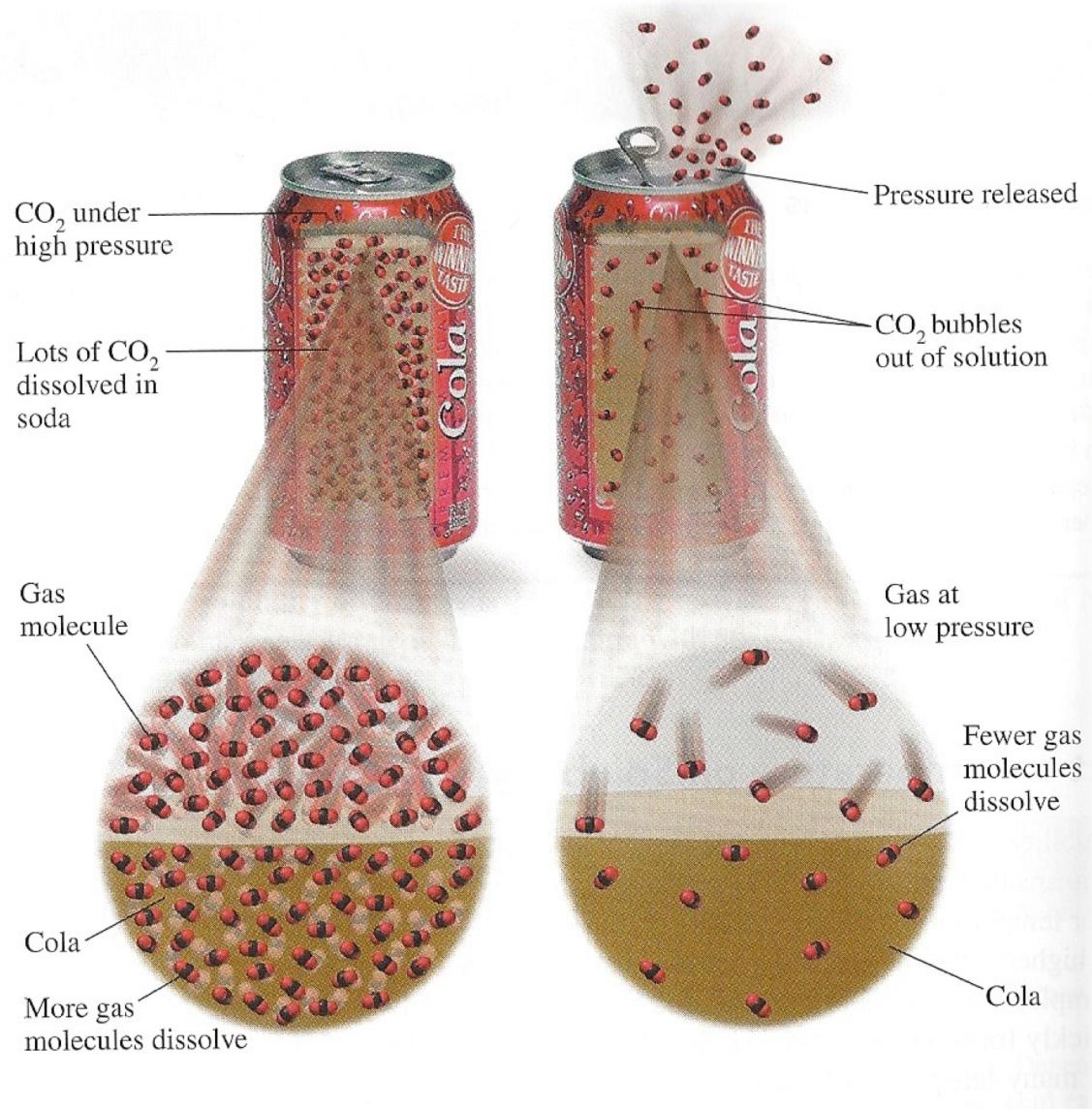
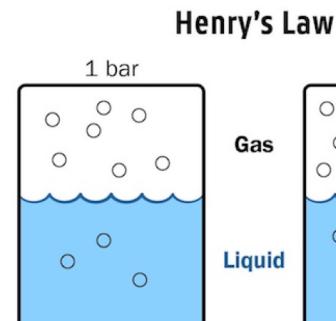
Figure 5—Fraction of dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate in water, as a function of pH (adapted from Daniels and others 1985).



# Solubility of CO<sub>2</sub> in a can

## Henry's Law:

**The solubility of a gas in a liquid is proportional to the pressure of gas above that liquid**



# Simple Method for Measurement of CO<sub>2</sub> in a food

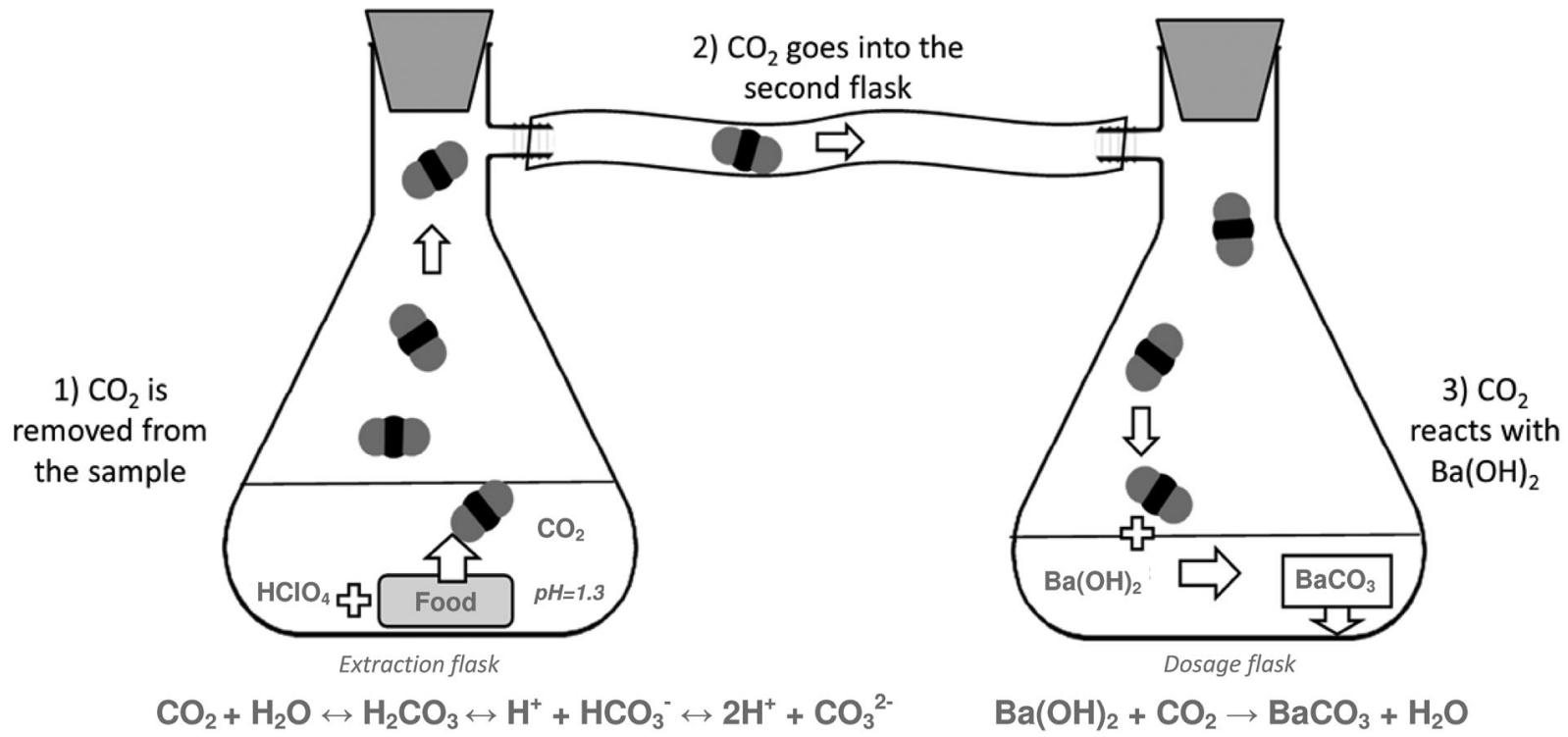


Figure 6—Example of experimental set-up to measure carbon dioxide content in liquid or solid food, and associated reactions (adapted from Gill 1988).

***Measurement of O<sub>2</sub> also possible (eg using luminescence sensors) but interactions with the food must be considered)***