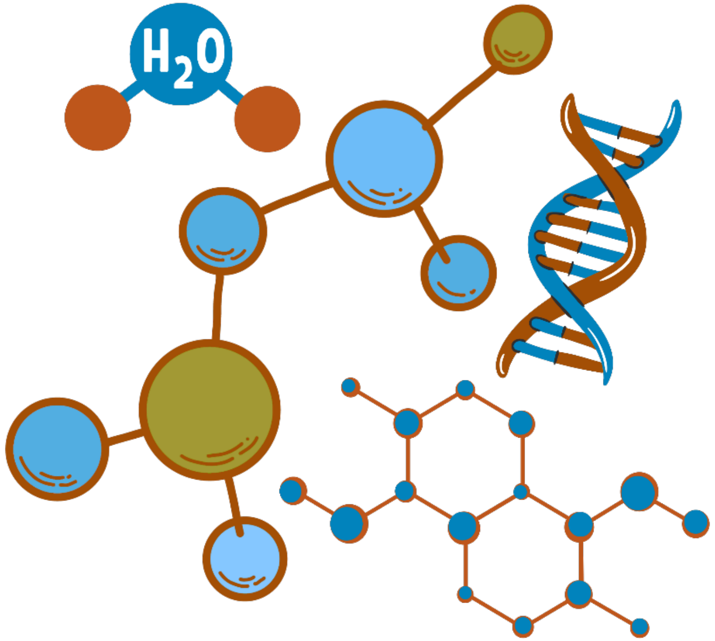
Introduction to Organic Chemistry
CHEM 109

جامعة الملك سعود
King Saud University
COLLEGE OF SCIENCES
CHEMISTRY DEPARTMENT

Chapter 4: Physical Properties and Intermolecular Forces



Chapter 4: Physical Properties and Intermolecular Forces

1. Physical Property

A **physical property** is defined as a characteristic of a substance that can be observed or measured without changing its chemical identity.

Examples; physical properties include color, density, the states of matter (gas, liquid, solid) , melting point, and boiling point.

2. Factors affecting the physical properties

2.1 Molecular weight

- **Increasing the molecular weight will increase boiling point and melting point .**
- *Example;* **ethane (CH_3CH_3) boils at -88.3 °C higher than methane (CH_4), which boils at -162 °C.**

2.2 Intermolecular forces (van der Waals forces)

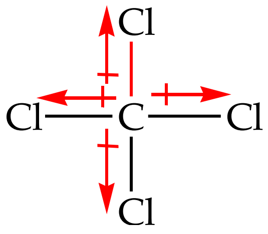
- **The forces that act between molecules are not as strong as those between ions.**

2. Factors affecting the physical properties

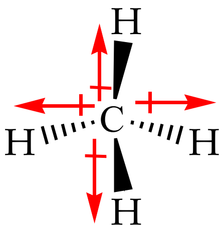
2.3 Intermolecular forces

A) Dipole-Dipole Forces

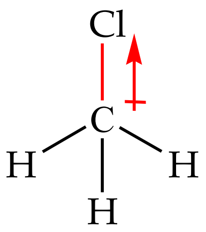
- **Dipole Moment (μ)** is a quantitative measure of the separation of positive and negative charges in a molecule.
- **Dipole Moment** depends on bond polarity and molecular shape.



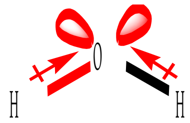
CCl_4 , $\mu = 0$



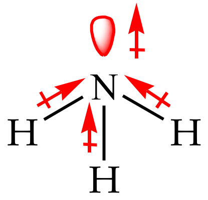
CH_4 , $\mu = 0$



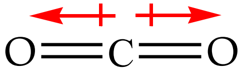
CH_3Cl , $\mu \neq 0$



H_2O , $\mu \neq 0$



NH_3 , $\mu \neq 0$



CO_2 , $\mu = 0$

- **Dipole-dipole forces** are between molecules with permanent dipoles.
- There is an interaction between $\delta+$ and $\delta-$ areas in each molecule; these are much weaker than ion-ion forces.
- Molecules align to maximize attraction of $\delta+$ and $\delta-$ parts of molecules.
- The more polar the molecule, the higher is its boiling point.

Table 2.1 Molecular Weights, Dipole Moments, Boiling Points of some organic substances

Substance	Molecular Weight	Dipole Moment μ (D)	Boiling Point (K)
Propane, $CH_3CH_2CH_3$	44	0.1	231
Dimethyl ether, CH_3OCH_3	46	1.3	248
Methyl chloride, CH_3Cl	50	1.9	249
Acetaldehyde, CH_3CHO	44	2.7	294
Acetonitrile, CH_3CN	41	3.9	355

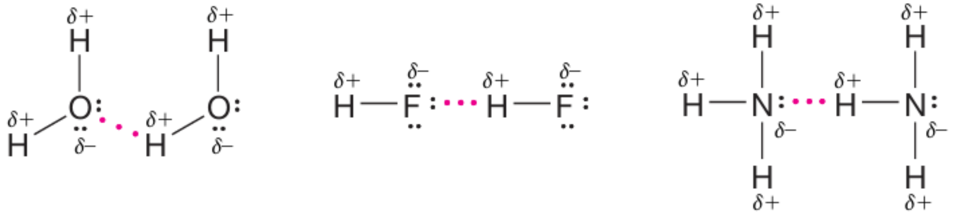
2. Factors affecting the physical properties

2.3 *Intermolecular forces*

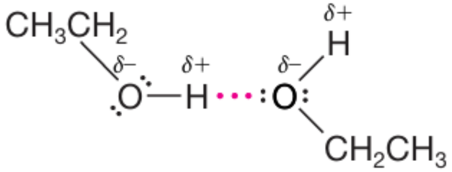
B) Hydrogen Bonds

- **Hydrogen bond is very strong dipole–dipole attractions occur between hydrogen atoms bonded to small, strongly electronegative atoms (O, N, or F) and nonbonding electron pairs on other electronegative atoms.**
- ***Example;* Ethanol (CH_3CH_2OH) has a boiling point of +78.5 °C; its isomer methyl ether (CH_3OCH_3) has a boiling point of -24.9 °C.**

Ethanol molecules are held together by hydrogen bonds whereas methyl ether molecules are held together only by weaker dipole-dipole interactions.



The red dots represent a hydrogen bond.



In Ethanol, a hydrogen atom covalently bonded to an oxygen atom, can form strong hydrogen bonds to each other.

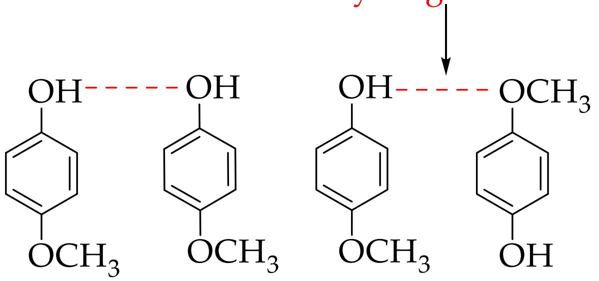
2. Factors affecting the physical properties

2.3 *Intermolecular forces*

B) Hydrogen Bonds

- **Hydrogen bonds consist of two types:**
  - **1) Intermolecular hydrogen bonds:**
    - **Occur between separate molecules in a substance.**
    - *Example;* **an intermolecular hydrogen bond in *p*-methoxyphenol.**
  - **2) Intramolecular hydrogen bonds:**
    - **Occur within one single molecule.**
    - *Example;* ***o*-methoxyphenol, both a hydrogen donor and a hydrogen acceptor must be present within one molecule**
- **Generally, Intramolecular hydrogen bonding reduces intermolecular interactions, which generally lowers melting point, boiling point, and solubility compared to compounds capable of intermolecular hydrogen bonding.**

Intermolecular hydrogen bond

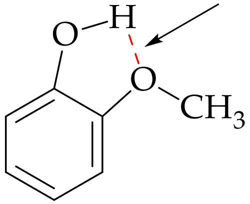


***p*-Methoxyphenol**

The hydrogen bonds occur between molecules

b.p = 243°C

Intramolecular hydrogen bond



***o*-Methoxyphenol**

The hydrogen bonds occur within molecule

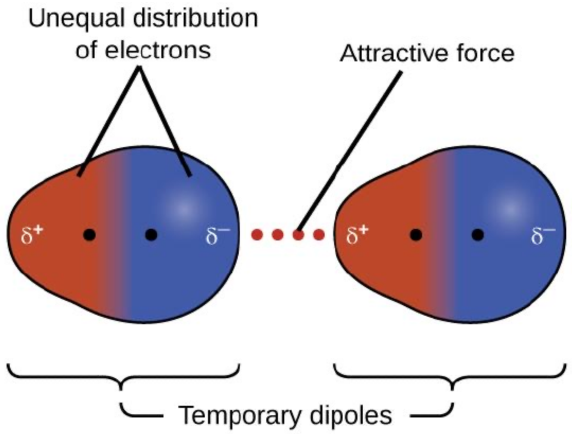
b.p = 205 °C

2. Factors affecting the physical properties

2.3 *Intermolecular forces*

C) London Dispersion Forces

- London or Dispersion Forces **result when a temporary dipole in a molecule caused by a momentary shifting of electrons induces an opposite and also temporary dipole in an adjacent molecule.**
- **These temporary opposite dipoles cause a weak attraction between the two molecules.**
- **Molecules which rely only on dispersion forces generally have low melting points and boiling points.**
- **Increasing the molecule size, increases dispersion forces, consequently, increasing the boiling point.** Methane **(**CH_4**) has a boiling point of** -162 °C **whereas** ethane **(**CH_3CH_3**) has a boiling point of** -88.2 °C**.**



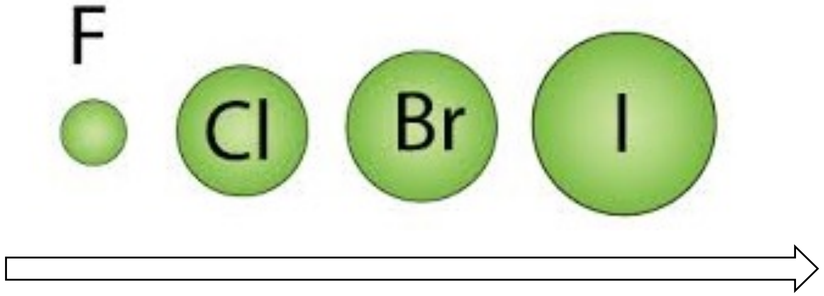
2. Factors affecting the physical properties

2.3 Intermolecular forces

C) London Dispersion Forces

Two important factors determine the magnitude of dispersion forces:

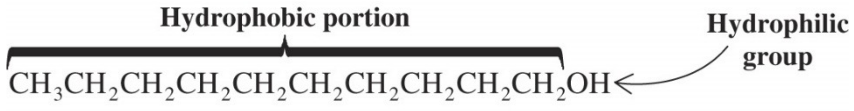
- **The relative surface area of the molecules;**
  - **Branching decrease such forces and therefore, decreasing boiling point.**
  - ***Example;* Pentane ($CH_3CH_2CH_2CH_2CH_3$) has a boiling point of 36.1 °C and Neopentane ($C(CH_3)_4$) has a boiling point of 9.5 °C.**
- **The relative polarizability of electrons of the atoms;**
  - **The electrons of large atoms such as iodine are loosely held and are easily polarized.**
  - **The electrons of small atoms such as fluorine are more tightly held and are much less polarizable.**
  - ***Example;* HI has a boiling point of -35 °C whereas HBr has a boiling point of -67 °C.**



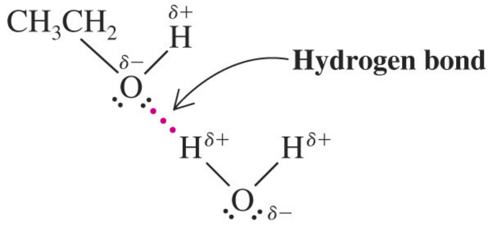
Polarizability increases with increasing size

3. Solubility

- Solubility of a substance could be explained by the intermolecular forces.
- A general rule for solubility is that "like dissolves like" in terms of comparable polarities.
- For compounds containing one hydrophilic group and thus capable of forming strong hydrogen bonds, the following approximate guidelines hold:
    - Compounds with one to three carbon atoms are water soluble.
    - Compounds with four or five carbon atoms are borderline.
    - Compounds with six carbon atoms or more are insoluble.
- In general, increasing the hydrophilic groups in a molecule will increase its solubility in polar solvent, in contrast, increasing the hydrophobic groups will decrease the solubility.



Decyl alcohol



4. Physical Properties of some Functional Groups

4.1 Physical properties of hydrocarbons

- **Hydrocarbons are nonpolar compounds and thus, the dispersion forces controlling their physical properties.**
- **Physical state;**

  C1 – C4 Hydrocarbons are gases, C5 - C17 hydrocarbons are liquids, and hydrocarbons with C18 or higher are wax-like solids.

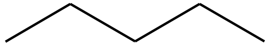
- **Boiling points and Melting points:**

  Boiling points of unbranched alkanes increase smoothly with number of carbons (molecular weight).

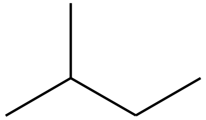
  However, increasing the degree of branching in an alkane decreases its boiling point.

- **Solubility:**

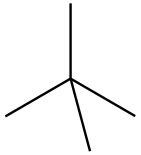
  Hydrocarbons as nonpolar compounds are soluble in nonpolar solvents such as carbon tetrachloride and benzene, but insoluble in polar solvents like water.



Pentane
b.p 36 °C
m.p -130 °C



Isopentane
b.p 28 °C
m.p -160 °C



Neopentane
b.p 10 °C
m.p -17 °C

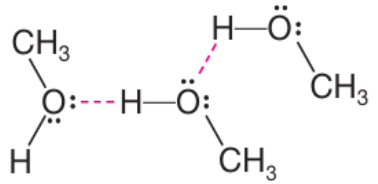
4. Physical Properties of some Functional Groups

4.2 Physical properties of alcohols and ethers

- Boiling points;
  - Ethers boiling points are roughly comparable to hydrocarbons of the same molecular weight.
  - Molecules of ethers cannot form hydrogen bond to each other.
  - Alcohols have considerably higher boiling point than ethers and hydrocarbons due to their ability to hydrogen bond to each other.
- Solubility;
  - Both alcohols and ethers can make hydrogen bond to water and have similar solubilities of about 8 g /100 mL in water.
  - Solubilities of alcohols in water are gradually decreases as the hydrocarbon portion increases.

Table 2.2 Physical properties of some alcohols and ethers

Name	Formula	m.p. (°C)	b.p. (°C)	Water solubility g/100 mL H_2O
Alcohols				
Methanol	CH_3OH	−97	64.7	∞
Ethanol	CH_3CH_2OH	−117	78.3	∞
Propyl alcohol	$CH_3CH_2CH_2OH$	−126	97.2	∞
Isopropyl alcohol	$CH_3CH(OH)CH_3$	−88	82.3	∞
Butyl alcohol	$CH_3CH_2CH_2CH_2OH$	−90	117.7	8.3
Isobutyl alcohol	$CH_3CH(CH_3)CH_2OH$	−108	108.0	10.0
tert-Butyl alcohol	$(CH_3)_3COH$	25	82.5	∞
Ethers				
Dimethyl ether	CH_3OCH_3	−138	−24.9	∞
Ethyl methyl ether	$CH_3OCH_2CH_3$	−115.2	10.8	∞
Diethyl ether	$CH_3CH_2OCH_2CH_3$	−116	34.6	7.5



Hydrogen bonding between molecules of methanol

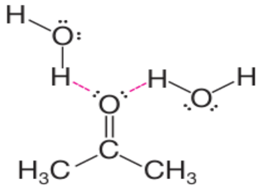
4. Physical Properties of some Functional Groups

4.3 Physical properties of aldehydes and ketones

- Boiling points;
  - The type of intermolecular forces in these compounds is dipole-dipole forces and cannot form hydrogen bond to each other.
  - They have lower boiling points than the corresponding alcohols.
- Solubility;
  - Aldehydes and ketones can form hydrogen bonds with water and therefore low molecular weight aldehydes and ketones have appreciable water solubility.

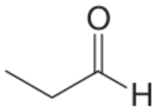
Table 2.3 Physical properties of aldehydes and ketones

Name	Formula	m.p. (°C)	b.p. (°C)	Water solubility
Aldehydes				
Formaldehyde	$HCHO$	−91	-21	Very soluble
Acetaldehyde	CH_3CHO	−125	21	∞
Propanal	CH_3CH_2CHO	−81	49	Very soluble
Butanal	$CH_3(CH_2)_2CHO$	−99	76	Soluble
Pentanal	$CH_3(CH_2)_3CHO$	−92	102	Slightly soluble
Benzaldehyde	C_6H_5CHO	−26	178	Slightly soluble
Ketones				
Acetone	CH_3COCH_3	−95	56.1	∞
Butanone	$CH_3COCH_2CH_3$	−86	80	Very soluble
2-Pentanone	$CH_3COCH_2CH_2CH_3$	−78	102	Soluble
Acetophenone	$C_6H_5COCH_3$	21	202	Insoluble

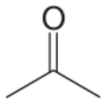


Hydrogen bonding (shown in red) between water molecules and acetone.

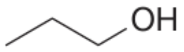
Butane
bp −0.5 °C
(MW = 58)



Propanal
bp 49 °C
(MW = 58)



Acetone
bp 56.1 °C
(MW = 58)



1-Propanol
bp 97.2 °C
(MW = 60)

4. Physical Properties of some Functional Groups

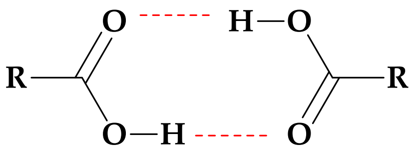
4.4 Physical properties of carboxylic acids and their derivatives: Carboxylic acids

Carboxylic acids

- Carboxylic acids are polar substances.
- Their molecules can form strong hydrogen bonds with each others and with water.
- Boiling points;
  - Generally, carboxylic acids have high boiling points than alcohols with comparable molecular weight due to the formation of a dimer of two molecules carboxylic acids by hydrogen bond.
- Solubility;
  - Carboxylic acids with up to 4 carbons are miscible with water.
  - As the length of the carbon chain increases, water solubility decreases.

Table 2.4 Physical properties of carboxylic acids

Name	Formula	m.p. (°C)	b.p. (°C)	Water solubility
Formic acid	HCOOH	8	100.5	∞
Acetic acid	CH_3CHO	16.6	118	∞
Propanoic acid	CH_3CH_2CHO	-21	141	∞
Butanoic acid	$CH_3(CH_2)_2CHO$	-6	164	∞
Pentanoic acid	$CH_3(CH_2)_3CHO$	-34	187	4.97
Benzoic acid	C_6H_5CHO	122	249	0.4



Dimer structure of two carboxylic acids

4. Physical Properties of some Functional Groups

4.5 Physical properties of carboxylic acids and their; Derivatives: Esters

Esters

- Esters are polar compounds, but, lacking a hydrogen attached to oxygen, their molecules cannot form strong hydrogen bonds to each other.
- Boiling points;
  - Esters have boiling points that are lower than those of acids and alcohols of comparable molecular weights.
  - The boiling points of esters are about the same as those of comparable aldehydes and ketones.
- Solubility;
  - Esters can make hydrogen bond to water and have appreciable water solubility.

Table 2.5 Physical properties of esters

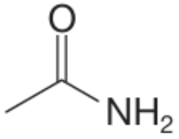
Name	Formula	m.p. (°C)	b.p. (°C)	Water solubility
Methyl format	$HCOOCH_3$	-99	31.5	Very soluble
Ethyl format	$HCOOCH_2CH_3$	-79	54	Soluble
Methyl acetate	CH_3COOCH_3	-99	57	24.4
Ethyl acetate	$CH_3COOCH_2CH_3$	-82	77	7.39
Propyl acetate	$CH_3COOCH_2CH_2CH_3$	-93	102	1.89

4. Physical Properties of some Functional Groups

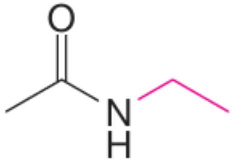
4.6 Physical properties of carboxylic acids and their Derivatives: Amides

Amides

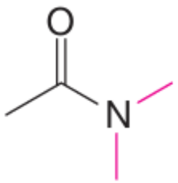
- Boiling points;
  - Amides with one or two hydrogens on nitrogen form strong hydrogen bonds and have high melting and boiling points.
  - On the other hand, *N,N*-disubstituted amides cannot form hydrogen bonds to each other and, therefor, have lower melting and boiling points.
  - Hydrogen bonding between amides in proteins and peptides is an important factor in determining their 3-dimentional shape.



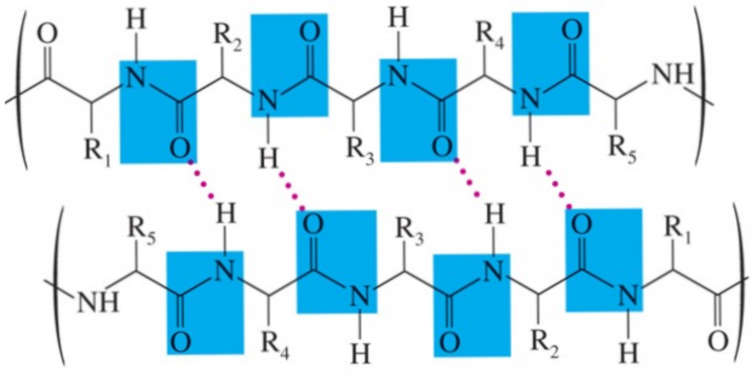
Ethanamide
bp 221 °C; mp 82 °C



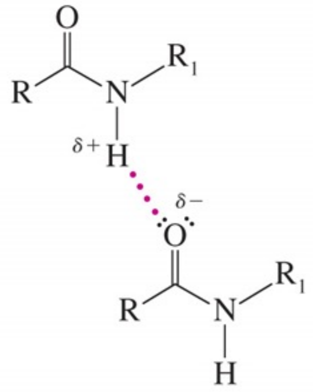
***N*-Ethylethanamide**
bp 205 °C



***N,N*-Dimethylethanamide**
bp 166 °C; mp -20 °C



Hydrogen bonding between amide groups of peptide chains



Hydrogen bonding between amide molecules

4. Physical Properties of some Functional Groups

4.7 Physical Properties of Amines

- Amines are moderately polar substances.
- Primary and secondary amines can form hydrogen bonds to each other and water.
- Tertiary amines cannot form hydrogen bonds to each other, but can form hydrogen bond to molecules of water.
- Boiling points;
  - They have boiling points that are higher than those of alkanes, but generally lower than those of alcohols of comparable molecular weight.
  - Tertiary amines have lower boiling points than primary or secondary amines of comparable molecular weights.
- Solubility;
  - Low molecular weight amines tend to be water soluble whether they are primary, secondary or tertiary.

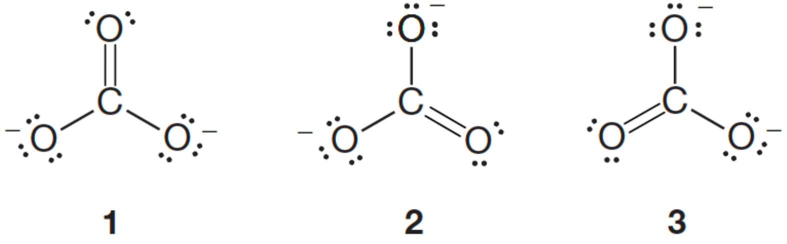
Table 2.6 Physical properties of amines

Name	Formula	m.p. (°C)	b.p. (°C)	Water solubility
Primary amines				
Methylamine	CH_3NH_2	-94	-6	Very soluble
Ethylamine	$CH_3CH_2NH_2$	-81	17	Very soluble
Butylamine	$CH_3(CH_2)_2CH_2NH_2$	-51	78	Very soluble
Isobutylamine	$(CH_3)_2CHCH_2NH_2$	-86	68	Very soluble
tert-Butylamine	$(CH_3)_3CNH_2$	-68	45	Very soluble
Aniline	$C_6H_5NH_2$	-6	184	3.7
Secondary amines				
Dimethylamine	$(CH_3)_2NH$	-92	7	Very soluble
Diethylamine	$(CH_3CH_2)_2NH$	-48	56	Very soluble
N-Methylaniline	$C_6H_5NHCH_3$	-57	196	Slightly soluble
Tertiary amines				
Trimethylamine	$(CH_3)_3N$	-117	2.9	Very soluble
Triethylamine	$(CH_3CH_2)_3N$	-115	90	14
Tripropylamine	$(CH_3CH_2CH_2)_3N$	-93	156	Slightly soluble

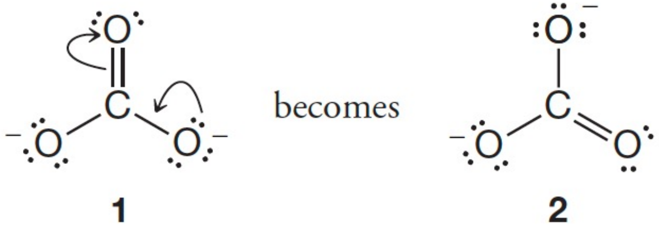
5. Resonance and Delocalization

5.1 Resonance Theory

- Resonance is defined as a way of describing bonding in certain molecules or ions by the combination of several contributing structures or forms (commonly call resonance structures).
- It is especially useful for analyzing delocalized electrons in cases where bonding cannot be represented by a single Lewis structure.
- Resonance structures differ only in the arrangement of electrons (not atom positions).
- Carbonate ion (CO_3^{-2}) can be drawn in three different, but equivalent structures:
- The resonance structures of carbonate ion can be presented be delocalizing the electron pair of its atoms using the curved arrows, which emphasizes to move the electron pairs NOT the re-position its atoms.



The curved arrows in structure 1, we change structure 1 into structure 2:

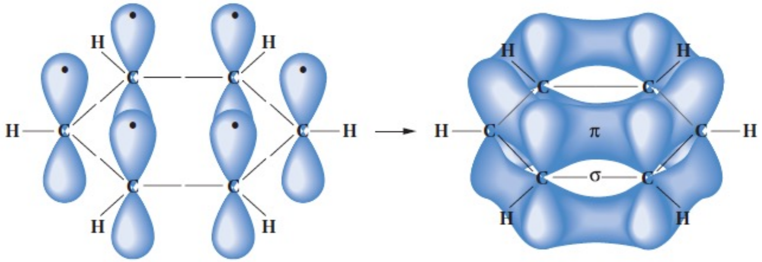


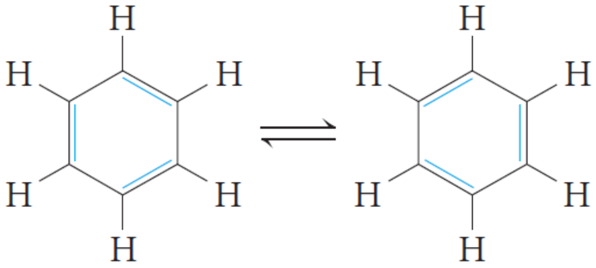
In a similar way we can change structure 2 into structure 3:

5. Resonance and Delocalization

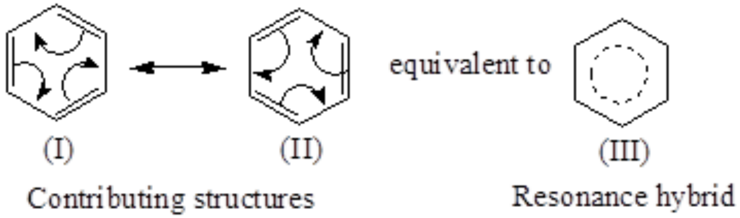
5.2 The Resonance Explanation for the Structure of Benzene

- **Benzene** is an aromatic molecule that has the molecular formula of (C_6H_6) which a ratio of (1:1) between carbon and hydrogen atoms indicating a highly unsaturated structure.
- **Kekulé** proposed that Benzene has **six-carbon atoms** that are located in the center of a regular **hexagon one hydrogen** atom attached to each carbon atom.
- His suggestion shows an **alternation between single and double bonds** through the ring via a conjugated system of double bonds.





The Kekulé structures for Benzene



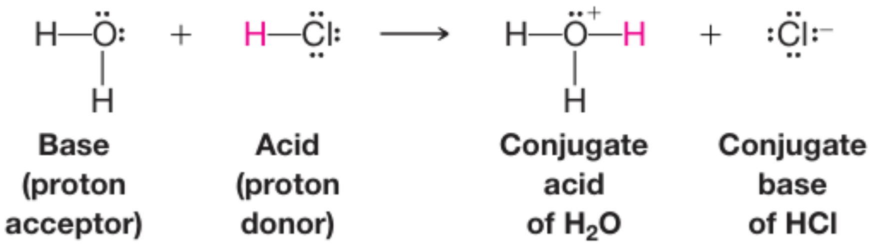
Resonance Model for Benzene

6. Acids and Bases

6.1 Bronsted–Lowry Acids and Base

Brønsted–Lowry acid–base reactions involve the transfer of protons.

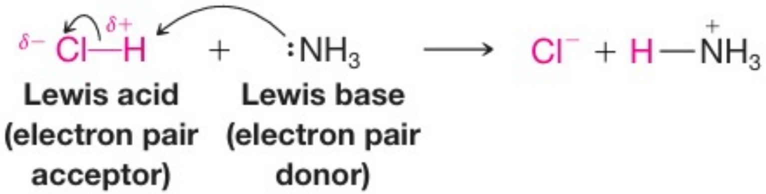
- Brønsted–Lowry acid is a substance that can donate (or lose) a proton.
- Brønsted–Lowry base is a substance that can accept (or remove) a proton.

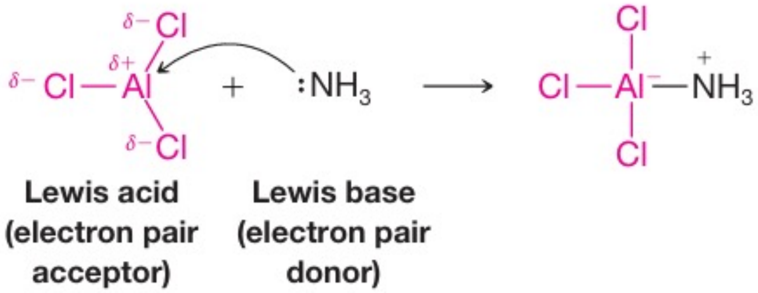


6.2 Lewis Acids and Bases

In Lewis acid–base theory, proton donors are not the only acids.

- Lewis's acid is electron pair acceptors (i.e., any electron-deficient atom and that have atoms with vacant orbital).
- Lewis's base is electron pair donors (i.e. Any electron-rich atom).





6. Acids and Bases

6.3 Heterolysis of Bonds to Carbon: Carbocations and Carbanions

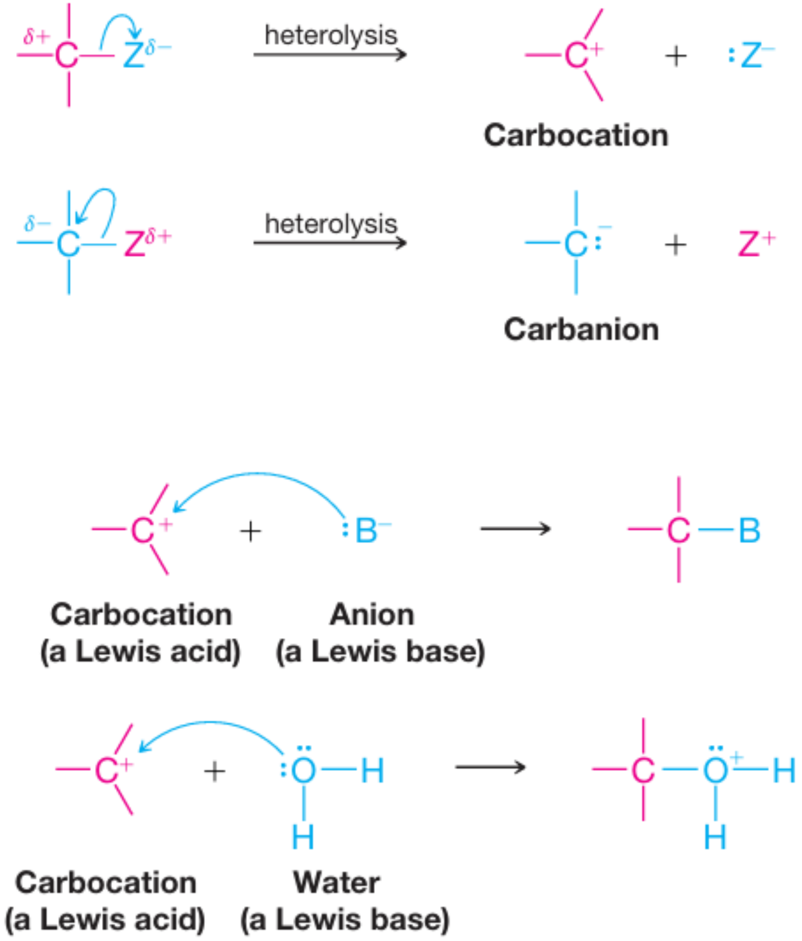
Heterolysis of a bond to a carbon atom can lead to either of two ions:

- A carbocation; an ion with a positive charge on the carbon atom.

  Example; Carbocations are electron deficient, and therefore carbocations are Lewis's acids.

- A carbanion; an ion with a negatively charged on the carbon atom.

  Example; Carbanions are electron rich (have an unshared electron pair) and therefore, carbanions are Lewis bases.



6. Acids and Bases

6.4 Electrophiles and Nucleophiles

- **Electrophiles** are reagents that seek electrons.

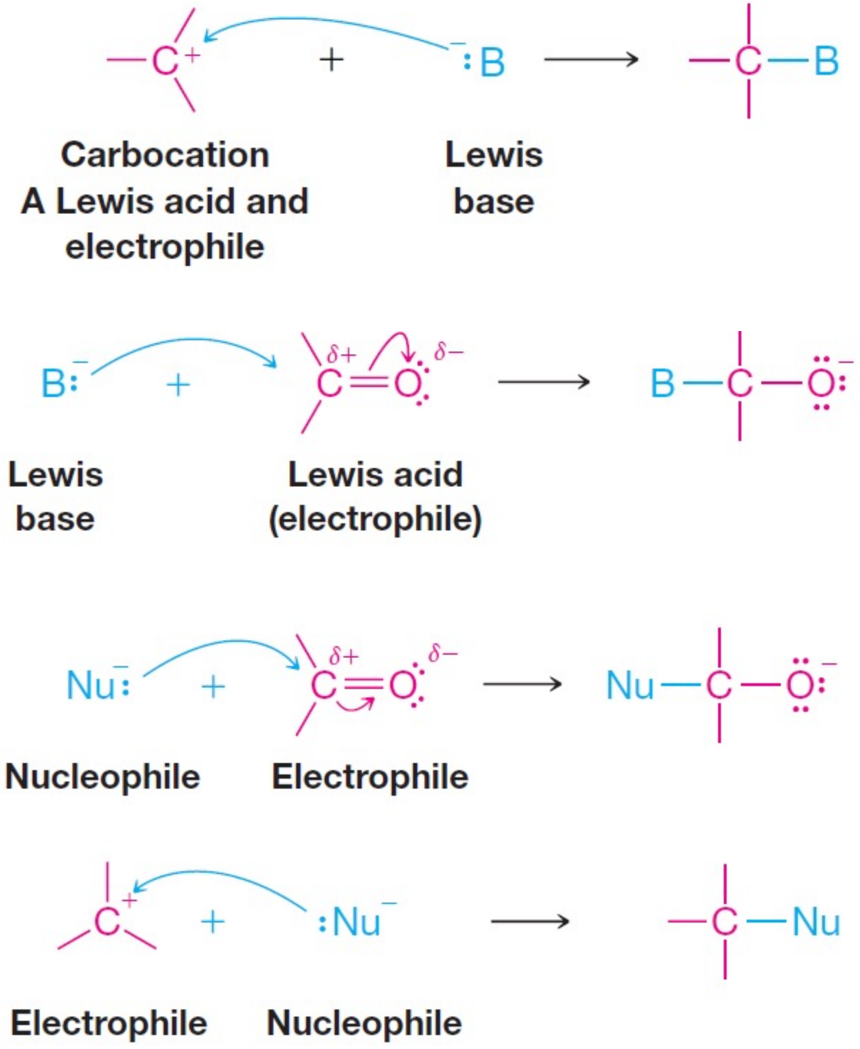
  Examples;

  - Lewis acids (electron pair acceptors).
  - Carbocations.
  - Carbon atoms that are electron poor because of bond polarity (i.e. Carbonyl carbon).

- **Nucleophile** is a Lewis base that seeks a positive center such as a positively charged carbon atom.

  Examples;

  - Lewis bases (electron pair donors).
  - Carbanions.



6. Acids and Bases

6.5 The Strength of Brønsted–Lowry Acids and Bases: K_a and pK_a

A) The Acidity Constant, K_a

- For any weak acid dissolved in water. Using a generalized hypothetical acid (HA), the expression for the acidity constant is:
- Generally;
  - A large value of K_a means the acid is a strong acid.
  - A small value of K_a means the acid is a weak acid.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

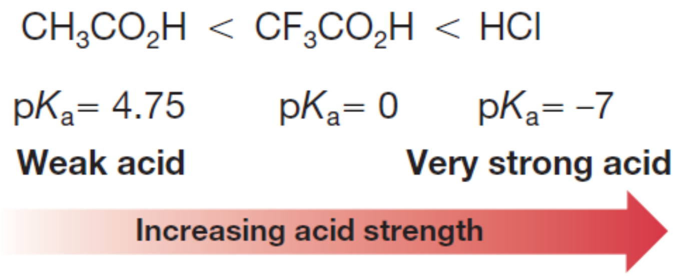
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

B) Acidity and pK_a

- The acidity constant, K_a, expressed as its negative logarithm, pK_a:

$$pK_a = -\log K_a$$

- The larger the value of the pK_a, the weaker is the acid.
- The stronger the acid, the weaker will be its conjugate base.
- The larger the pK_a of the conjugate acid, the stronger is the base

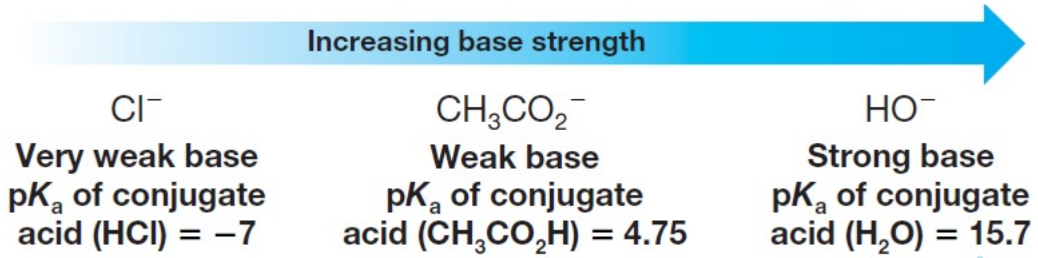


$CH_3CO_2H < CF_3CO_2H < HCl$

$pK_a = 4.75$ $pK_a = 0$ $pK_a = -7$

Weak acid **Very strong acid**

Increasing acid strength



Increasing base strength

Cl^-
Very weak base
pK_a of conjugate acid (HCl) = −7

$CH_3CO_2^-$
Weak base
pK_a of conjugate acid (CH_3CO_2H) = 4.75

HO^-
Strong base
pK_a of conjugate acid (H_2O) = 15.7

6. Acids and Bases

6.6 Relationships Between Structure and Acidity

A) Periodic Table Trend

- **Bond Strength To The Proton**

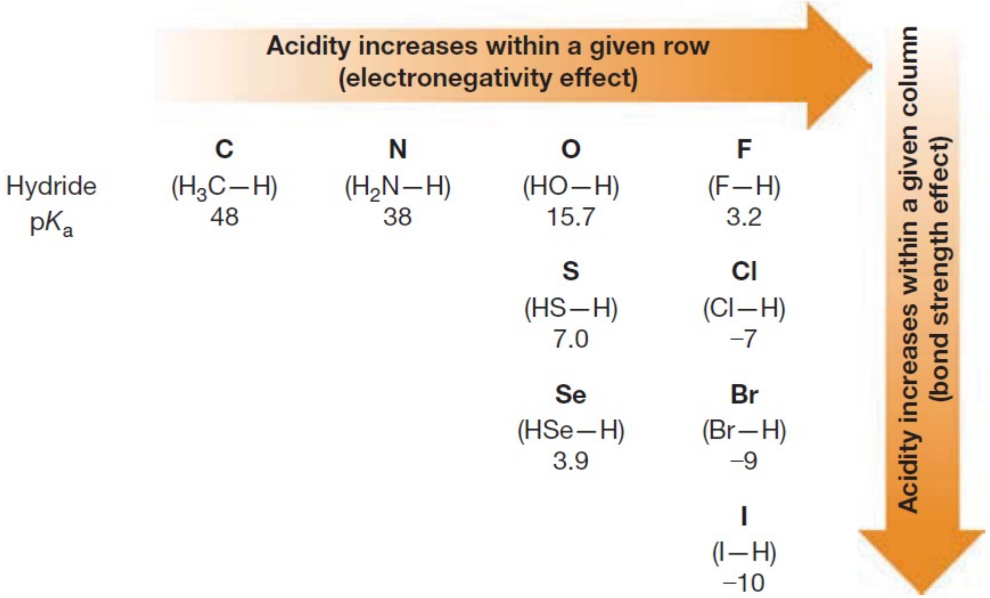
  Acidity increases from top to bottom in a given column with decreasing bond strength.

- **Electronegativity of The Atom Bonded To The Hydrogen**

  Acidity increases from left to right across a given row with increasing electronegativity.

B) The Effect of Hybridization

- **A *sp* carbon atom is effectively more electronegative than a *sp*^{2} carbon, which in turn is more electronegative than a *sp*^{3} carbon. Alkyne hydrogen is weakly acid and Alkene and alkane hydrogens are essentially not acidic.**



Hydride pK_a	C	N	O	F
	(H_3C-H) 48	(H_2N-H) 38	($HO-H$) 15.7	($F-H$) 3.2
			S ($HS-H$) 7.0	Cl ($Cl-H$) −7
			Se ($HSe-H$) 3.9	Br ($Br-H$) −9
				I ($I-H$) −10

Relative Acidity of the Hydrocarbons

$$HC{\equiv}CH > H_2C{=}CH_2 > H_3C{-}CH_3$$

6. Acids and Bases

6.6 Relationships Between Structure and Acidity

C) Inductive Effects

- Inductive effects are electronic effects transmitted through bonds. The inductive effect of a group can be electron donating or electron withdrawing.
- The electron donating decreases acidity.
- The electron withdrawing increases acidity.

Electron-withdrawing substituents (-I)

$-CHO, -COCH_3, -COOH, -NO_2, -NH_2, -OH, -OCH_3$

Electron-donating substituents (+I)

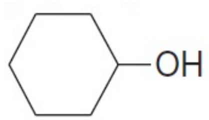
$-CH_3, -C_2H_5$

6. Acids and Bases

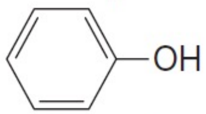
6.7 Carboxylic Acids, Phenols and Alcohols as Acids

- Carboxylic acids are weak acids, having pK_a values in the range of 3–5.
- Phenol is weak acid, having pK_a values of 9.89.
- Alcohols, have pK_a values in the range of 15–18, and essentially do not give up a proton unless exposed to a very strong base.
- Phenol is a weak acid compared with a carboxylic acid such as acetic acid, and is a much stronger acid than alcohols such as cyclohexanol.

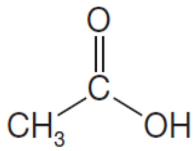
Carboxylic acid > Phenol > Alcohol



Cyclohexanol
pK_a = 18



Phenol
pK_a = 9.89



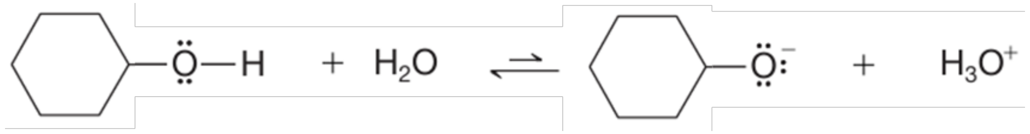
Acetic acid
pK_a = 4.75

6. Acids and Bases

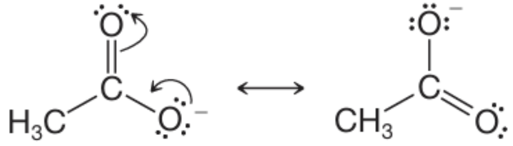
6.7 Carboxylic Acids, Phenols and Alcohols as Acids

- Acidity increases when
  - The conjugate base is stabilized by resonance.
  - and electron-withdrawing inductive effects.
- Delocalization of the negative charge is possible in a carboxylate anion, but it is not possible in an alkoxide ion.
- The inductive electron-withdrawing effect of the carbonyl group in carboxylic acids contributes to the acidity of functional group.
- Phenol is more acidic than cyclohexanol because its conjugate base, the phenoxide ion, is stabilized by resonance, this resonance stabilizes the conjugate base more than it stabilizes phenol itself, increasing acidity.

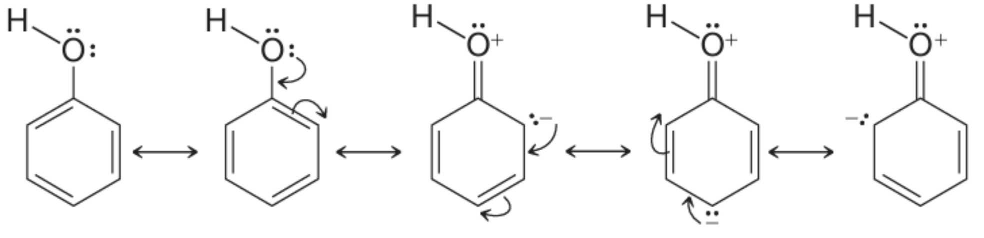
No resonance stabilization in cyclohexoxide anion



Resonance stabilization in acetate ion



Resonance stabilization in phenol

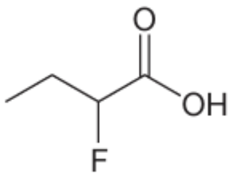


1a 1b 2 3 4

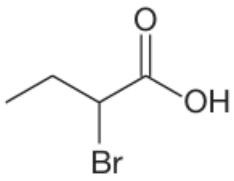
6. Acids and Bases

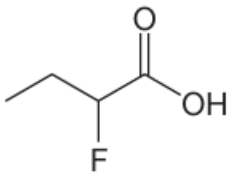
6.7 Carboxylic Acids, Phenols and Alcohols as Acids

- **Fluorine** is much more electronegative than **bromine**; therefore it will be able to disperse the negative charge of the anion formed when the proton is lost.
- The fluorine is closer to the carboxyl group where it will be better able to disperse the negative charge in the anion formed when the proton is lost.
- An electron-withdrawing group increases the acidity of a phenol.

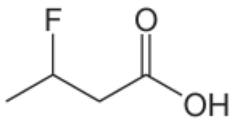


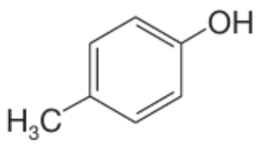
Stronger acid

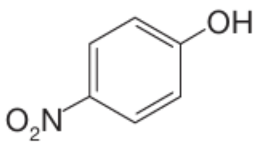




Stronger acid







Stronger acid

6. Acids and Bases

6.8 Organic Compounds as Bases

- An organic compound is a potential base if it contains:

A) π bond

  - Alkenes react with a strong acid by accepting a proton.

B) an atom with an unshared electron pair.

  - **Alcohols, ethers, amines** and compounds containing a carbonyl group act as bases in the presence of a strong acid such as HCl and H_2SO_4.
  - **Amines:** Aromatic amines less basic than aliphatic amines.
  - **Electron-donating groups** increase the basicity of amines, and electron-withdrawing groups decrease their basicity.