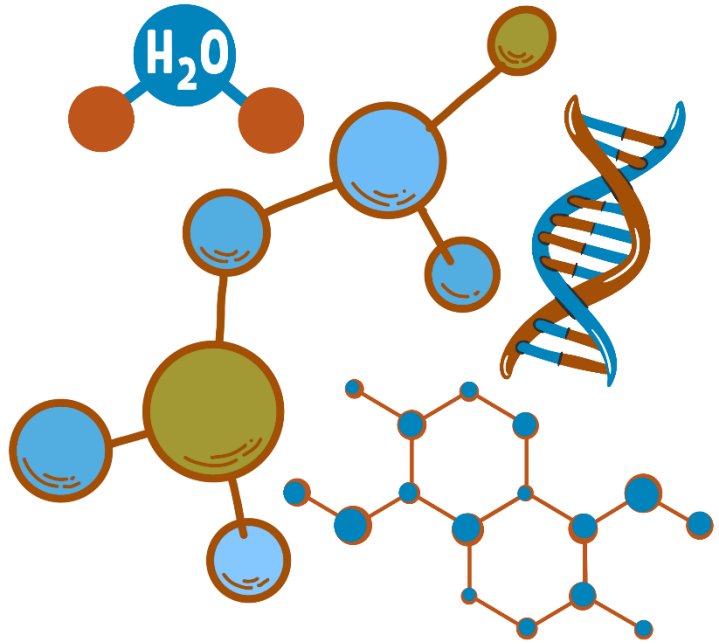
Introduction to Organic Chemistry
CHEM 108

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Chapter 4: Physical Properties and Intermolecular Forces



Chapter 4: Physical Properties and Intermolecular Forces

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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. Types of Intermolecular Forces

2.1. Intermolecular forces (van der Waals forces)

- **Van der Waals forces are a type of intermolecular force that includes weak attractions between molecules.**
- **Van der Waals force occur between all atoms and molecules, including nonpolar ones.**
- **The forces that act between molecules are not as strong as those between ions.**
- **The relative surface area of the molecules;**
  - **Branching decrease such forces and therefore, decreasing boiling point.**
  - ***Example;***

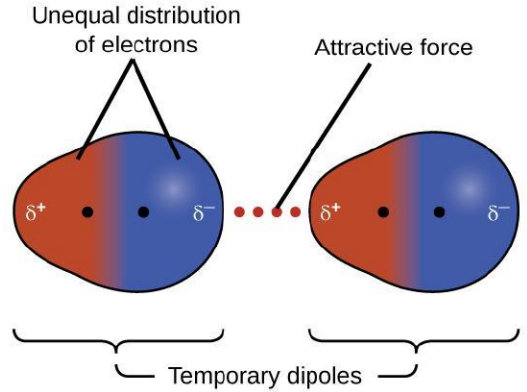
    Pentane ($CH_3CH_2CH_2CH_2CH_3$) has a boiling point of 36.1 °C and Neopentane ($C(CH_3)_4$) has a boiling point of 9.5 °C.

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2. Types of Intermolecular Forces

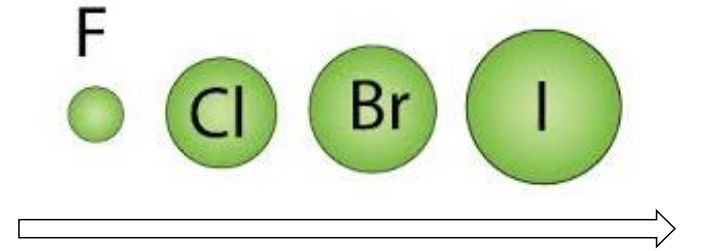
2.2. London Dispersion Forces

- 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 causing a weak attraction between the two molecules.
- Molecules which rely only on dispersion forces generally have low melting points and boiling points.



- The relative polarizability of electrons of the atoms;
  - The electrons of large atoms such as iodine are loosely held and are easily polarized, whereases 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 HF has a boiling point of 19.5 °C.



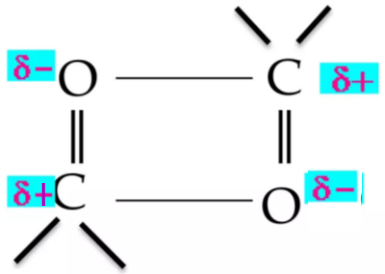
Polarizability increases with increasing size

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2. Types of Intermolecular Forces

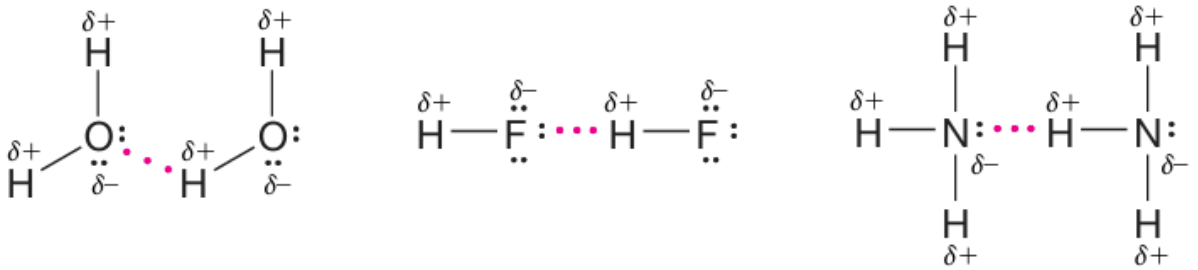
2.3. Dipole-dipole Forces

- Dipole-dipole forces refers to the electrostatic forces between two permanent polar molecules.
- There is an interaction between δ+ and δ- areas in each molecule; these are much weaker than ion-ion forces.



2.4. Hydrogen Bonds

- Hydrogen bond is very strong dipole–dipole attractions occur between hydrogen atoms bonded to small, strongly electronegative atoms (N, O, or F) and nonbonding electron pairs on other electronegative atoms.



The red dots represent a hydrogen bond.

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2. Types of Intermolecular Forces

2.4. Hydrogen Bonds

- **Hydrogen bonds consist of two types:**

  1) Intermolecular hydrogen bonds:

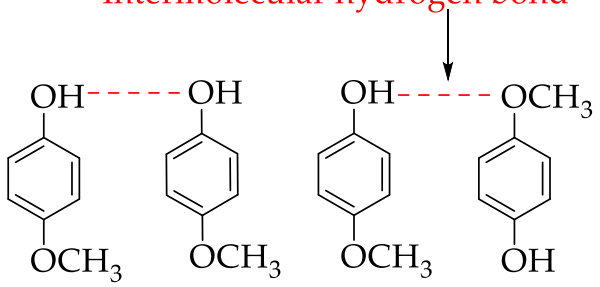
  Occur between separate molecules in a substance.

  2) Intramolecular hydrogen bonds:

  Occur within one single molecule.

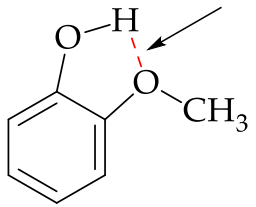
- **Generally, Intramolecular hydrogen bonding reduces intermolecular interactions, which generally lowers melting point, boiling point, and solubility compared to compounds capable of intermolecular hydrogen bonding.**

Intermolecular hydrogen bond



***p*-Methoxyphenol**
m.p = 243 °C

Intramolecular hydrogen bond



***o*-Methoxyphenol**
m.p = 204-206 °C

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3. Physical Properties of Some Functional Groups

3.1. Physical Properties of Hydrocarbons

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

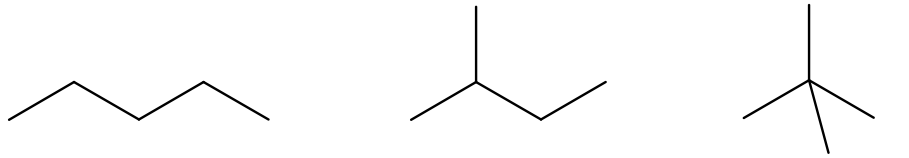
  C1–C4 Hydrocarbons are gases, C5-C17 hydrocarbons are liquids, and hydrocarbons with C18 or higher are wax-like solids.

- **Boiling points and Melting points:**

  Effect of Molecular weight; **Increasing the molecular weight will increase, the boiling point and melting point increase.**

  - ***Example;*** **Methane (CH_4) has a boiling point of -162 °C whereas ethane (CH_3CH_3) has a boiling point of -88.2 °C.**

  Effect of Branching; **Increasing the degree of branching in an alkane decreases its boiling point.**



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

- **Solubility:**

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

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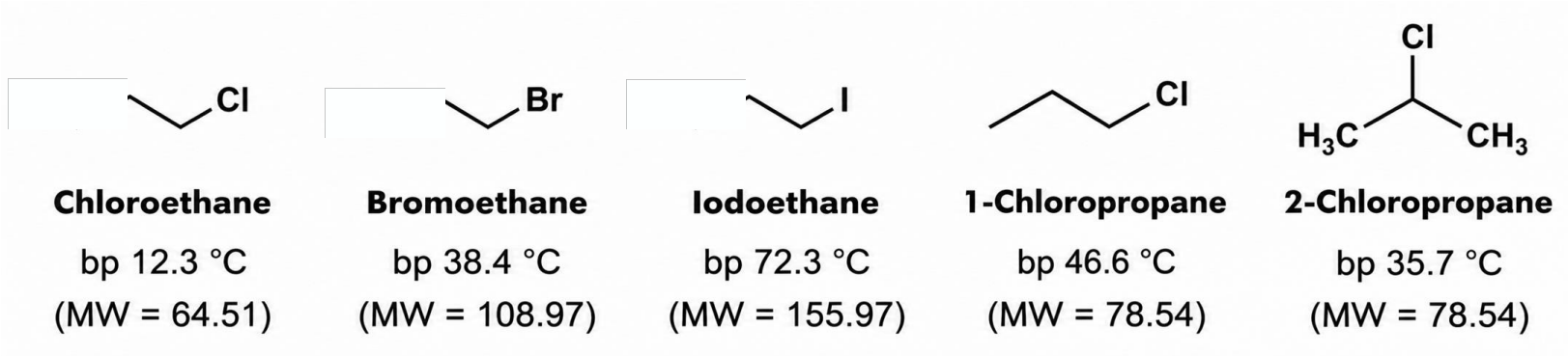
3. Physical Properties of Some Functional Groups

3.2. Physical Properties of Alkyl Halides (Haloalkanes)

- **Boiling points;**
  - **Boiling points generally increase with molecular mass and halogen size:**

$$R–F < R–Cl < R–Br < R–I$$

  - **Branching decreases boiling points.**



Chloroethane	Bromoethane	Iodoethane	1-Chloropropane	2-Chloropropane
bp 12.3 °C	bp 38.4 °C	bp 72.3 °C	bp 46.6 °C	bp 35.7 °C
(MW = 64.51)	(MW = 108.97)	(MW = 155.97)	(MW = 78.54)	(MW = 78.54)

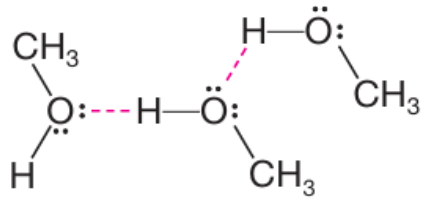
- **Solubility;**
  - **Alkyl halides are poorly soluble in water but soluble in organic solvents.**
  - **Water solubility generally decreases as the hydrocarbon portion increases**

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3. Physical Properties of Some Functional Groups

3.3. Physical Properties of Alcohols, Thiols, Ethers and Epoxides

- **Boiling points;**
  - **Thiols** form very weak hydrogen bonds; therefore, they have lower boiling points than the corresponding alcohols.
  - **Alcohols** have considerably higher boiling points than **thiols**, **ethers**, and **hydrocarbons** due to their ability to hydrogen bond to each other.
  - **Thiols** form very weak hydrogen bonds; therefore, they have lower boiling points than the corresponding alcohols.
  - **Ethers** and **epoxides** cannot form hydrogen bonds with each other but can form hydrogen bonds with water. Their boiling points are roughly comparable to hydrocarbons of similar molecular weight.



Hydrogen bonding between molecules of methanol

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	∞
Thiols				
Methanethiol	CH_3SH	−123	6.0	2.3
Ethanethiol	CH_3CH_2SH	−147.1	35.9	0.68
Propyl mercaptan	$CH_3CH_2CH_2SH$	−113.2	67.8	0.19
Isopropyl mercaptan	$CH_3CH(SH)CH_3$	−130.5	54.9	0.48
Isobutyl mercaptan	$(CH_3)_2CHCH_2SH$	−144.9	87.9	-
tert-butyl mercaptan	$(CH_3)_3CSH$	1.0	64.3	-
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

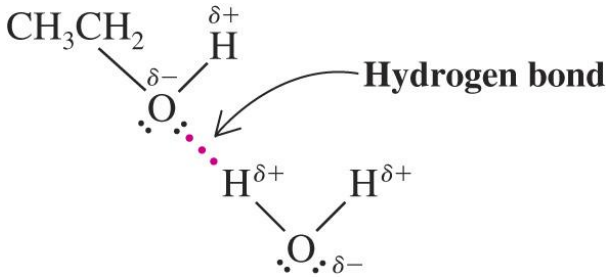
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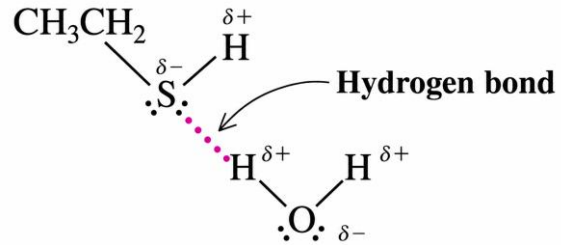
3. Physical Properties of Some Functional Groups

3.3. Physical Properties of Alcohols, Thiols, Ethers and Epoxides

- **Solubility;**

  - Both alcohols and ethers can make hydrogen bond to water and have similar solubilities of about 8 g /100 mL in water.
  - Thiols are less soluble in water than corresponding alcohols because the –SH group forms weaker hydrogen bonds with water.
  - The water solubility of alcohols and thiols gradually decreases as the hydrocarbon portion increases.







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3. Physical Properties of some Functional Groups

3.4. Physical Properties of Aldehydes and Ketones

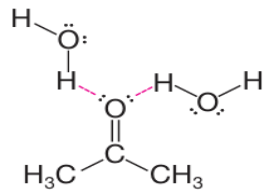
- **Boiling points;**
  - The type of intermolecular forces in these compounds is dipole-dipole forces and cannot form hydrogen bond to each other.
  - They have lower boiling points than the corresponding alcohols.

Table 2.3 Physical properties of aldehydes and ketones

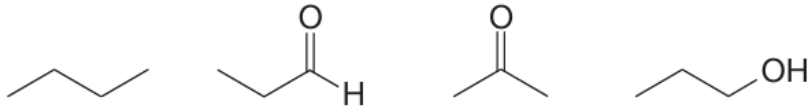
Name	Formula	m.p. (°C)	b.p. (°C)	Water solubility
Aldehydes				
Formaldehyde	HCHO	–91	-21	Very soluble
Acetaldehyde	CH_3CHO	–125	21	∞
Propanal	CH_3CH_2CHO	–81	49	Very soluble
Butanal	$CH_3(CH_2)_2CHO$	–99	76	Soluble
Pentanal	$CH_3(CH_2)_3CHO$	–92	102	Slightly soluble
Benzaldehyde	C_6H_5CHO	–26	178	Slightly 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

- **Solubility;**

Aldehydes and ketones can form hydrogen bonds with water and therefore low molecular weight aldehydes and ketones have appreciable water solubility.



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



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3. Physical Properties of some Functional Groups

3.5. Physical Properties of Carboxylic Acids and Their Derivatives

Carboxylic acids

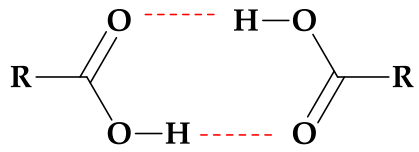
- Carboxylic acids are polar substances.
- Their molecules can form strong hydrogen bonds with each others and with water.

- **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.

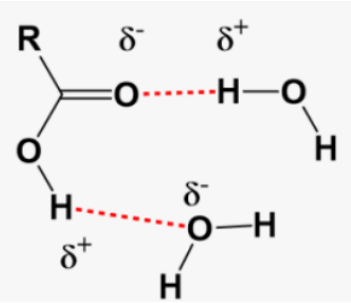
- **Solubility;**
  - Carboxylic acids with up to 4 carbons are miscible with water.
  - As the length of the carbon chain increases, water solubility decreases.
  - Aromatic carboxylic acids are insoluble in water due to their hydrophobic nature.

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_3COOH	16.6	118	∞
Propanoic acid	CH_3CH_2COOH	-21	141	∞
Butanoic acid	$CH_3(CH_2)_2COOH$	-6	164	∞
Pentanoic acid	$CH_3(CH_2)_3COOH$	-34	187	4.97
Benzoic acid	C_6H_5COOH	122	249	0.4



Dimer structure of two carboxylic acids



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3. Physical Properties of some Functional Groups

3.5. Physical Properties of Carboxylic Acids and Their Derivatives

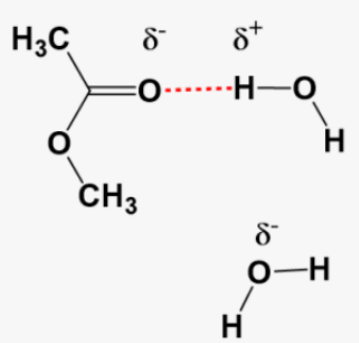
Esters

- Esters are polar compounds, but lacking a hydrogen attached to oxygen, their molecules cannot form strong hydrogen bonds to each other.

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

- **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.



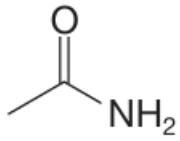
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3. Physical Properties of some Functional Groups

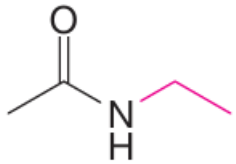
3.5. Physical Properties of Carboxylic Acids and Their Derivatives

Amides

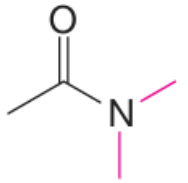
- **Boiling points;**
  - **Amides with one or two hydrogens on nitrogen form strong hydrogen bonds and have high melting and boiling points.**
  - **On the other hand, *N,N*-disubstituted amides cannot form hydrogen bonds to each other and, therefor, have lower melting and boiling points.**



Ethanamide
bp 221 °C; mp 82 °C

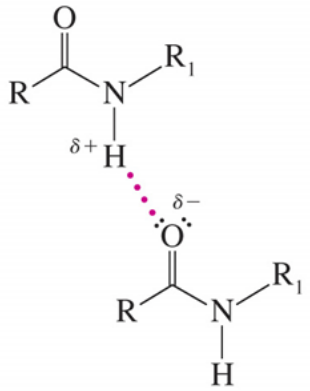


***N*-Ethylethanamide**
bp 205 °C

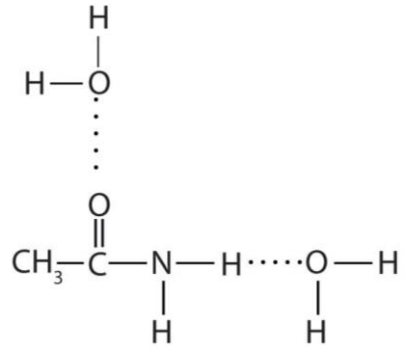


***N,N*-Dimethylethanamide**
bp 166 °C; mp -20 °C

- **Solubility;**
  - **Amides are soluble in water due to the polar nature of the amide group and they can make hydrogen bond to water.**



Hydrogen bonding between amide molecules



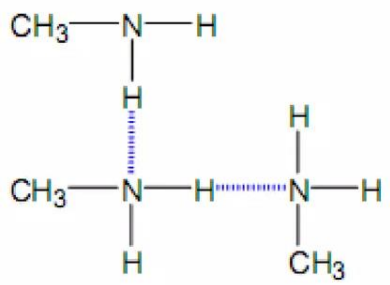
Hydrogen bonding between amide and water molecules

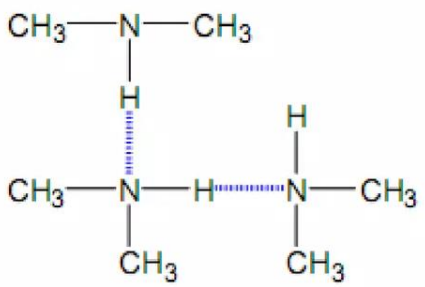
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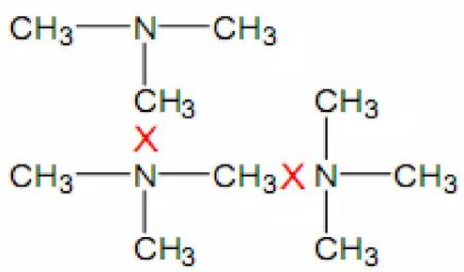
3. Physical Properties of some Functional Groups

3.6. Physical Properties of Amines

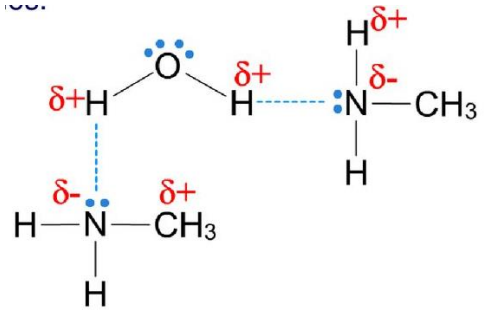
- **Amines are moderately polar substances.**
- **Primary and secondary amines can form hydrogen bonds to each other and water.**
- **Tertiary amines cannot form hydrogen bonds to each other but can form hydrogen bond to molecules of water.**







- **Solubility;**
  - **Low molecular weight amines tend to be water soluble whether they are primary, secondary or tertiary.**



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3. Physical Properties of some Functional Groups

3.6. Physical Properties of Amines

- **Boiling points;**
  - Tertiary amines have lower boiling points than primary or secondary amines of comparable molecular weights.
  - They have boiling points that are higher than those of alkanes, but generally lower than those of alcohols of comparable molecular weight.

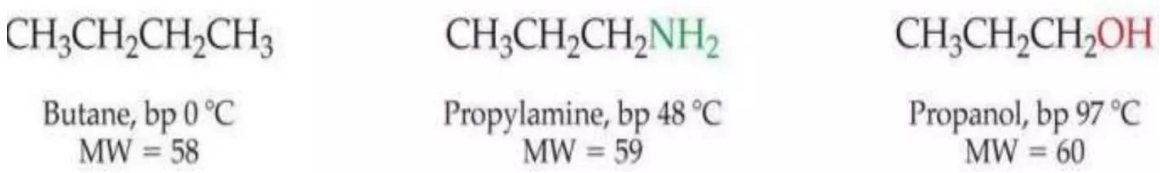
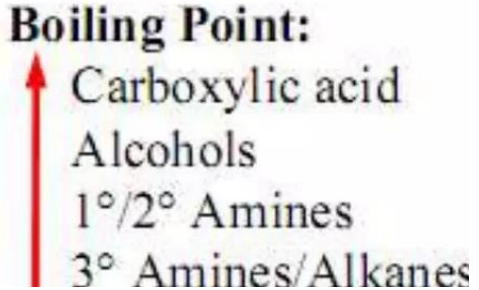


Table 2.6 Physical properties of amines

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

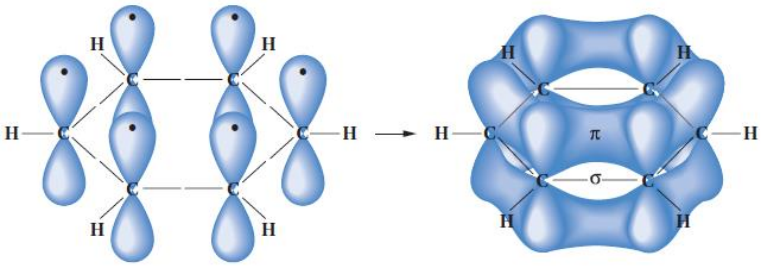


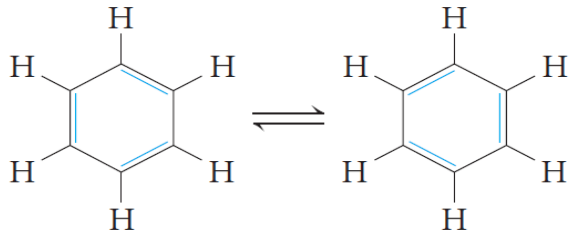
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4. Resonance and Delocalization

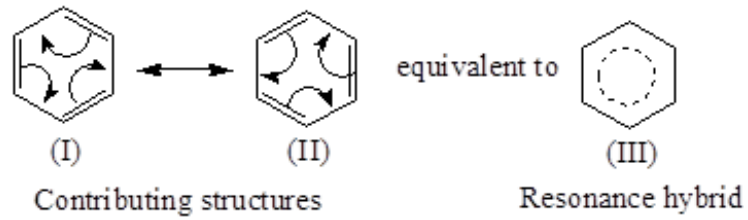
4.1. The Resonance Explanation for the Structure of Benzene

- **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**).
- **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

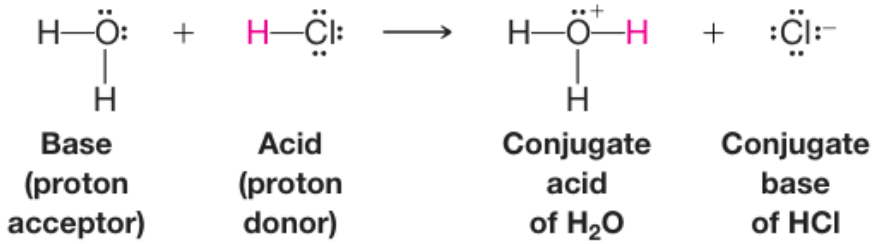
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5. Acids and Bases

5.1. Bronsted–Lowry Acids and Base

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

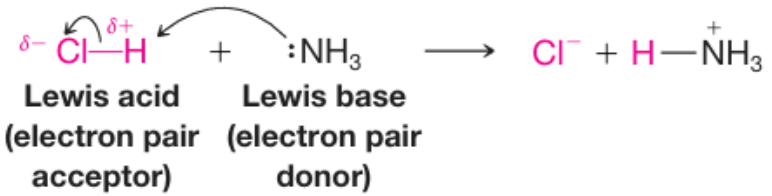
- **Brønsted–Lowry acid is a substance that can donate (or lose) a proton.**
- **Brønsted–Lowry base is a substance that can accept (or remove) a proton.**

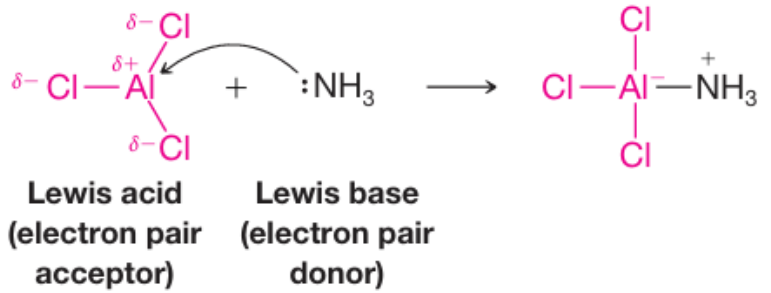


5.2. Lewis Acids and Bases

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).**





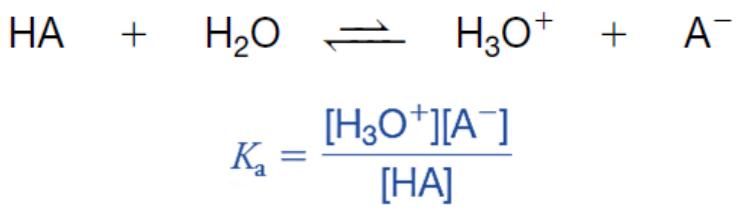
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5. Acids and Bases

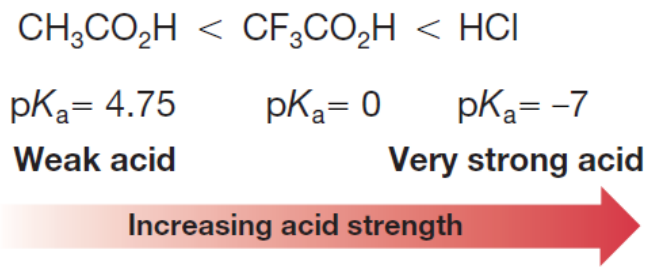
5.3. The Strength of Brønsted–Lowry Acids and Bases: Ka and pKa

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.

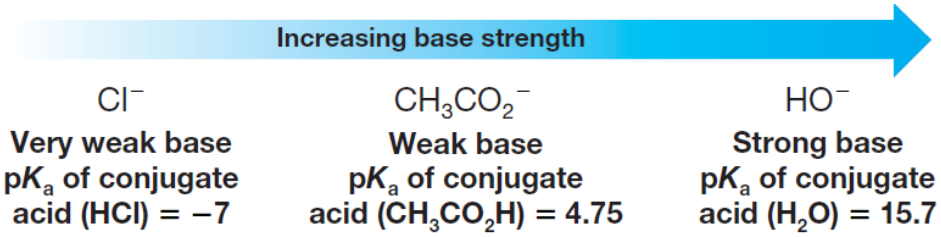


B) Acidity and pK_a

- 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.



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5. Acids and Bases

5.4. Relationships Between Structure and Acidity

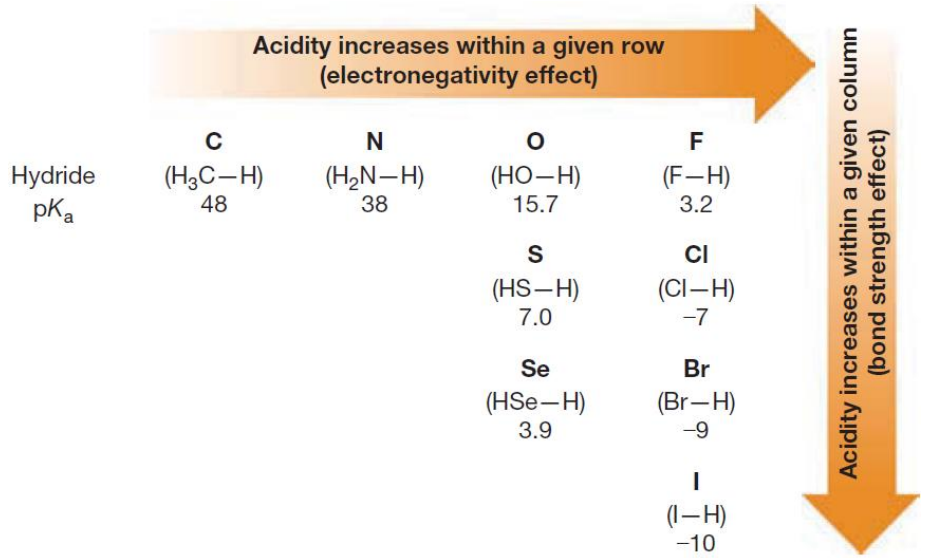
A) Periodic Table Trend

- **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.**
- **Example; Alkyne hydrogen is weakly acid and Alkene and alkane hydrogens are essentially not acidic.**

Relative Acidity of the Hydrocarbons

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

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5. Acids and Bases

5.4. Relationships Between Structure and Acidity

C) Inductive Effects

- The electron withdrawing increases acidity. Electron-withdrawing substituents (-I); -OH, -SH, -CHO, -$COCH_3$, -COOH, -NO_2, -NH_2, -OCH_3
- The electron donating decreases acidity, Electron-donating substituents (+I); -CH_3, -C_2H_5

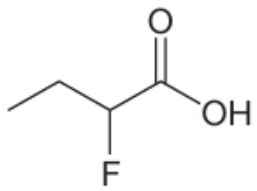
Compound	pK_a		Compound	pK_a
HCO_2H	3.75		$CH_3CH_2CH_2CO_2H$	4.82
CH_3CO_2H	4.74		$ClCH_2CH_2CH_2CO_2H$	4.53
FCH_2CO_2H	2.65		$CH_3CHClCH_2CO_2H$	4.05
$ClCH_2CO_2H$	2.85		$CH_3CH_2CHClCO_2H$	2.89
$BrCH_2CO_2H$	2.90		$C_6H_5CO_2H$	4.20
ICH_2CO_2H	3.10		p-$O_2NC_6H_4CO_2H$	3.45
Cl_3CCO_2H	0.77		p-$CH_3OC_6H_4CO_2H$	4.45

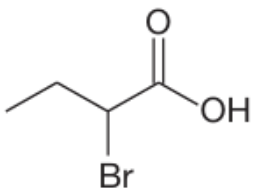
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5. Acids and Bases

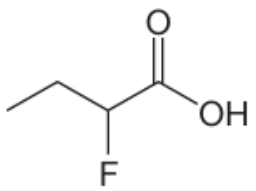
5.5. Carboxylic Acids, Phenols and Alcohols as Acids

- **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.**

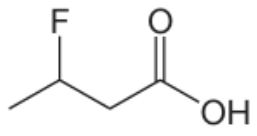


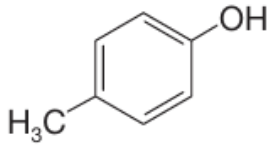


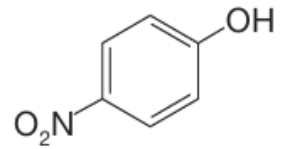
Stronger acid



Stronger acid







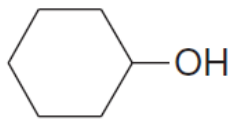
Stronger acid

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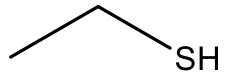
5. Acids and Bases

5.5. Carboxylic Acids, Phenols and Alcohols as Acids

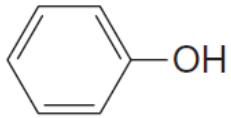
- **Carboxylic acids are weak acids, having pK_a values in the range of 3–5.**
- **Phenol is weak acid, having pK_a values of 9.89.**
- **Thiols are weak acids, typically having pKa values in the range of about 10–11, and are more acidic than alcohols.**
- **Alcohols, have pK_a values in the range of 15–18, and essentially do not give up a proton unless exposed to a very strong base.**



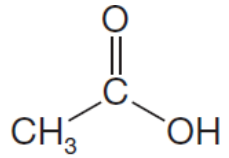
Cyclohexanol
pK_a = 18



Ethanethiol
pK_a= 10.6



Phenol
pK_a = 9.89



Acetic acid
pK_a = 4.75

- **Phenol is a weak acid compared with carboxylic acids such as acetic acid but is slightly more acidic than thiols and much more acidic than alcohols such as cyclohexanol.**

Carboxylic acid > Phenol > Thiol > Alcohol

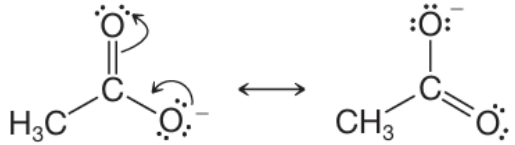
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5. Acids and Bases

5.5. Carboxylic Acids, Phenols and Alcohols as Acids

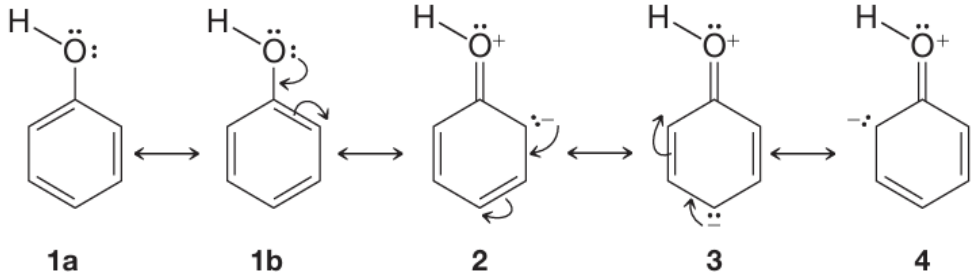
- **Acidity increases with**
  - **The conjugate base is stabilized by resonance; Delocalization of the negative charge is possible in a carboxylate anion, but it is not possible in an alkoxide ion.**

Resonance stabilization in acetate ion

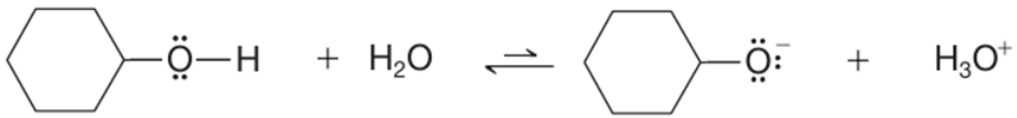


- **Phenol is more acidic than cyclohexanol because its conjugate base, *the phenoxide ion*, is stabilized by resonance, this resonance stabilizes the conjugate base more than it stabilizes phenol itself, increasing acidity.**

Resonance stabilization in phenol



No resonance stabilization in cyclohexoxide anion



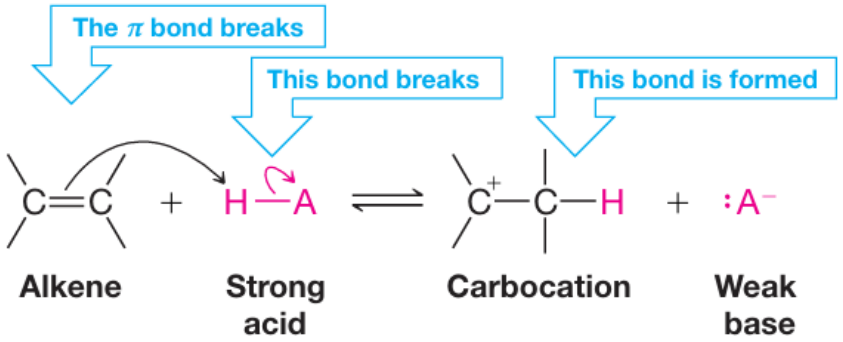
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5. Acids and Bases

5.6. Organic Compounds as Bases

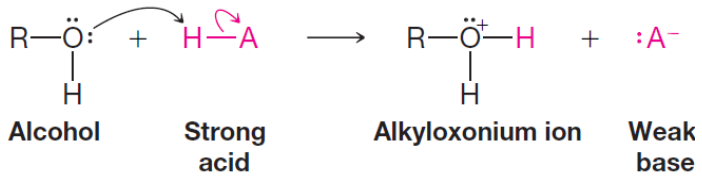
- **An organic compound is a potential base if it contains:**

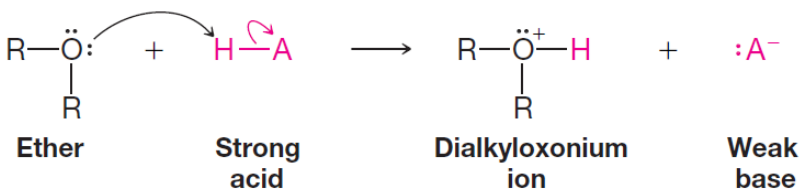
A) π bond; Alkenes react with a strong acid by accepting a proton.

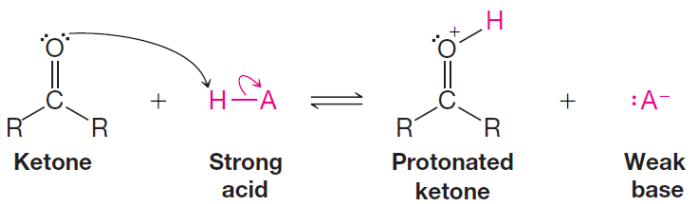


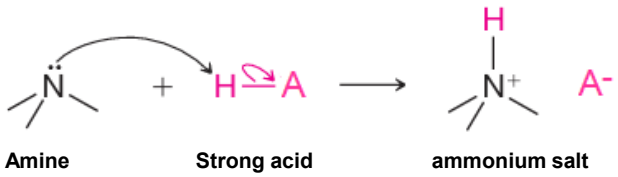
B) An atom with an unshared electron pair.

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.







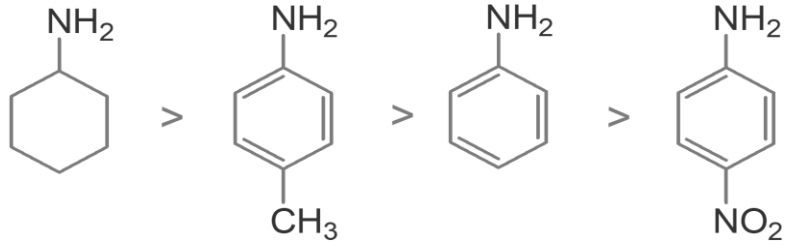


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5. Acids and Bases

5.6. Organic Compounds as Bases

- **Amines:** Aromatic amines less basic than aliphatic amines.
- **Electron-donating groups** increase the basicity of amines, and electron-withdrawing groups decrease their basicity.



5.7. Heterolysis of Bonds to Carbon: Carbocations and Carbanions

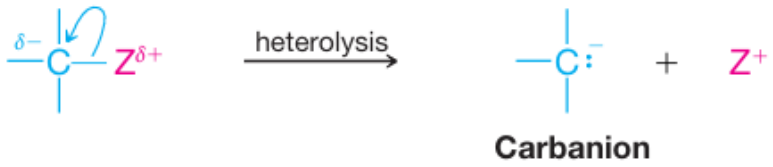
Heterolysis of a bond to a carbon atom can lead to either of two ions:

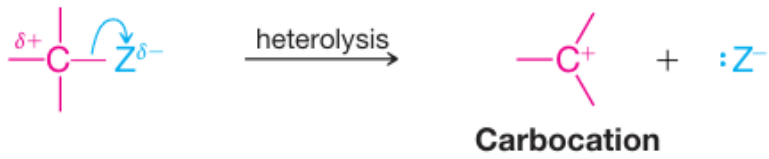
- **A carbocation;** an ion with a **positive charge** on the carbon atom.

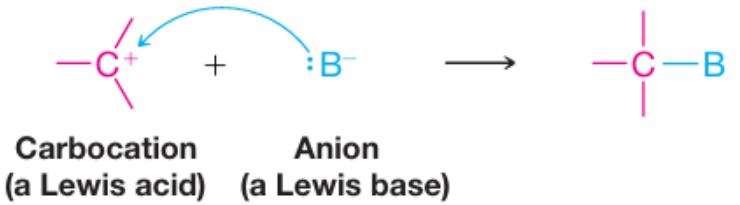
  Example; Carbocations are **electron deficient**, and therefore carbocations are **Lewis's acids**.

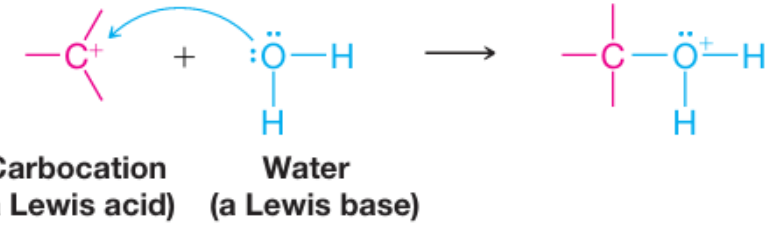
- **A carbanion;** an ion with a **negatively charged** on the carbon atom.

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









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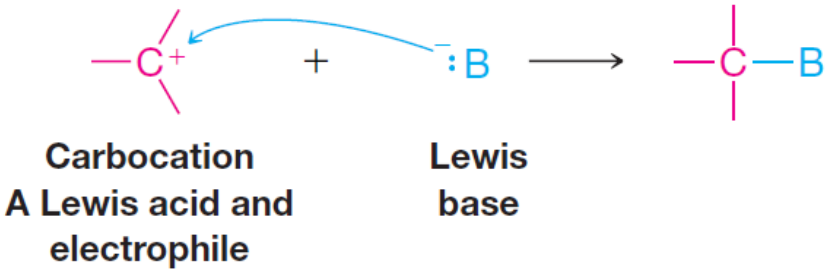
5. Acids and Bases

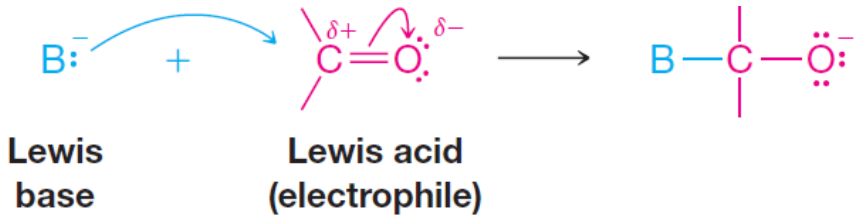
5.8. Electrophiles and Nucleophiles

- **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).

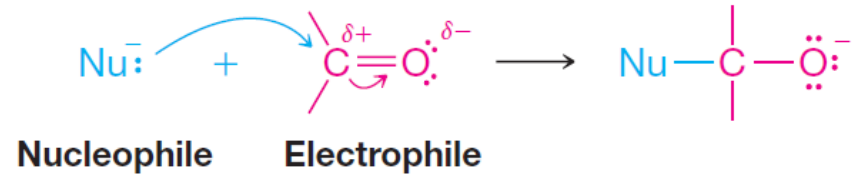


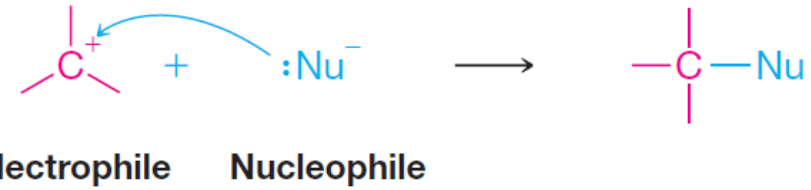


- **Nucleophile** is a Lewis base that seeks a positive center such as a positively charged carbon atom.

Examples;

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



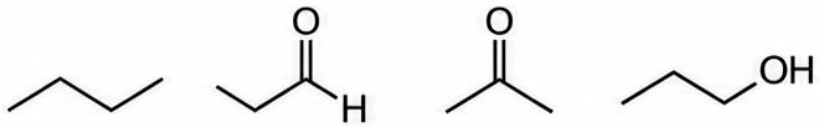


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6. Practice Problems

1) Compare the following compounds. Give the requested order and a brief reason for your answer.

a) Arrange the following compounds in increasing order of boiling point.



Butane Propanal Acetone 1-Propanol

b) Arrange the following isomers in decreasing order of boiling point.



Pentane Isopentane Neopentane

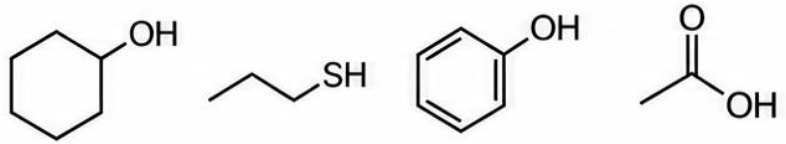
c) Arrange the following alkyl halides in increasing order of boiling point.



Fluoroethane Chloroethane Bromoethane Iodoethane

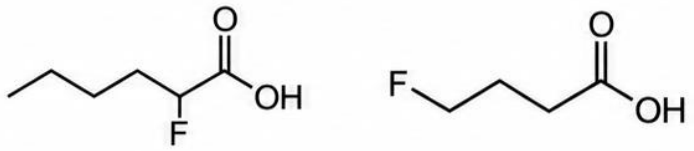
2) Compare the acidity (and basicity) of the following compounds. Give the requested order and a brief reason for your answer.

a) Arrange the following compounds in increasing order of acidity.



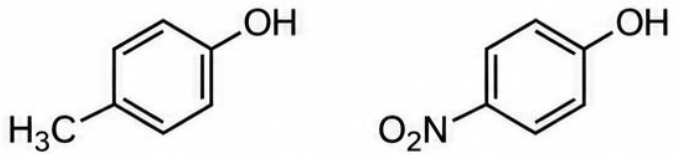
Cyclohexanol Ethanethiol Phenol Acetic acid

b) Which of the following carboxylic acids is stronger? Explain your answer.



2-Fluorobutanoic acid 4-Fluorobutanoic acid

c) Which of the following phenols is more acidic? Explain your answer.



p-Cresol *p*-Nitrophenol