CHEM 2.5

Standard 91165 Demonstrate understanding of the properties of selected organic compounds

Click **here** for the NCEA page for this standard. This standard can be divided into 3 parts Please read <u>this document</u>.

1. Introduction to organic chemistry

- a. Functional groups
- b. Naming and drawing organic compounds
- c. Isomers
 - i. Structural
 - ii. Geometrical

2. Physical and chemical of functional groups

- a. Physical properties of organic substances
- b. Type of organic reactions
- c. Alkane

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- i. Substitution reactions
- d. Alkene and alkyne
 - Addition reactions
 - 1. Markovnikov rule
 - 2. Addition polymer
 - ii. Oxidation reactions
- e. Haloalkanes
 - i. Type of haloalkane
 - ii. Substitution reactions
 - iii. Elimination reactions
 - 1. Anti-Markovnikov rule
- f. Alcohols
 - i. Substitution reactions
 - ii. Elimination reactions
 - iii. Oxidation reactions
- g. Amines
- h. Carboxylic acids
- i. Identifying unknown organic substances
- 3. Overall reaction scheme

Introduction to organic chemistry

There are three major themes for this part of the standard

- 1) Functional groups
- 2) Naming and drawing organic compounds
 - a) Naming organic compounds
 - b) Drawing organic compounds
- 3) Isomers
 - a) Structural isomers
 - b) Geometrical isomers (cis and trans isomers)
- Organic chemistry is the chemistry of carbon based compounds.
- Since living organism on earth are mostly composed of organic substances, therefore it is an important part of chemistry.
- Although the organic chemistry is rather basic in level 2 (and even level 3), it is a VERY important part of chemistry and is part of the first year of biomedical science and health science programme which is the path to medical school as well as pharmacy, food science, and engineering, in University of Auckland (my Alma Mater).
- The most basic form of organic compounds involve **carbon** and **hydrogen** atoms only.
 - They are called **hydrocarbons**.
 - The simplest of them is the alkane.
 - A hydrocarbon with carbon to carbon single bond only.
- The more complicated organic compounds involve other elements such as oxygen and nitrogen.
- One of the very important in organic chemistry is
 - Carbon 4 bonds
 - Nitrogen 3 bonds
 - Oxygen 2 bonds
 - Hydrogen and halogen 1 bond

Functional groups

- Most of the chemical reaction in organic chemistry involves the functional group the molecule contains.
- Only functional group part of the molecule changes in a particular chemical reaction and leaving the rest of the molecule unchanged.
- Below are the functional groups for CHEM 2.5



Exercise for functional groups

Circle and name the functional group(s) for the molecules below.



Naming organic compounds

- The system of naming organic compounds commonly used is called IUPAC
 IUPAC stands for International Union of Pure and Applied Chemistry
- The table below is a summary of the naming system
 - \circ $\$ -#- is the location of the chain 1
- Saturation describes the molecules contains C=C or C=C
 - \circ $\,$ Molecules that contains $\mbox{C-C}$ bond only are saturated
 - Molecules that contains double or triple bonds are "unsaturated"

Branched chain Or sub-group	Main chain (longest continuous chain)	saturation	Major Functional group
Halogens -F #-floro -Cl #-chloro -Br #-bromo -I #-iodo	1 × C - meth	C-C bond only an	Contains -OH -#-ol
	2 × C - eth	C=C -#-en	
	3 × C - prop	C≡C -#-yn	Contains
	4 × C - but		-NH ₂ -#-amine*
Branched chain 1 × C - #-methyl 2 × C - #-ethyl 3 × C - #-propyl And so on	5 × C - pent		Contains
	6 × C - hex		
	7 × C - hept		СОН
Amine* #-amino	8 × C - oct		oic acid*
			None of the above e
*carbon of carboxylic acid is always the 1 st carbon Between # and # use , Between # and alphabet use - If two or more of the same branched chain or functional group add: di for 2× tri for 3× tetra for 4× eg. 1,2-diol If two or more branched chains present, they are arranged in alphabetical order *-NH ₂ is treated as branched chain if other major functional group present or it contains multiple C bonds (ene and yne)			

Table 1.1 - Table summary IUPAC naming system for CHEM 2.5

¹ Location should be the smallest number for the major functional group

Naming organic compounds

- Naming starts from the right to the left of the table
 - 1. Identify major functional group
 - 2. Saturation
 - 3. Main chain
 - 4. Branched chain
- Example 1



• Example 2



• Example 3



• Example 4



- 1. It contains -COOH oic acid
- 2. No C=C anoic acid
- 3. Three carbons in the main chain propanoic acid
- 4. No branched chain propanoic acid
- 1. No major functional group <u>e</u>
- 2. Contains C=C between 1st carbon and 2nd carbon <u>-1-ene</u>
- 3. Four carbons in the main chain but-1-ene
- 4. No branched chain but-1-ene

- 1. No major functional group <u>e</u>
- 2. Contains C-C bond only ane
- 3. Six carbons in the main chain hexane
- 4. Two bromine branched on 2^{nd} and 3^{rd} carbon

2,3-dibromohexane

- 1. Contains -OH on the 2nd carbon -2-ol
- 2. Contains C-C bond only <u>an</u>-2-ol
- 3. Four carbons in the main chain butan-2-ol
- One CH₃ branched chain on the 2nd carbon <u>2-methyl</u>butan-2-ol

• More complicated example 1- identifying longest chain

Identify the longest unbranched chain





- 1. Contains NH_2 on the 2nd carbon <u>-2-amine</u>
- 2. C-C bond only an-2-amine
- 3. Four carbons in the main chain **<u>but</u>an-2-amine**
- 4. No branched chain butan-2-amine

• More complicated example 2 - multiple branched chain



- Although it contains amine, since molecule contain C=C therefore amine would be treated as branched chain. <u>e</u>
- 2. It contains C=C on the 1^{st} and 2^{nd} carbon <u>-1-en</u>e
- 3. Four carbons in the main chain **<u>but</u>-1-ene**
- 4. It contains the following branched chains in alphabetical order
 - a. amino on the 4^{th} carbon
 - b. dichloro both on the 3rd carbon
 - c. Methyl on the 2nd carbon

Therefore the name would be

4-amino-3,3-dichloro-2-methylbut-1-ene

Exercise for naming organic compounds

Name the following molecules





Н





Drawing organic compounds

- Below are the steps for drawing organic compounds
 - 1. Draw the main chain
 - 2. Draw the functional group
 - 3. Draw the branched chain (or sub group)
 - a. Starting from the main functional group carbon
 - 4. Fill the rest of the bonds with hydrogen atoms
 - a. MAKE SURE CARBON HAS 4 BONDS ONLY!
- Example 1: 3-bromohexan-2-ol
 - 1. Draw the main chain
 - hex = 6 carbons



- 2. Draw the functional group
 - **-2-ol** = OH on the 2^{nd} carbon



- 3. Draw the branched chain
 - **3-bromo** = Br on the 3^{rd} carbon



4. Fill the rest of the bonds with hydrogen atoms



- Example 2: 3,4-dimethylpentanoic acid
 - 1. Draw the main chain
 - pent = 5 carbons

- 2. Draw the functional group
 - **anoic acid** = COOH on the 1^{st} carbon



- 3. Draw the branched chain
 - **3,4-dimethyl** =CH₃ on the 3rd and 4th carbons (start counting from the COOH group)



4. Fill the rest of the bonds with hydrogen atoms



Exercise for drawing organic compounds

- 1. Draw the following organic compounds
 - a. 4-bromobutan-1-ol
 - b. 2,3-dimethylbut-2-ene
 - c. 1,1,3-trichloropropane
- 2. Draw the molecules 2-ethylpropan-2-ol
 - a. Explain why the naming is wrong
 - b. Give the proper IUPAC name

Isomers

- Isomers are molecules that are similar but different in one way or another
- There are two types of isomers for CHEM 2.5
 - Structural isomers
 - Geometric isomers (*cis* and *trans*)

Structural isomers

- Structural isomers is also called constitutional isomers.
 - They are compounds with the **same atom composition** (molecular formula) but **arranged in different order** (structural formula)
 - Because of their different structural arrangement, therefore the IUPAC name will be different.
 - $\circ~$ Below is an example of structural isomer with a molecular formula $C_4 H_{10} O$



butan-1-ol Chemical Formula: C₄H₁₀O



butan-2-ol Chemical Formula: C₄H₁₀O



2-methylpropan-2-ol Chemical Formula: C₄H₁₀O



2-methylpropan-1-ol Chemical Formula: C₄H₁₀O

- All of the molecules above has the molecular formula of C₄H₁₀O but they have different structure resulting in a different name.
- Structural isomers can be drawing in an orderly manner
 - 1. Draw a simple straight chain with functional group on the 1st carbon
 - 2. Move the functional group along the main chain
 - 3. Create a branched chain on the 2nd carbon and functional group on the 1st carbon
 - a. Then functional on the next etc
 - b. Remember there are no 1-methyl
 - 4. Repeat step 3 but branched chain on the 3rd carbon etc
 - 5. Name the compounds to ensure that there are no repeats

- Example #1 draw all the structural isomers contains amine with the molecular of $C_5H_{13}N$
 - 1. Draw a simple straight chain with functional group on the 1st carbon



2. Move the functional group along the main chain



Create a branched chain on the 2nd carbon and functional group on the 1st carbon
 a. Then functional on the next etc



- 4. Repeat step 3 but branched chain on the 3rd carbon etc
- 5. Name the compounds to ensure that there are no repeats







2-methylbutan-1-amine



3-methylbutan-1-amine



3-methylbutan-2-amine

ŃН₂ Н

н Н

Η̈́

Exercise for structural isomers

Draw and name all possible isomers that contains a carboxylic acid with molecular formula $C_6H_{12}O_2$

Geometric isomers (cis and trans isomers)

- Geometric isomers is a type of stereoisomers where molecules have the same composition and same arrangement order but different position in space.
- In CHEM 2.5 the geometric isomers is the only stereoisomer
 - C = C is **rigid** and is **not able to rotate**.
 - When both of the double bond carbons contain two different atoms or group of atoms
 - If one of the carbon contains two of the same atoms or group
 - No geometric isomer
 - There would be two possibilities of arrangement
 - On the same side of the double bond called *cis*
 - On the opposite side of the double bond called *trans*
 - For example but-2-ene





trans but-2-ene

Example for geometric isomer for 1,2-dibromoethene





cis 1,2-dibromoethene *trans* 1,2-dibromoethene

Exercise for geometric isomer

1. Draw the two possible geometric isomers for 1-bromobut-1-ene.

2. Explain with diagrams why but-2-ene has geometric isomers whereas but-1-ene and 2-methylprop-1-ene does not have geometric isomer.

Physical and chemical of functional groups

This part of the standards can be divided into

- 1. Physical properties of organic substances
- 2. Type of organic reactions
- 3. Alkane
 - a. Substitution with halogen under UV to form haloalkane
- 4. Alkene and alkyne
 - a. Addition reactions
 - i. Markovnikov rule (major and minor product)
 - ii. Addition polymer
 - b. Oxidation
- 5. Haloalkanes
 - a. Type of haloalkane
 - b. Substitution reactions
 - c. Elimination reactions
 - i. Anti-Markovnikov rule
- 6. Alcohols
 - a. Type of alcohol
 - b. Substitution reactions
 - c. Elimination reactions
 - d. Oxidation
- 7. Amines
 - a. Acid and base reaction with
- 8. Carboxylic acids
 - a. Acid and base reaction with
- 9. Identifying unknown organic substances

Physical properties of organic substances

- For organic compounds the physical properties is governed by the
 - Length of the carbon chain
 - Functional group present in the molecule
 - For boiling point and melting point
 - For the same functional group boiling point increases as the chain length increases
 - With the same chain length, below are the boiling point ranking from highest to lowest.
 - Carboxylic acid
 - Amine
 - Alcohol
 - Haloalkane
 - Alkane and alkene
 - This depends on the **polarity of the functional group**. **Increase** in **polarity** of the functional group, **increase** in **boiling point**.
- For solubility
 - Most organic compounds with the exception of
 - Alcohol
 - Carboxylic acid
 - Amine

That has 5 or less carbons are soluble with water.

- They forms two layers with water (and aqueous solution) just like mixing oil with water.
- This is because their they contain a **strongly polar functional group**.
- For organic compounds the **chemical properties** is governed by the **functional group presents**.
 - Hence the word **functional**

Type of organic reactions

- There are
 - Substitution
 - An atom or group of atoms is replaced by another atom or group of atoms.
 - Addition
 - Atoms and group of atoms is inserted into the molecules by breaking of C=C or C=C.
 - Elimination
 - Two neighbour atoms or group of atoms is removed to form a C=C.
 - Oxidation
 - Reaction that involves **removal of H atoms** or **addition of O atoms**.
 - Acids and bases
 - **Donates** or **accepts hydrogen ions**.

Exercise for physical properties and types of organic reactions

Draw the following substances and identify them as soluble in water or not

1. 2-methylpropan-2-ol

2. Tetrachloromethane

3. Chloroethene

4. 2-methylpropanoic acid

5. 2-amino-2-methylpropanoic acid

6. tetrafloroethene

Alkane

- As mentioned before, alkanes are **saturated hydrocarbons**.
- It has a general formula of $C_n H_{2n+2}$.
- Alkane composes the major component of crude oil.
- They are generally inert for chemical reaction except for **combustion**.
 - That is why they are commonly used as **organic solvent**.
 - For example, hexane.
 - The only other reaction it involves is **substitution** with **elemental halogen under UV light**.

Substitution

- One of the hydrogen atom is replaced with a **halogen atom** from **halogen** forming a **haloalkane** and **hydrogen halide**.
- For example reaction between **propane** with **chlorine** to form **chloroalkane** and **hydrogen chloride**.
- As mentioned before alkane is unreactive, therefore **UV light** is needed to provide sufficient energy for the reaction to occur.



• The position for the substitution does not have to be on the 1st carbon.

Exercise for Alkane

- 1. Write a balanced equation for the following (organic compounds can be drawn)
 - a. 2-methylbutane mixed with bromine under sunlight
 - b. Hexane mixed with iodine under sunlight
 - c. Methane mixed with chlorine under sunlight
 - d. Ethane mixed with fluorine under sunlight

Alkene and alkyne

- Alkene and alkyne are unsaturated hydrocarbons
 - Alkene has a general formula of $C_n H_{2n}$
 - Alkyne has a general formula of $C_n H_{2n-2}$
- Their reactions involve in the C=C or C=C leaving the rest of the molecule unchanged
- There are two types of reaction for alkene
 - Addition reactions
 - Oxidation reactions

Addition reactions

1. Addition of hydrogen with platinum catalyst to form alkane



2. Addition of water under acidic condition $(H_2SO_{4(aq)})$ to form **alcohol**



3. Addition of halogen to form dihaloalkane



4. Addition of hydrogen halide to form haloalkane



Markovnikov rule

- In an addition reaction of water or hydrogen halides (HF, HCl, HBr, or HI) to an asymmetrical alkene or alkyne, the hydrogen atom prefer bonded to the carbon atom that had the greatest number of hydrogen atoms to form the major product.
- For example addition of water to propene



• A common phrase, hydrogen rich gets richer.

Addition polymers

- Polymers are long chain molecules formed by joining smaller molecules (monomer) together.
 - \circ $\;$ They can occur naturally or artificially using fossil fuel based chemicals
 - Artificial polymers are commonly known as plastics
- Addition polymers is when monomers joins together to form polymer by breaking of double bonds.
- Repeating unit is the part of the polymer which the monomer used to be.
- It is important to draw the **alkene** in **H shape** where the **double bond** is the **center of the H**.
- For example.

Polypropylene is an addition polymer made out of the monomer propene.

- Draw 2 repeating units of the **polymer**.
- Put a bracket around the **repeating unit**.



Oxidation reactions

- Alkene can be oxidised by
 - Acidified potassium permanganate $KMnO_4/H^+$.
 - Observation **Purple to Colourless**.
 - Acidified potassium dichromate $K_2Cr_2O_7/H^+$.
 - Observation **Orange to Green**.
- The **double bond is broken** and each of the **carbon of the double bond** is inserted with two **alcohol groups** on each of the carbon forming a **diol**.
- For example oxidation of propene



Exercise for Alkene and alkyne

Draw the **organic product(s)** for the following reactions. Label major and minor when appropriate.

- 1. But-1-ene reacted with dilute $H_2SO_{4(aq)}$
- 2. 2-methylpropene reacted with hydrogen chloride gas
- 3. Pent-2-ene reacted with acidified potassium dichromate
- 4. cis hex-2-ene reacted with bromine water
- 5. 2-methylbut-1-ene reacted with hydrogen chloride gas

Haloalkane

- Haloalkane is a commonly used as a base material for many of the organic synthesis.
 - Halogens are group XVII elements
 - Fluorine (**F**)
 - Chlorine (CI)
 - Bromine (Br)
 - Iodine (I)
- They are often produced in an **industrial scale** by reacting **alkane** with **halogen gas** with **petroleum products** then separated by **fractional distillation**.
- There are two types of reaction for haloalkane
 - Substitution reactions
 - Elimination reactions
- Types of haloalkane
 - There are three types of **haloalkane** (R = the rest of the chain)
 - Primary haloalkane



• Secondary haloalkane



• Tertiary haloalkane



Substitution reactions

- Haloalkane undergoes two substitution reactions where the halogen atom is replaced by
 - **-OH** using the reagent **KOH**_(aa) (or NaOH_(aa)) to form **alcohol**



Elimination reactions

• The **halogen atom** and a **neighbouring hydrogen** are **removed** forming a **C=C** using the reagent of **KOH**_(alc) forming **hydrogen halide** byproduct.



Anti-Markovnikov rule

- Similar to addition reaction, there could be **two possible products** (a **major** and a **minor**) if the molecule is **asymmetrical**.
- Opposite to the Markovnikov, If there are two neighboring carbon with hydrogen, the one with the **less hydrogen atom** is favored to form the **major** product.



Exercise for haloalkane

1. Compare and contrast the reactions between the reactions of 2-chlorohexane reacted with potassium hydroxide under different conditions. Identify the types of reactions and provide the structure and name of all organic products and their relationship between them.

2. Complete the diagram below



- 3. Draw the structure of both reactants and organic products of the following reactions.
 - a. 1,5-dichlorohexane with alcoholic potassium hydroxide.
 - b. 2-bromopentane with alcoholic ammonia.
 - c. 2-florobutane with alcoholic potassium hydroxide.
 - d. 1-chloropropane with aqueous potassium hydroxide.

Alcohol

- Alcohol in chemistry refers to organic compounds that contain -OH group.
- The alcohol in beverages is ethanol which is produced by the fermentation by yeast in an **anaerobic environment**.
- There similar to haloalkane there are **three types of alcohols** (R = the rest of the chain)
- There are **three types** of reaction for alcohol
 - Substitution reactions
 - Elimination reactions
 - Oxidation reactions

Types of alcohol

• Primary alcohol



• Secondary alcohol



• Tertiary alcohol



Substitution reactions

- Alcohol undergoes two substitution reactions where the -OH is replaced by
 - -CI using the reagent PCI_5 , PCI_3 or $SOCI_2$



• -Br using the reagent HBr_(conc)



Elimination reactions

- The -OH group and a hydrogen from a neighbouring carbon is removed to form C=C reagent H₂SO_{4(conc)}.
- Similar to the elimination of haloalkane, when there are two possible positions to remove the hydrogen, it could results in a major and minor product depending on the number of hydrogen atom on the carbon.
 - The hydrogen poor gets poorer



Oxidation

• Primary alcohol can be oxidised to carboxylic acid by KMnO₄/H⁺ or K₂Cr₂O₇/H⁺



Exercise for alcohol

- 1. Draw the structure of products for ethanol reactions with
 - a. Potassium dichromate
 - b. $H_2SO_{4(conc)}$ c. $SOCI_2$

2. Draw the possible products when 3-methylbutan-2-ol is reacted with $H_2SO_{4(conc)}$

Amine

- Amine is a base.
 - Repeat this statement 10 times.
- For CHEM 2.5 only reaction is **amine** acting as a **base**.
 - From CHEM 2.6 a base is a H^+ acceptor.
 - Amine is a weak base, partially dissociate forming an equilibrium mixture.
 - The lone pair electrons of the nitrogen atom accepts an hydrogen ion.
 - It will turn red litmus blue.
 - Dissociate in water forming OH⁻
 - Reacts with hydrochloric acid forming chloride salt.



Carboxylic acid

- Carboxylic acid is an acid (DUH!)
 - From CHEM 2.6 an acid is a H⁺ donor
 - Carboxylic acid is a weak acid, partially dissociate forming an equilibrium mixture.
 - The the hydrogen atom of the -OH in the acid group acts as an H⁺ source.
 - It will turn **blue litmus red.**
 - **Dissociate** in water forming H_3O^+ .
 - Reacts with sodium hydroxide forming sodium salt and water.



Exercise for amine and carboxylic acid

- 1. Draw the organic products for
 - a. Propanoic acid with sodium hydroxide
 - b. Hexan-3-amine with hydrochloric acid
- 2. Discuss the follow steps and identify all the reactions below and draw all the organic products.
 - Propan-1-ol is reacted with concentrated sulfuric acid, the mixture is then distilled.
 - The organic product is then reacted with bromine water.
 - The product is then extracted by organic solvent then the organic solvent is then removed by evaporation.
 - The product then mixed with alcoholic ammonia.

Identifying unknown organic substances

- There are many ways to to identify unknown organic substances with a combination of **chemical and physical properties**, I personally find the following steps helpful.
 - 1. Acid and base
 - a. Add moist red litmus and blue litmus paper
 - i. Red litmus turns blue
 - 1. Amines
 - ii. Blue litmus turns red
 - 1. Carboxylic acids
 - b. Or use sodium carbonate solution (or sodium hydrogencarbonate)
 - i. Bubbles form
 - ii. acid + carbonate \rightarrow salt + water + carbon dioxide
 - 1. Carboxylic acids

2. Test alkene

- a. New sample add bromine water to a new sample
 - i. Colour change from **brown** to **colourless** quickly
 - 1. Alkenes
 - ii. Single layer form
 - 1. Alcohol, amine or carboxylic acid with 5 or less carbons

3. Test alcohol or alkene

- a. New sample add
 - i. Acidified potassium permanganate
 - 1. Purple to colourless
 - ii. Acidified potassium dichromate
 - 1. Organic to green
 - 2. Alcohols or alkenes

Exercise for identifying unknown organic substances

Identify three unlabelled bottle containing organic substance of one of the followings:

- Propan-1-ol
- Hex-1-ene
- butanoic acid

Design series of chemical test to determine which of the sample is which.

Provide observations for each test and classify all the chemical reactions to justify your answers.

Overall reaction scheme

