

Chapter 1. Molecular formula and molar mass

- elemental analysis
- combustion analysis
- calculation of the percentage composition

What is the empirical formula of a compound that consists of 64.6 % C and 10.8 % H? What is the molecular formula?

Does the compound contain π -bonds or rings? If so, how many?

Reading:
Pavia
Chapter 1
Don't need 1.2

1. Molecular Formula

Need to know

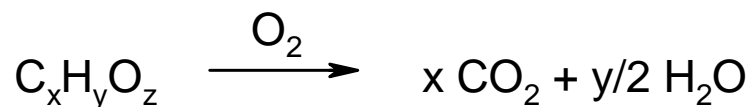
which elements: qualitative analysis

how much of each element: quantitative analysis

} elemental analysis

For organic compounds important:

Combustion analysis



Problem: cannot determine % oxygen!

Solution: determine % of all other elements,

then get % O by difference from 100 %

elemental analysis \longrightarrow empirical formula $\xrightarrow{\text{molar mass}}$ molecular formula

1. Molecular Formula continued

Example

An elemental analysis gives 40.0 % C, 6.71 % H.

Give the **empirical** and the **molecular** formula.

A. Empirical formula

Step 1: Is oxygen present? How much?

$$40.0 + 6.71 < 100 \% \Rightarrow \text{yes, } 53.3 \% \text{ O}$$

Step 2: Convert mass (40 % C is 40 g C in 100 g compound) to amount of substance.

$$n(\text{C}) = \frac{40.0 \text{ g}}{12.011 \text{ g/mol}} = 3.33 \text{ mol}$$

$$n(\text{H}) = \frac{6.71 \text{ g}}{1.0078 \text{ g/mol}} = 6.66 \text{ mol}$$

$$n(\text{O}) = \frac{53.3 \text{ g}}{15.9994 \text{ g/mol}} = 3.33 \text{ mol}$$

$$n = \frac{m}{M} \quad \text{units: } \text{mol} = \frac{\text{g}}{\text{g/mol}}$$



1. Molecular Formula continued

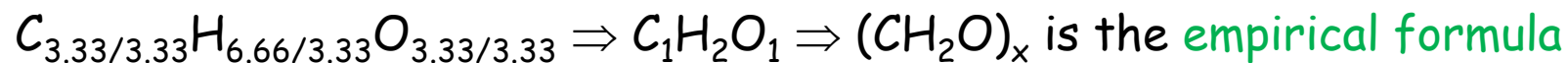
Example continued

An elemental analysis gives 40.0 % C, 6.71 % H.

Give the empirical and the molecular formula.

A. Empirical formula continued

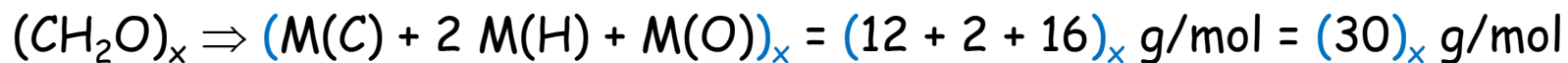
Step 3: Convert rational numbers. Divide by smallest number.



B. Molecular formula

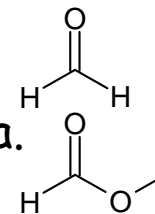
Step 1: Obtain the molar mass, M.

Step 2: Find x.



For M 30 g/mol $\Rightarrow x = 1 \Rightarrow CH_2O$ is the molecular formula.

For M 60 g/mol $\Rightarrow x = 2 \Rightarrow C_2H_4O_2$ is the molecular formula.



2. Index of hydrogen deficiency, U

- also called **unsaturation** number (therefore U)
- first piece of structural information from a molecular formula

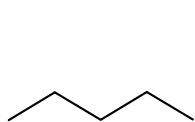
saturated: **alkane: C_nH_{2n+2}** (maximum # H possible)

unit of unsaturation: ring or π -bond: **reduces # H by 2**

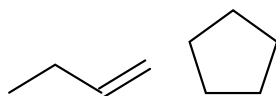
unsaturated: **cycloalkane** }
 alkene } : C_nH_{2n}
 alkyne: C_nH_{2n-2}

Examples

A. Index from a structure (trivial)



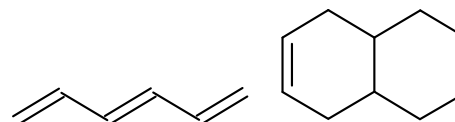
U = 0



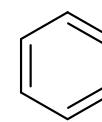
U = 1



U = 2



U = 3



U = 4

2. Index of hydrogen deficiency, U, continued

Examples continued

B. Index from a molecular formula

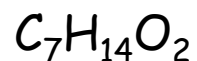
$$U = te + 1 - \frac{1}{2}(m - tr)$$

te: tetravalent \Rightarrow C, Si

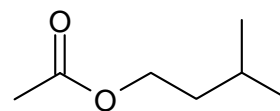
tr: trivalent \Rightarrow N, P

(d: divalent \Rightarrow O, S)

m: monovalent \Rightarrow H, X

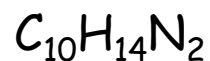


$$U = 7 + 1 - \frac{1}{2}(14 - 0) = 8 - 7 = 1$$

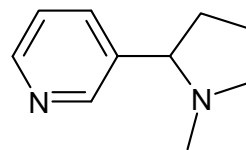


isopentylacetate

one ring or C=C or C=O: need spectroscopic support



$$U = 10 + 1 - \frac{1}{2}(14 - 2) = 11 - 6 = 5$$



nicotine

3. Rule of 13

- gives information about a *possible* molecular formula
- obtained from molar mass, M

Idea: divide M by 13, gives base formula of C and H only

$$\frac{M}{13} = n + \frac{r}{13} \Rightarrow C_n H_{n+r}$$

Example

M 94 g/mol

$$\frac{94}{13} = 7 + \frac{3}{13} \Rightarrow C_7 H_{10} \Rightarrow \text{read as "7 non-H atoms"} \Rightarrow 7 \text{ C or}$$

6 C plus 1 O or

5 C plus 2 O...

$7 \times 13 = 91$

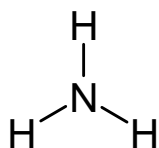
\Rightarrow gives **general idea** of how big the molecule is!

Further: U? Structures? (For 7 C, or for 6 C and 1 O...)

4. Nitrogen rule

Nitrogen peculiarity:

even atomic mass but odd number of electrons



⇒ molar mass is odd for an odd number of N atoms!

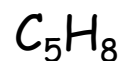
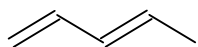
Example

Unknown with M 136 g/mol, 70.6 % C, 5.9 % H.

Give the molecular formula and the unsaturation number.

Propose two vastly different structures (different skeleton, functional groups).

Food for thought on rounding

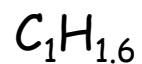


M 68 g/mol

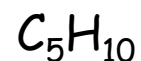
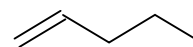
88.2 % C, 11.8 % H

$$n(C) = \frac{88.2g}{12g/mol} = 7.35mol$$

$$n(H) = \frac{11.8g}{1g/mol} = 11.8mol$$



too far from 2 to round!



M 70 g/mol

85.7 % C, 14.3 % H

$$n(C) = \frac{85.7g}{12g/mol} = 7.14mol$$

$$n(H) = \frac{14.3g}{1g/mol} = 14.3mol$$

