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, 1.6

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

$$C_xH_yO_z \xrightarrow{O_2} x\ CO_2 + y/2\ H_2O$$

Problem: cannot determine % oxygen!

Solution: determine % of all other elements,
then get % O by difference from 100 %

elemental analysis → empirical formula —(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?

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

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

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

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

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

$\Rightarrow C_{3.33}H_{6.66}O_{3.33}$

$$n = \frac{m}{M}$$

units: $mol = \frac{g}{g/mol}$

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.

$C_{3.33/3.33}H_{6.66/3.33}O_{3.33/3.33} \Rightarrow C_1H_2O_1 \Rightarrow (CH_2O)_x$ is the empirical formula

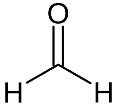
B. Molecular formula

Step 1: Obtain the molar mass, M.

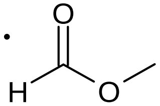
Step 2: Find x.

$(CH_2O)_x \Rightarrow (M(C) + 2\ M(H) + M(O))_x = (12 + 2 + 16)_x$ g/mol $= (30)_x$ g/mol

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)

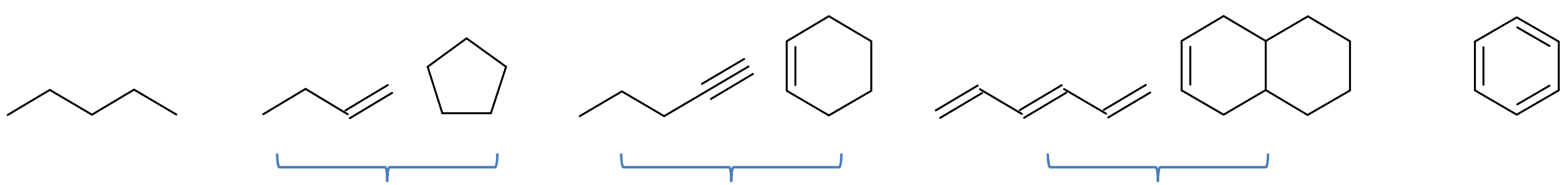
unit of unsaturation: ring or π-bond: reduces # H by 2

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 ⇒ C, Si

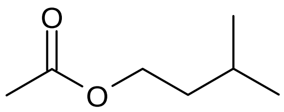
tr: trivalent ⇒ N, P

(d: divalent ⇒ O, S)

m: monovalent ⇒ H, X

$C_7H_{14}O_2$

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

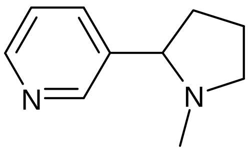


isopentylacetate

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

$C_{10}H_{14}N_2$

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



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

$$\frac{M}{13} = n + \frac{r}{13} \quad \Rightarrow C_nH_{n+r}$$

Example

M 94 g/mol

$$\frac{94}{13} = 7 + \frac{3}{13} \quad \Rightarrow C_7H_{10} \quad \Rightarrow \text{read as "7 non-H atoms"} \Rightarrow \text{7 C or}$$

6 C plus 1 O or

5 C plus 2 O…

7 x 13 = 91

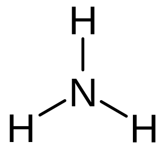
$\Rightarrow$ gives general idea of how big the molecule is!

Further: U? Structures?

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).