INTRODUCTION TO SPECTROSCOPY

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5th Edition

MOLECULAR FORMULAS AND WHAT CAN BE LEARNED FROM THEM

1.1 ELEMENTAL ANALYSIS AND CALCULATIONS

TABLE 1.1
CALCULATION OF PERCENTAGE COMPOSITION FROM COMBUSTION DATA

$$\underset{9.83\text{ mg}}{C_xH_yO_z} + \text{excess } O_2 \longrightarrow \underset{23.26\text{ mg}}{x\,CO_2} + \underset{9.52\text{ mg}}{y/2\,H_2O}$$

$$\text{millimoles } CO_2 = \frac{23.26\text{ mg } CO_2}{44.01\text{ mg/mmole}} = 0.5285\text{ mmoles } CO_2$$

$$\text{mmoles } CO_2 = \text{mmoles C in original sample}$$

$$(0.5285\text{ mmoles C})(12.01\text{ mg/mmole C}) = 6.35\text{ mg C in original sample}$$

$$\text{millimoles } H_2O = \frac{9.52\text{ mg } H_2O}{18.02\text{ mg/mmole}} = 0.528\text{ mmoles } H_2O$$

$$(0.528\text{ mmoles } H_2O)\left(\frac{2\text{ mmoles H}}{1\text{ mmole } H_2O}\right) = 1.056\text{ mmoles H in original sample}$$

$$(1.056\text{ mmoles H})(1.008\text{ mg/mmole H}) = 1.06\text{ mg H in original sample}$$

$$\%\,C = \frac{6.35\text{ mg C}}{9.83\text{ mg sample}} \times 100 = 64.6\%$$

$$\%\,H = \frac{1.06\text{ mg H}}{9.83\text{ mg sample}} \times 100 = 10.8\%$$

$$\%\,O = 100 - (64.6 + 10.8) = 24.6\%$$

TABLE 1.2
CALCULATION OF EMPIRICAL FORMULA

Using a 100-g sample:

64.6% of C = 64.6 g

10.8% of H = 10.8 g

$$24.6\% \text{ of O} = \frac{24.6 \text{ g}}{100.0 \text{ g}}$$

$$\text{moles C} = \frac{64.6 \text{ g}}{12.01 \text{ g/mole}} = 5.38 \text{ moles C}$$

$$\text{moles H} = \frac{10.8 \text{ g}}{1.008 \text{ g/mole}} = 10.7 \text{ moles H}$$

$$\text{moles O} = \frac{24.6 \text{ g}}{16.0 \text{ g/mole}} = 1.54 \text{ moles O}$$

giving the result

$C_{5.38}H_{10.7}O_{1.54}$

Converting to the simplest ratio:

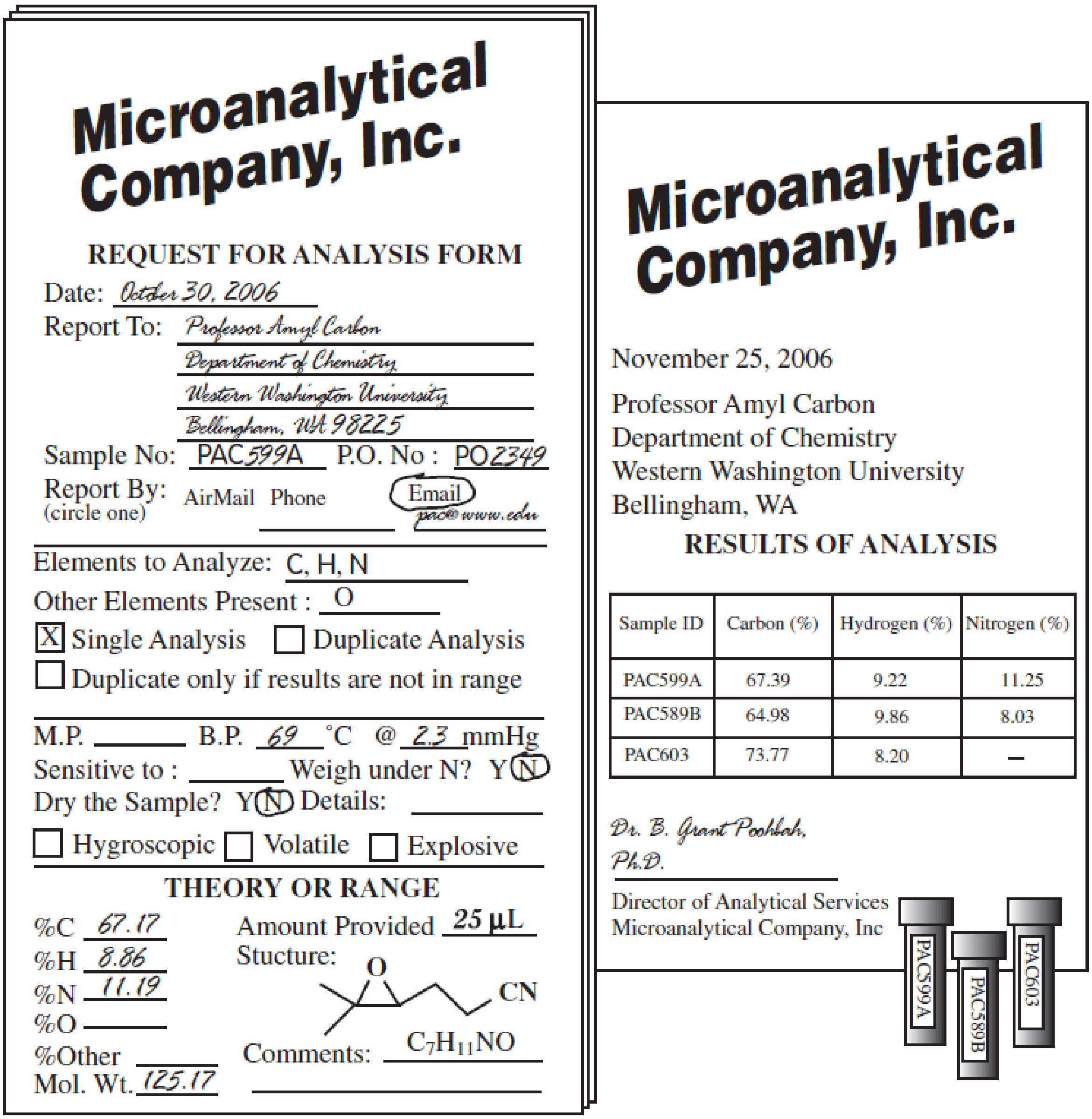
$$C_{\frac{5.38}{1.54}}\,H_{\frac{10.7}{1.54}}\,O_{\frac{1.54}{1.54}} = C_{3.49}H_{6.95}O_{1.00}$$

which approximates

$C_{3.50}H_{7.00}O_{1.00}$

or

$C_7H_{14}O_2$



Microanalytical Company, Inc.

REQUEST FOR ANALYSIS FORM

Date: October 30, 2006

Report To: Professor Amyl Carbon
Department of Chemistry
Western Washington University
Bellingham, WA 98225

Sample No: PAC599A P.O. No: PO2349

Report By: (circle one) AirMail Phone Email pac@www.edu

Elements to Analyze: C, H, N

Other Elements Present: O

[X] Single Analysis [ ] Duplicate Analysis

[ ] Duplicate only if results are not in range

M.P. ______ B.P. 69 °C @ 2.3 mmHg

Sensitive to: ______ Weigh under N? Y (N)

Dry the Sample? Y (N) Details: ______

[ ] Hygroscopic [ ] Volatile [ ] Explosive

THEORY OR RANGE

%C 67.17
%H 8.86
%N 11.19
%O ______
%Other ______
Mol. Wt. 125.17

Amount Provided 25 µL

Stucture: O CN

Comments: $C_7H_{11}NO$

Microanalytical Company, Inc.

November 25, 2006

Professor Amyl Carbon
Department of Chemistry
Western Washington University
Bellingham, WA

RESULTS OF ANALYSIS

Sample ID	Carbon (%)	Hydrogen (%)	Nitrogen (%)
PAC599A	67.39	9.22	11.25
PAC589B	64.98	9.86	8.03
PAC603	73.77	8.20	–

Dr. B. Grant Poohbah, Ph.D.
Director of Analytical Services
Microanalytical Company, Inc

1.2 DETERMINATION OF MOLECULAR MASS

1.3 MOLECULAR FORMULAS

Ethane provides a simple example. After quantitative element analysis, the empirical formula for ethane is found to be $\mathbf{CH_3}$. A molecular mass of 30 is determined. The empirical formula weight of ethane, 15, is half of the molecular mass, 30. Therefore, the molecular formula of ethane must be $2(CH_3)$ or C_2H_6.

1.4 INDEX OF HYDROGEN DEFICIENCY

Frequently, a great deal can be learned about an unknown substance simply from knowledge of its molecular formula. This information is based on the following general molecular formulas:

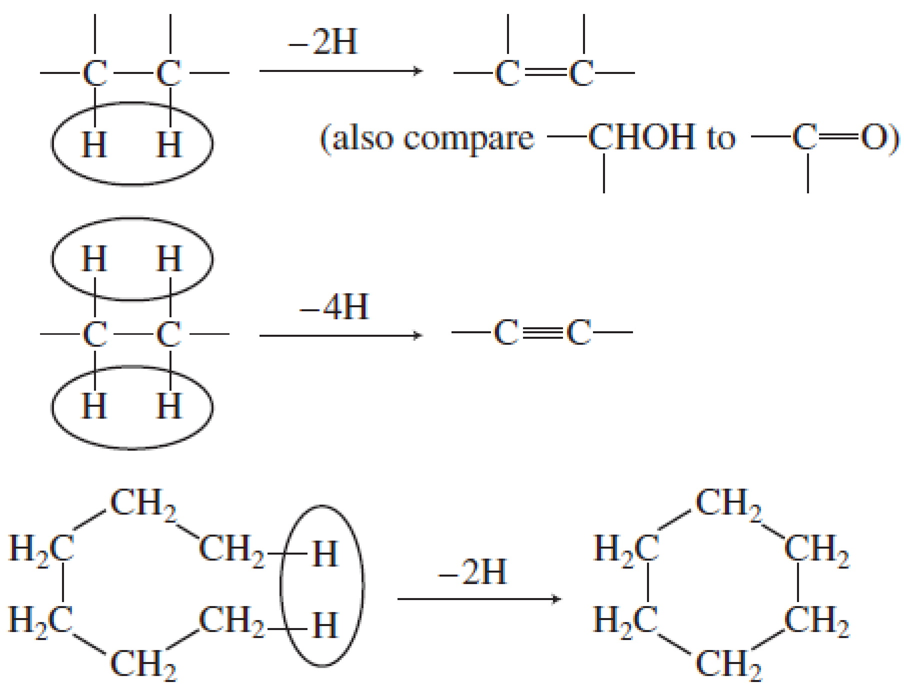
alkane	C_nH_{2n+2}	Difference of 2 hydrogens
cycloalkane or alkene	C_nH_{2n}	Difference of 2 hydrogens
alkyne	C_nH_{2n-2}	

1. To convert the formula of an open-chain, saturated hydrocarbon to a formula containing Group V elements (N, P, As, Sb, Bi), one additional hydrogen atom must be *added* to the molecular formula for each such Group V element present. In the following examples, each formula is correct for a two-carbon acyclic, saturated compound:

C_2H_6, C_2H_7N, $C_2H_8N_2$, $C_2H_9N_3$

2. To convert the formula of an open-chain, saturated hydrocarbon to a formula containing Group VI elements (O, S, Se, Te), *no change* in the number of hydrogens is required. In the following examples, each formula is correct for a two-carbon, acyclic, saturated compound:

C_2H_6, C_2H_6O, $C_2H_6O_2$, $C_2H_6O_3$



3. To convert the formula of an open-chain, saturated hydrocarbon to a formula containing Group VII elements (F, Cl, Br, I), one hydrogen must be *subtracted* from the molecular formula for each such Group VII element present. In the following examples, each formula is correct for a two-carbon, acyclic, saturated compound:

C_2H_6, C_2H_5F, $C_2H_4F_2$, $C_2H_3F_3$

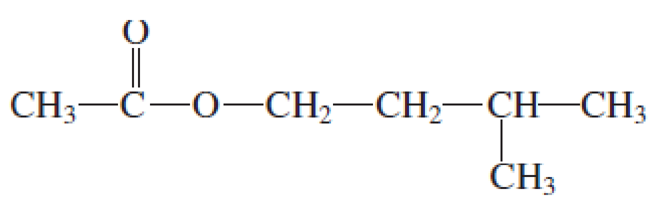
TABLE 1.3

CORRECTIONS TO THE NUMBER OF HYDROGEN ATOMS WHEN GROUP V AND VII HETEROATOMS ARE INTRODUCED (GROUP VI HETEROATOMS DO NOT REQUIRE A CORRECTION)

Group	Example	Correction	Net Change
V	C—H → C—NH_2	+1	Add nitrogen, add 1 hydrogen
VI	C—H → C—OH	0	Add oxygen (no hydrogen)
VII	C—H → C—Cl	–1	Add chlorine, lose 1 hydrogen

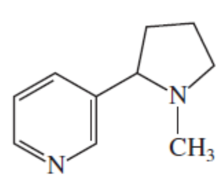
Example 1:

The unknown substance introduced at the beginning of this chapter has the molecular formula $C_7H_{14}O_2$.



Example 2:

Nicotine has the molecular formula $C_{10}H_{14}N_2$.



1.5 THE RULE OF THIRTEEN

$$\frac{M}{13} = n + \frac{r}{13}$$

The base formula thus becomes

$$C_nH_{n+r}$$

$$U = \frac{(n - r + 2)}{2}$$

To comprehend how the Rule of Thirteen might be applied, consider an unknown substance with a molecular mass of 94 amu. Application of the formula provides

$$\frac{94}{13} = 7 + \frac{3}{13}$$

According to the formula, $n = 7$ and $r = 3$. The base formula must be

$$C_7H_{10}$$

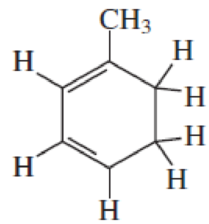
The index of hydrogen deficiency is

$$U = \frac{(7 - 3 + 2)}{2} = 3$$

TABLE 1.4
CARBON/HYDROGEN EQUIVALENTS FOR SOME COMMON ELEMENTS

Add Element	Subtract Equivalent	Add ΔU	Add Element	Subtract Equivalent	Add ΔU
C	H_{12}	7	^{35}Cl	C_2H_{11}	3
H_{12}	C	−7	^{79}Br	C_6H_7	−3
O	CH_4	1	^{79}Br	C_5H_{19}	4
O_2	C_2H_8	2	F	CH_7	2
O_3	C_3H_{12}	3	Si	C_2H_4	1
N	CH_2	$\frac{1}{2}$	P	C_2H_7	2
N_2	C_2H_4	1	I	C_9H_{19}	0
S	C_2H_8	2	I	$C_{10}H_7$	7

A substance that fits this formula must contain some combination of three rings or multiple bonds. A possible structure might be

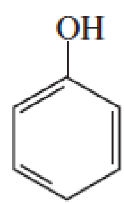


C_7H_{10}

$U = 3$

1. Base formula = C_7H_{10} $\quad U = 3$
2. Add: $+ O$
3. Subtract: $- CH_4$
4. Change the value of U: $\quad \Delta U = 1$
5. New formula = C_6H_6O
6. New index of hydrogen deficiency: $\quad U = 4$

A possible substance that fits these data is



C_6H_6O

$U = 4$

There are additional possible molecular formulas that conform to a molecular mass of 94 amu:

$C_5H_2O_2$	$U = 5$	C_5H_2S	$U = 5$
C_6H_8N	$U = 3\frac{1}{2}$	CH_3Br	$U = 0$

1.6 THE NITROGEN RULE

Another fact that can be used in determining the molecular formula is expressed as the **Nitrogen Rule.** This rule states that when the number of nitrogen atoms present in the molecule is odd, the molecular mass will be an odd number; when the number of nitrogen atoms present in the molecule is even (or zero), the molecular mass will be an even number. The Nitrogen Rule is explained further in Chapter 3, Section 3.6.