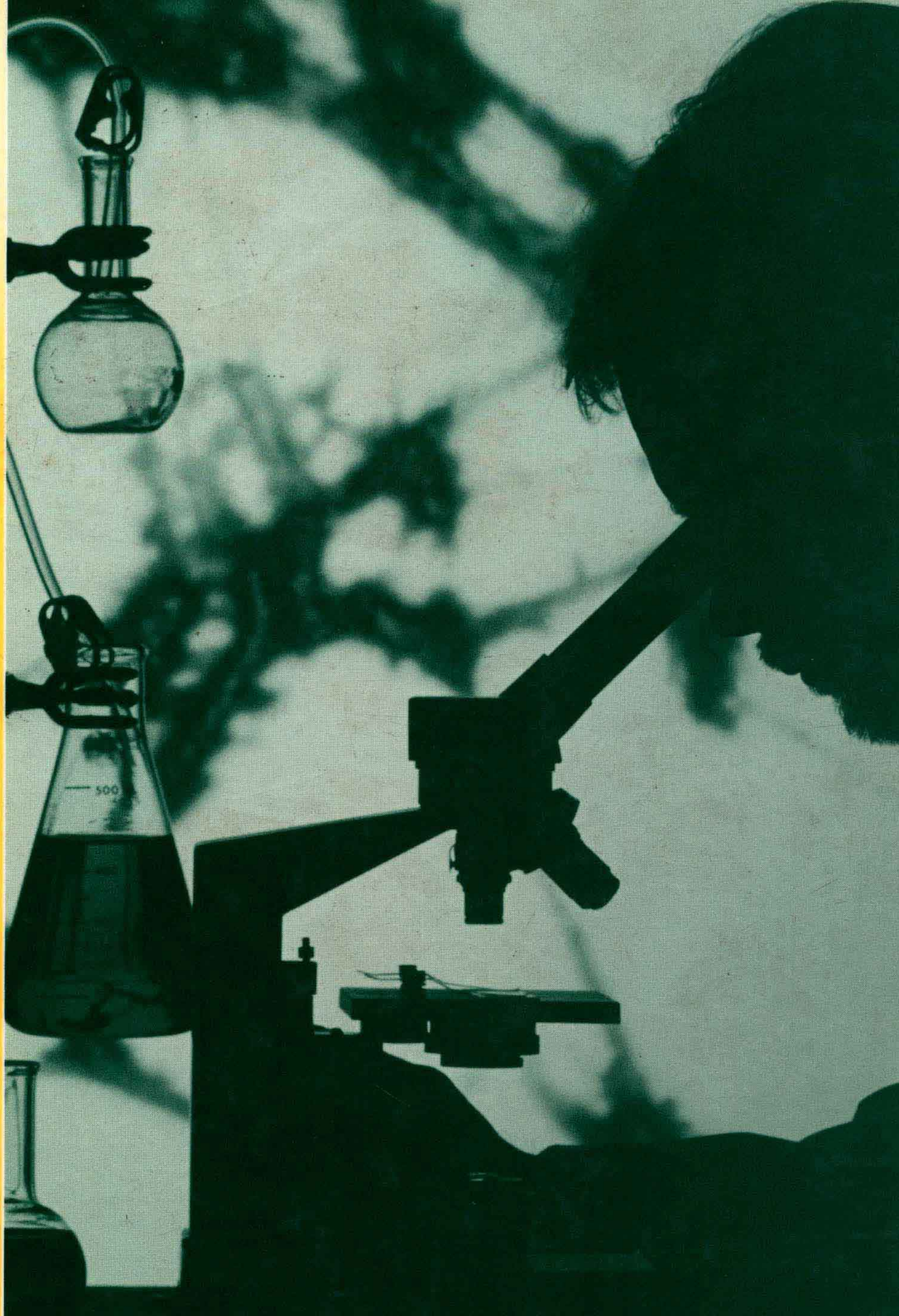

Rod O'Connor

ADVANCED PROBLEMS IN APPLIED CHEMISTRY

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PREFACE

This is not a "textbook" of chemistry. Instead, it is designed as an introduction for the beginning student, or as a review for those more advanced in the field but somewhat "rusty" in certain areas. The book deals with methods and skills used in solving problem situations in some of the more important, and practical, areas of chemistry, and it is best used in conjunction with a chemistry textbook or other supplementary material. The book's purpose is to provide practice and/or review for those seeking competency or proficiency in chemical problem solving, especially in the areas of chemical equilibrium, stoichiometry, and thermochemistry.

It is not essential that all Units be studied or that they be followed in any particular sequence. You may wish to concentrate your efforts on those Units whose topics represent areas of some difficulty, thus needing extra practice, or on Units in which you have some particular interest in achieving greater proficiency

Each Unit begins with a brief summary of pertinent background information. Following this introduction are brief statements of learning objectives at two levels, *competency* and *proficiency*. The distinction between these levels is basically that we would consider a *competency* level to be roughly that of a C to B student in a typical university chemistry class, while the *proficiency* level corresponds to that of a typical B+ to A student. (All *proficiency* level material is identified by an asterisk [*].)

Immediately following the statements of objectives are *Pre-Test* questions, at both levels. Successful completion of the *competency* level questions offers you a choice of proceeding on to *proficiency* level work, working an *competency* level problems for added practice, or terminating — if the *competency* level is sufficient for your personal needs. If you have difficulties with the *competency level Pre-Test*, then you should study the "Methods" work at that level. Successful completion of the *proficiency level Pre-Test*, or the final *Self-Test* questions based on the *proficiency* level "Methods" work, offers you the choice of terminating or proceeding on to the more challenging *Relevant Problems* of your choice.

The *Relevant Problems* are arranged in four categories: (A) *Agriculture and Marine Sciences*, (B) *Biological and Medical Sciences*, (I) *Industrial Chemistry*, and (E) *Environmental Sciences*. Problem solving may thus be practiced in an area related to personal interests or, by working problems from more than one set, as exercises in examining a broad scope of chemical applications.

Your comments, questions, or suggestions would be welcomed. Please, address any correspondence to

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INTRODUCTION

PROBLEM SOLVING

Some people seem to have an intuitive grasp of how to approach a problem to obtain a rapid and efficient solution. Although there is little doubt that some are more gifted than others in this respect, it is a talent that can be acquired. Proficiency in this skill, as in all skills, improves with practice.

When a mechanically inept customer takes his car to a mechanic with the complaint that it is getting poor gas mileage and makes a "funny rumbling sound," this poses a problem for the mechanic. Although the talented mechanic might not express it this way, his approach to this problem involves certain distinguishable phases:

1. Identification of what he wants to find out
2. Recognition of what information is given that might be useful
3. Identification of other information needed, but not given (i.e., information that must be obtained from memory and from other sources)
4. Selection of a method of attack on the problem
5. Manipulation of information and tools to achieve a solution
6. Checking that the solution is probably satisfactory

For the mechanic, these steps might involve:

1. Finding out what is causing the poor gas mileage and unusual engine noise
2. Given: poor mileage + "funny rumbling sound"
3. Other information: memory of previous experience with similar problems + application of various suitable test instruments + other pertinent observations
4. Selecting parts to be replaced, adjustments to be made, and tools to be used
5. Fixing the engine
6. Test driving

This system is a general one for solving all kinds of problems. It is the basis for most scientific research, and it is the key to solving all sorts of mathematical problems. The more problems you solve, the easier it becomes, until you, like the competent mechanic, can solve problems without formally thinking out each step of the method. Until the stage of "intuitive" proficiency is reached, however, it is worthwhile to proceed slowly and systematically through the various phases of problem solving.

Let us illustrate the approach by a "case study" of three problems.

PROBLEM 1

A dozen assorted ball bearings weighs 180g. What is the average mass of a bearing in this assortment?

SOLUTION

Step 1: Find: *mass per bearing* (in grams)
Step 2: Given: *180g per dozen* (of bearings)
Step 3: Needed, not given: *How many items per dozen?*
Answer (from memory): 12 per dozen
Step 4: Method of attack:
Divide mass by number to find average mass of each. Use unity factor method.
Step 5: Manipulation:

$$\frac{180\text{g}}{\cancel{\text{dozen}}\text{ (bearings)}} \times \frac{1\ \cancel{\text{dozen}}}{12} = \frac{180\text{g}}{12\text{ (bearings)}} = 15\text{g (per bearing)}$$

Step 6: Check:
a. Dimensions canceled properly
b. Math check:
$15\text{g} \times 12 = 180\text{g}$

PROBLEM 2

A manufacturing concern plans to distribute nut/bolt/washer sets. Each set will consist of one 18.5g nut, one 31.0g bolt, and two 5.50g washers. The sets will be sold in "1-dozen set" packages. What will be the net mass of each package?

SOLUTION

Step 1: Find: *net mass of a "1-dozen" package of the sets*
Step 2: Given: *1 nut/set @ 18.5g/nut; 1 bolt/set @ 31.0g/bolt;*
washers/set @ 5.50g/washer; 1 dozen per package
Step 3: Needed, not given:
How many items per dozen?
Answer (from memory): 12 per dozen
What does "net mass" mean?
Answer (from memory): mass of package contents (i.e., 1 dozen sets)
Step 4: Method of attack:
Find the mass of each set and multiply by the number of sets per package.
Use unity factor method where appropriate.
(*Note:* Often there is no unique method of attack. Here, for example, we might have decided to find the mass of 1 dozen nuts, 1 dozen bolts, and 2 dozen washers and then added these together.)

Step 5: Manipulation:

$$\left[\frac{18.5\text{ g}}{1\ \cancel{\text{nut}}} \times \frac{1\ \cancel{\text{nut}}}{1\text{ set}}\right] + \left[\frac{31.0\text{ g}}{1\ \cancel{\text{bolt}}} \times \frac{1\ \cancel{\text{bolt}}}{1\text{ set}}\right] + \left[\frac{5.50\text{ g}}{1\ \cancel{\text{washer}}} \times \frac{2\ \cancel{\text{washers}}}{1\text{ set}}\right]$$

$$= \frac{[18.5 + 31.0 + (2)(5.50)]\text{ g}}{1\text{ set}} = \frac{60.5\text{ g}}{1\text{ set}}$$

$$\frac{60.5\text{ g}}{1\ \cancel{\text{set}}} \times \frac{1\ \cancel{\text{dozen sets}}}{1\text{ pkg}} \times \frac{12}{1\ \cancel{\text{dozen}}} = \frac{(60.5 \times 12)\text{ g}}{1\text{ pkg}}$$

Estimate

$$6.05 \times 10^1 \times 1.2 \times 10^1 \times 6 \times 1 \times 10^2\ (\sim 600)$$

Solve

$$\frac{(6.05 \times 1.2 \times 10^2)\text{ g}}{1\text{ pkg}} = 7.26 \times 10^2\text{ g} \quad (726\text{ g/pkg})$$

Step 6: Check:
a. Dimensions canceled properly
b. Arithmetic rechecked for accuracy

*PROBLEM 3

What is the maximum mass of nut/bolt/washer sets, as described in Problem 2, that could be prepared from 8.00kg of nuts, 18.2kg of bolts, and 12.2kg of washers?

SOLUTION

Step 1: Find: maximum mass of sets from given masses of components
Step 2: Given: 8.00kg of nuts, 18.2kg of bolts, 12.2kg of washers
Step 3: Needed, not given:
Composition of a set
Answer: (Given in Problem 2)
1 nut + 1 bolt + 2 washers
Masses of components
Answer: (Given in Problem 2)
18.5g/nut, 31.0 g/bolt, 5.50 g/washer
Mass of a set
Answer: (Found during solution to Problem 2)
60.5g/set
Step 4: Method of attack:
The word "maximum" in the problem suggests that there is some limitation other than just the sum of the masses of the components given. It must be recognized that we can no longer make sets when we run out of any one component. Thus, the *maximum* mass of sets will correspond

to the mass obtainable from the limiting component (i.e., the *smallest* of the masses of sets obtainable from the masses of each component available). Since we are dealing with masses (rather than numbers), some appropriate equivalents would be useful in constructing unity factors:

18.5g nuts = 60.5g sets
31.0g bolts = 60.5g sets
(2 × 5.50)g washers = 60.5g sets

Then we must calculate the mass of sets obtainable by using up all of each component available and select the smallest of these values as the limit on the mass of sets obtainable.

Step 5: Manipulation:
From nuts

$$\frac{60.5\text{g sets}}{18.5\text{g nuts}} \times \frac{8.00\text{kg nuts}}{1} = 26.2\text{kg sets}$$

From bolts

$$\frac{60.5\text{g sets}}{31.0\text{g bolts}} \times \frac{18.2\text{kg bolts}}{1} = 35.5\text{kg sets}$$

From washers

$$\frac{60.5\text{g sets}}{11.0\text{g washers}} \times \frac{12.2\text{kg washers}}{1} = 67.1\text{kg sets}$$

Since our calculations show that we shall run out of nuts when 26.2kg of sets have been constructed, the maximum mass of sets obtainable is 26.2kg.

Step 6: Check:
a. Dimensions cancel
b. Arithmetic rechecked for accuracy
c. Logic rechecked

Each new problem poses its own unique challenges, and there is no "magic formula" for problem solving. The stepwise approach suggested should prove useful in establishing a systematic technique. Facility will improve with practice.

Contents

PART I

STOICHIOMETRY

UNIT 1

CHEMICAL FORMULAS

A chemical formula uses a combination of element symbols and subscript numbers to represent a compound or polyatomic grouping:

sodium chloride	methane	nitrate ion
$NaCl$	CH_4	NO_3^-

Three general types of formulas are of considerable utility in chemistry. *Empirical formulas*, indicating only the simplest whole number ratio of combined atoms, are most useful for simple inorganic compounds such as potassium bromide (KBr) or magnesium sulfate ($MgSO_4$). Such formulas reveal little information about more complex species. Carbon, for example, forms a tremendous variety of covalent compounds (organic compounds), and empirical formulas provide no real description of most organic compounds. Such different species as benzene and acetylene, for example, are both represented by CH, while a number of complex sugars have the empirical formula CH_2O. (Does this seem appropriate for a "carbohydrate"?)

Molecular formulas indicate the *actual* number of each kind of atom in a unique chemical combination. Such formulas thus distinguish between benzene (C_6H_6) and acetylene (C_2H_2). Molecular formulas, such as $C_6H_{12}O_6$ for glucose, are sufficient for many purposes, including stoichiometric calculations.

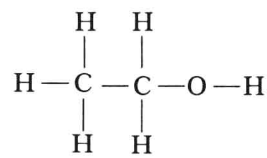
Structural formulas of various types show how atoms are connected in molecules or polyatomic ions. These formulas may be relatively simple, such as $CH_3CH_2CH_3$ for propane, or—in expanded forms—they may offer more sophisticated descriptions of structure, ranging from two-dimensional formulations to representations of three-dimensional characteristics. To write structural formulas, we need to know a fair amount about chemical bonding and some common conventions. The experimental evidence required and its interpretation may be quite complex.

Empirical and molecular formulas can be determined from relatively simple experimental data, using rather straightforward mathematical techniques. Since more knowledge and experience are required for interpreting structural information, we shall reserve this topic for more detailed texts.

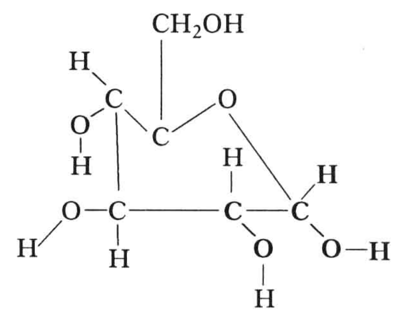
a compressed structural formula for ethyl alcohol

C_2H_5OH

an expanded structural formula for ethyl alcohol



a 3-dimensional structural formula for α-D-glucose



OBJECTIVES

(1) Given the percentage composition of a compound, be able to calculate its empirical formula

(2) Given the formula weight and the empirical formula of a compound, be able to calculate its molecular formula

(3) Given appropriate analytical data for a binary (two-element) compound, be able to calculate its empirical formula

*(4) Given appropriate analytical data for a multielement compound, be able to calculate its empirical formula

*(5) Given the empirical formula of a volatile compound and vapor density data, be able to calculate the molecular formula

PRE-TEST

Necessary Atomic Weights:

carbon (C)	12.01	nitrogen (N)	14.01
copper (Cu)	63.54	oxygen (O)	16.00
hydrogen (H)	1.008	sulfur (S)	32.06

(1) A red-orange dye called Alizarin is an organic compound consisting of 70.02% carbon, 3.36% hydrogen, and 26.64% oxygen (each analysis being accurate to ± 0.01%). What is the empirical formula for Alizarin? ____________

(2) The formula weight of Alizarin is 240.2. What is its molecular formula? ____________

(3) A sulfide of copper was treated with acid in such a way as to convert essentially all the sulfur to hydrogen sulfide (H_2S). If a 0.8144g sample of the copper salt produced 0.1744g of hydrogen sulfide, what was the empirical formula of the original salt? ____________

*(4) Combustion of a 0.3082g sample of hexamethylenediamine, a compound used in the production of Nylon-66, formed 0.7003g of carbon dioxide and 0.3821g of water. A separate nitro- gen assay, using 1.270g of the compound, produced 0.3723g of ammonia (NH_3). What is the empirical formula of the original compound? ____________

*(5) The vapor density of a sample of hexamethylenediamine, corrected to standard temperature and pressure (STP), was reported as 5.19g liter^{-1}. Using the information that 22.4 liters of gas, under ideal conditions, contains 1.00 mole of the gas at STP, calculate the molecular formula of this compound. ______________

ANSWERS AND DIRECTIONS

(1) $C_7H_4O_2$, (2) $C_{14}H_8O_4$, (3) Cu_2S. If all are correct, go on to *(4) and *(5) or to Relevant Problems, Unit 1. If you missed any, study Methods, Sections 1.1 through 1.3. *(4) C_3H_8N, *(5) $C_6H_{16}N_2$. If both are correct, go on to Relevant Problems, Unit 1.

If you missed either, study Methods, Sections 1.4 and 1.5.

METHODS

1.1 Empirical Formula from Percentage Composition

Each chemical element has its own atomic weight (Table 1.1), which may be thought of as the average mass of an atom of the element, expressed in *amu* (atomic mass units). The empirical formula of a compound shows the relative *number* of atoms, while the percentage composition of a compound shows the *mass* relationships. If we think of the percentage of an element in a compound as "amu's of element per 100 amu of compound," we can use such data with atomic weights to obtain the relative numbers of atoms.

For example, let's consider a simple compound of carbon and hydrogen, propane (81.72% C, 18.28% H). Using unity factors we can determine an atomic ratio:

$$\frac{81.72 \text{ amu (C)}}{100 \text{ amu (cpd)}} \times \frac{100 \text{ amu (cpd)}}{18.28 \text{ amu (H)}} \times \frac{1 \text{ atom (C)}}{12.01 \text{ amu (C)}} \times \frac{1.008 \text{ amu (H)}}{1 \text{ atom (H)}}$$

$$= 0.3752 \text{ atom(C)/atom(H)}$$

We could express this as an empirical formula, $C_{0.3752}H_1$, but conventionally we use only whole numbers in empirical formulas. What is the simplest number that can be multiplied by both 0.3752 and 1 to yield whole numbers? If we note that 0.3752 is about 3/8 (Table 1.2), then it is apparent that we should multiply both subscripts by 8:

$$C_{(3/8 \times 8)}H_{(1 \times 8)} = C_3H_8$$

In general, such a procedure will work for relatively simple compounds. With the more complex compounds it is usually more profitable to omit calculation of an empirical formula, if an accurate molecular weight is available, and determine the molecular formula directly.

Note that it does not matter which element is selected for "comparison." Had we chosen to calculate atoms (H)/atom (C) for propane, for example, we would have obtained $C_1H_{2.67}$ and, noting that 2.67 is about $2\frac{2}{3}$ (8/3), whole numbers would have been obtained by multiplying by 3:

$$C_{(1 \times 3)}H_{(8/3 \times 3)} = C_3H_8$$

Table 1.1 **Atomic Weights of Some Common Elements**
(four significant figures)

Symbol	*Name*	*Atomic Weight*	*Symbol*	*Name*	*Atomic Weight*
Al	aluminum	26.98	H	hydrogen	1.008
As	arsenic	74.92	I	iodine	126.9
B	boron	10.81	Li	lithium	6.939
Ba	barium	137.3	Mg	magnesium	24.31
Br	bromine	79.91	Mn	manganese	54.94
C	carbon	12.01	N	nitrogen	14.01
Ca	calcium	40.08	Na	sodium	22.99
Cl	chlorine	35.45	O	oxygen	16.00
Cu	copper	63.54	P	phosphorus	30.97
Cr	chromium	52.00	S	sulfur	32.06
F	fluorine	19.00	Si	silicon	28.09
Fe	iron	55.85	Zn	zinc	65.37

(See Appendix A for complete listing.)

Table 1.2 **Some Decimal/Fraction Equivalents**

Decimal	*Fraction*	*Decimal*	*Fraction*	*Decimal*	*Fraction*
$0.08\overline{3}$	1/12	$0.36\overline{36}$	4/11	0.625	5/8
$0.09\overline{09}$	1/11	0.375	3/8	$0.63\overline{63}$	7/11
$0.\overline{11}$	1/9	0.4	2/5	0.66	2/3
0.125	1/8	$0.41\overline{66}$	5/12	0.7143	5/7
0.1429	1/7	0.4286	3/7	$0.72\overline{72}$	8/11
$0.16\overline{6}$	1/6	$0.4\overline{4}$	4/9	0.75	3/4
$0.18\overline{18}$	2/11	$0.45\overline{45}$	5/11	$0.7\overline{7}$	7/9
0.2	1/5	0.5	1/2	0.8	4/5
0.22	2/9	0.5454	6/11	$0.81\overline{81}$	9/11
0.25	1/4	$0.5\overline{5}$	5/9	$0.83\overline{3}$	5/6
$0.27\overline{27}$	3/11	0.5714	4/7	0.8571	6/7
0.2857	2/7	$0.583\overline{3}$	7/12	0.875	7/8
$0.3\overline{3}$	1/3	0.6	3/5	$0.8\overline{8}$	8/9

(A bar above a number, or pair of numbers, indicates repetitive digits, e.g., $1.3\overline{3} = 1.33333 \ldots$.)

EXAMPLE 1

Lactic acid, formed in the body during muscle activity, consists of 40.00% C, 6.71% H, and 53.29% O. What is its empirical formula?

SOLUTION

Since the compound contains three elements, we'll have to find atomic ratios twice, using the same "comparison" element. Let's try hydrogen:

$$1.\quad \frac{40.00 \text{ amu (C)}}{100 \text{ amu (cpd)}} \times \frac{100 \text{ amu (cpd)}}{6.71 \text{ amu (H)}} \times \frac{1 \text{ atom (C)}}{12.01 \text{ amu (C)}} \times \frac{1.008 \text{ amu (H)}}{1 \text{ atom (H)}}$$

$$= 0.500 \text{ atom (C)/atom (H)}$$

$$2.\quad \frac{53.29 \text{ amu (O)}}{100 \text{ amu (cpd)}} \times \frac{100 \text{ amu (cpd)}}{67 \text{ amu (H)}} \times \frac{1 \text{ atom (O)}}{16.00 \text{ amu (O)}} \times \frac{1.008 \text{ amu (H)}}{1 \text{ atom (H)}}$$

$$= 0.500 \text{ atom (O)/atom (H)}$$

Hence, the empirical formula for lactic acid is $C_{0.5}H_1O_{0.5}$ or, in conventional whole-number form,

$$C_{(0.5 \times 2)}H_{(1 \times 2)}O_{(0.5 \times 2)} = CH_2O$$

Note that subscripts of unity (1) are understood and not written.

EXERCISE 1

Phenylpyruvic acid is produced in the body in abnormal amounts as the result of a molecular disease called phenylketonuria, which causes irreversible brain damage. Phenylpyruvic acid is composed of 65.85% C, 4.91% H, and 29.24% O. What is its empirical formula?

(answer, page 13)

1.2 Molecular Formula from Formula Weight and Empirical Formula

The formula weight of a compound is the sum of all atomic weights of its component atoms, as expressed by its molecular formula. For example, for glucose, $C_6H_{12}O_6$, the formula weight is determined by

$$C_6 \text{ (6 carbons)}: 6 \times 12.01 = 72.06$$

$$H_{12} \text{ (12 hydrogens)}: 12 \times 1.008 = 12.096$$

$$O_6 \text{ (6 oxygens)}: 6 \times 16.00 = 96.00$$

$$180.2 \quad \text{(rounded to four figures)}$$

An *empirical* formula weight can be calculated in the same way. The molecular formula of a compound can then be determined by multiplying the subscript numbers in the empirical formula by the ratio of formula weight to empirical formula weight, since this shows us how many times the empirical formula is contained in the molecular formula.

EXAMPLE 2

The formula weight of lactic acid (Example 1) is 90.08. What is its molecular formula?

SOLUTION

From Example 1, the empirical formula is CH_2O, for which the empirical formula weight is

$$\begin{aligned} C\!: \; 1 \times 12.01 &= 12.01 \\ H_2\!: \; 2 \times 1.008 &= 2.016 \\ O\!: \; 1 \times 16.00 &= 16.00 \\ \hline & 30.03 \quad \text{(to four-places)} \end{aligned}$$

Then:

$$\frac{\text{form. wt.}}{\text{emp. form. wt.}} = \frac{90.08}{30.03} = 3$$

So the molecular formula is given by

$$C_{(1 \times 3)}H_{(2 \times 3)}O_{(1 \times 3)} = C_3H_6O_3$$

EXERCISE 2

Ethylene glycol, the compound most commonly employed in antifreeze preparations for automobile radiators, has the empirical formula CH_3O. Its molecular weight is 62.07. What is its molecular formula?

(answer, page 14)

1.3 Empirical Formula from Analytical Data

Quantitative chemical analysis can provide data useful in determining an empirical formula. In the simplest case, that of a binary (two-element) compound, it is necessary only to convert a weighed sample of the compound completely to a new compound of either of the original elements and to obtain the weight of the new compound, whose chemical formula is known. Using these weights and appropriate unity factors, it is easy to find the percentage composition, from which the empirical formula can be determined (Section 1.1). It is necessary only to recognize that there is a direct conversion between the mass units of amu and grams (as described in Unit 3), so that atomic or formula weight ratios can be expressed using any mass units.