# CALCULATIONS OF
# *Quantitative Analysis*

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# CALCULATIONS OF QUANTITATIVE ANALYSIS

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# PREFACE

Quantitative analysis presents to the student for the first time a mathematical interpretation of chemical data which have been accumulated as a result of his own experimental work. A course in quantitative analysis must provide thorough training in laboratory practice and technic, adequate explanation and instruction in fundamental physical and chemical laws as applied to the chemical system, and a basic working knowledge of the concepts of elementary mathematics as applied to these principles.

A thorough training in the methods of analytical calculations is of advantage because it provides a more fundamental understanding of the underlying principles of the various analytical determinations studied. In addition, application of mathematics to a wide variety of problems provides the student with a basic knowledge of many determinations which otherwise would be completely neglected in the ordinary course in quantitative analysis.

In arranging this book, the author has kept in mind the fact that most instructors wish to devote as much time as possible to lectures on chemical theories as applied to analytical chemistry. Consequently, the book was written in lecture style with careful sequence of thought so that the student can learn the methods of calculation from assigned readings and problems. Sufficient examples are provided to enable the student to see how each new type of problem should be approached.

The method of working problems involving percentage is so quickly developed that calculations of this type can be understood by the time the first laboratory experiment has been completed. If gravimetric analysis is considered first in the laboratory, the book is studied in its present sequence. If titrimetric analysis is to be considered first, Chapter I and Chapter II through the section on chemical factors are assigned, followed by Chapter III on the fundamental calculations of titrimetric analysis and solution strength. The problems selected were chosen on the basis of material presented in standard text-books of elementary quantitative analysis.

In order to stimulate the student's interest and imagination, as well as to supply the answer to the question so often raised in the student's mind as to the value of this type of work, the author has included a number of problems which have direct bearing on industrial applications from such fields as metallurgy, geology, and water analysis. In such problems, sufficient information is given to enable the student to understand the principles of the determinations involved and the nature of the procedures.

The author wishes to acknowledge his indebtedness to Dr. A. R. Choppin, Dean of the College of Chemistry and Physics at Louisiana State University for many helpful suggestions and criticisms. He also wishes to thank Professor Fritz Feigl, Ministerio da Agricultura, Laboratorio da Produção Mineral, Rio de Janeiro, for his criticisms and encouragement and Professor M. G. Mellon of Purdue University who read the manuscript and made many constructive criticisms.

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CHAPTER I

# INTRODUCTION

A study of chemical calculations is customarily included as a special branch of the study of quantitative analysis. The student in quantitative analysis has already had sufficient chemistry to give him a knowledge of the working tools necessary to understand the basic calculations called for in this course. Because many students have forgotten parts of their elementary chemistry course, it may be well to review the definitions and fundamental concepts of general chemistry which are most needed for the present studies.

The smallest quantity of an element which is capable of entering into chemical combination is the *atom*. An atom is made up of electrons and protons. The *electron* may be considered as the ultimate indivisible negatively charged particle. It has a mass of 0.0005484 (on a basis of $O_2/2$ having a mass of 16.00) atomic weight units. The *proton* is the positive nucleus of the hydrogen atom and is considered the building unit from which the nuclei of the heavier elements are made. A *positron* is the smallest known positively charged particle. It has the same mass as the electron. When atoms combine they form molecules. *Molecules* may be defined as the smallest units of a chemical compound which still retain the properties of the compound. When molecular compounds like acids, bases and salts are placed in water or other suitable solvents they dissociate, that is, break up into their individual ions. An *ion* is a particle which is electrically charged. The electrical charge carried by an ion determines the chemical combining power of the ion or of the atom from which it comes. The chemical combining power of atoms or ions is called *valence*, and is usually expressed by a number which indicates the relative combining power of the atom or ion as compared to hydrogen which is taken as unity. Valences of some of the more common ions are listed in Table 1.

As an aid in determining valences, the following considerations should prove helpful. Where ions are discussed it is customary to represent these ions by appropriate symbols. Thus, sodium ion is represented by the symbol, $Na^+$. We all know by this time that such a symbol serves as a chemical shorthand telling us that we are concerned with *sodium ion* having a valence of plus one. Similarly, $SO_4^{--}$ represents the *sulfate ion* having a valence of minus two.

Now let us consider a compound having the formula, TlCl (thallous chloride). At first glance we might have difficulty stating the valency of the thallous ion, since we have seldom encountered this ion before. In spite of the fact that we don't remember the valence of thallium, we can still determine its charge by noting that the compound is electrically neutral. Since we must all remember that the chloride ion, $Cl^-$, has a charge of minus one, it is obvious that if the TlCl is neutral, Tl must have a valence of plus one.

TABLE 1

VALENCES OF SOME COMMON IONS

*Monovalent*

| CATIONS | ANIONS |
|---|---|
| Ammonium ($NH_4^+$) | Bromate ($BrO_3^-$) |
| Cuprous ($Cu^+$) | Bromide ($Br^-$) |
| Hydrogen ($H^+$) | Chlorate ($ClO_3^-$) |
| Mercurous ($Hg^+$) | Chloride ($Cl^-$) |
| Potassium ($K^+$) | Cyanide ($CN^-$) |
| Silver ($Ag^+$) | Dihydrogen phosphate ($H_2PO_4^-$) |
| Sodium ($Na^+$) | Fluoride ($F^-$) |
| | Hydrogen carbonate ($HCO_3^-$) |
| | Hydroxide ($OH^-$) |
| | Iodate ($IO_3^-$) |
| | Iodide ($I^-$) |
| | Nitrate ($NO_3^-$) |
| | Nitrite ($NO_2^-$) |
| | Periodate ($IO_4^-$) |
| | Permanganate ($MnO_4^-$) |
| | Thiocyanate ($NCS^-$) |

*Divalent*

| CATIONS | ANIONS |
|---|---|
| Barium ($Ba^{++}$) | Carbonate ($CO_3^{--}$) |
| Calcium ($Ca^{++}$) | Chromate ($CrO_4^{--}$) |
| Cupric ($Cu^{++}$) | Dichromate ($Cr_2O_7^{--}$) |
| Ferrous ($Fe^{++}$) | Monohydrogen phosphate ($HPO_4^{--}$) |
| Lead ($Pb^{++}$) | Oxalate ($C_2O_4^{--}$) |
| Magnesium ($Mg^{++}$) | Oxygen ($O^{--}$) |
| Mercuric ($Hg^{++}$) | Sulfate ($SO_4^{--}$) |
| Stannous ($Sn^{++}$) | Sulfite ($SO_3^{--}$) |
| Strontium ($Sr^{++}$) | Thiosulfate ($S_2O_3^{--}$) |
| Zinc ($Zn^{++}$) | |

*Trivalent*

| | |
|---|---|
| Aluminum ($Al^{+++}$) | Ferricyanide ($Fe(CN)_6^{---}$) |
| Cerous ($Ce^{+++}$) | Phosphate ($PO_4^{---}$) |
| Chromic ($Cr^{+++}$) | |
| Ferric ($Fe^{+++}$) | |

*Tetravalent*

| | |
|---|---|
| Ceric ($Ce^{++++}$) | Ferrocyanide ($Fe(CN)_6^{----}$) |
| Stannic ($Sn^{++++}$) | |
| Zirconium ($Zr^{++++}$) | |

*Note:* Atoms in the elementary state have a valence of zero. Also, many ions exist as complexes rather than in simple forms as ordinarily indicated.

Other important terms which must be part of the vocabulary of any chemist are atomic weight and molecular weight. *Atomic weight* may be defined as that weight of an element referred to a fixed basis of oxygen taken as sixteen, $O_2/2 = 16.000$. *Molecular weight* may be defined as the sum of the atomic weights of all the atoms in the molecule of an element or a compound. It is to be noted that nothing has been said about the units in which atomic and molecular weights are expressed. The reason for this is that atomic weights, and consequently molecular weights, are relative weights. That is, sodium with its atomic weight of 22.997 is merely compared to one atom of oxygen which has an atomic weight of 16.000; oxygen being the primary standard on which all atomic weights are based. The atomic weight of oxygen was arbitrarily set at 16.000. Actually, atomic weights and molecular weights can be expressed in pounds, ounces, tons, grains, grams, etc. It is general practice, however, to express these weights in grams. The *gram atomic weight* is the atomic weight expressed in grams. Likewise, the *gram molecular weight* is the molecular weight expressed in grams.

### GRAM EQUIVALENT WEIGHT

One of the fundamental concepts of chemistry is that of equivalent weight. *Gram equivalent weight* may be defined as that weight of substance which corresponds to one gram atomic weight of hydrogen, i.e., 1.0080 grams of hydrogen. The term *corresponds to* can be explained on the basis of the equation

$$H \longrightarrow H^+ + e,$$

where H is a hydrogen atom, $H^+$ is a hydrogen ion (proton), and $e$ is one electron. Using this as the basis for defining gram equivalent weight, our definition can be made to apply to double decomposition reactions and neutralization reactions. In addition, oxidation-reduction reactions which involve the gain and loss of electrons can be defined in terms of this equation since one hydrogen atom is shown to be capable of releasing one electron. This will be discussed under the topic of oxidation-reduction in Chapter V.

Gram equivalent weights of acids and bases can usually be determined by inspection. For example, the equivalent weight of HCl is equal to the molecular weight since that weight actually contains 1 gram atom of hydrogen. Likewise, one gram molecular weight of $HNO_3$ contains 1 gram atom of hydrogen. In the case of $H_2SO_4$ the equivalent weight would ordinarily be equal to one-half the gram molecular weight, since the gram molecular weight contains 2 gram atoms of hydrogen. In the case of KOH the gram equivalent weight is equal to the gram molecular weight, since the gram molecular weight contains the exact amount of hydroxide ion necessary to react with 1 gram atom of hydrogen. $Ca(OH)_2$ contains sufficient hydroxide ions to react exactly with 2 gram atoms of hydrogen. Therefore, its gram equivalent weight is equal to one-half its gram molecular weight.

To determine the gram equivalent weights of salts all we need do is picture the salt in terms of its hydrogen equivalent. Thus, in the case of NaCl we know that it is a salt which corresponds to the acid HCl. Knowing that the equivalent weight of HCl is the same as the molecular weight of HCl, we reason that the equivalent and molecular weights of NaCl must also be the same. Now let us note that in every case considered so far, the gram equivalent weight could have been obtained by dividing the gram molecular weight by the total valence of either the anion or cation of the substance in question. With this in mind we can set up a simple rule for determining gram equivalent weights:

$$\text{Gram equivalent weight } (GEW)^* = \frac{\text{gram molecular weight } (GMW)}{\text{total valence of either cation or anion involved in the reaction}}.$$

Since this rule deviates somewhat from our observations in the preceding paragraph, some explanation is due to account for these differences. The main difference is in the words *involved in the reaction.* The reason for adding these words is that in some compounds more than one equivalent weight is possible, and the particular equivalent weight we want depends on the reaction in which we are interested at that moment. Thus, in the case of Mohr's salt, which has the formula $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, reactions are possible involving ferrous ions, ammonium ions, or sulfate ions. The *GEW* will depend on which ion we are talking about,

$$GEW \text{ (in respect to } Fe^{++}) = \frac{GMW \text{ of } FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}{2} = \frac{392}{2} = 196 \text{ grams.}$$

$$GEW \text{ (in respect to } NH_4^{+}) = \frac{GMW \text{ of } FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}{2} = \frac{392}{2} = 196 \text{ grams.}$$

$$GEW \text{ (in respect to } SO_4^{++}) = \frac{GMW \text{ of } FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O}{4} = \frac{392}{4} = 98 \text{ grams.}$$

* The expression used here applies only to ordinary neutralization and double decomposition reactions. Equivalent weights of oxidizing and reducing agents are discussed in Chapter V. Where complex ion formation is encountered equivalency is determined according to the particular reaction involved.

Another important example of the significance of the words *involved in the reaction*, which will be considered later, is the case of certain reactions such as the neutralization of $Na_2CO_3$. Here neutralization may occur when the sodium hydrogen carbonate has been formed (as indicated when phenolphthalein is used as the indicator)

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl, \qquad (1)$$

or neutralization may be considered to be that point at which all sodium carbonate has been converted to carbonic acid (as is the case when methyl orange is used as the indicator)

$$Na_2CO_3 + 2HCl \longrightarrow H_2CO_3 + 2NaCl. \qquad (2)$$

The *GEW* of sodium carbonate for equation (1) would be $\frac{Na_2CO_3}{1}$, while for equation (2) it would be $\frac{Na_2CO_3}{2}$.

The illustration above also points out the significance of the words *total valence*. By total valence we mean the ordinary valence of the ion in question multiplied by the subscript of that ion in the particular formula concerned.

## PROBLEMS

1. Calculate the gram molecular weights for the following:
   a) $CaCO_3$ b) $NaCl$ c) $KCl$ d) $H_2SO_4$ e) $NH_4NO_3$ f) $HCl$ g) $FeCl_3 \cdot 6H_2O$ h) $Al_2O_3$ i) $Pb(NO_3)_2$
2. Calculate the gram equivalent weights of the compounds listed in Problem 1.
3. Find the gram molecular weights and gram equivalent weights of the following compounds. Where more than one gram equivalent weight is possible, calculate all of them and indicate the particular ion each *GEW* refers to.
   a) $Ag_2SO_4$ b) $KHC_2O_4$ c) $K_2C_2O_4 \cdot H_2O$ d) $KHF_2$ e) $K_2SO_4 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ f) $Mg_2P_2O_7$
4. What are the valences of the ions indicated in the following formulas?
   a) $Zr(NO_3)_4$ b) $Ce_2(SO_4)_3$ c) $Ce(SO_4)_2$ d) $UO_2SO_4$ e) $Na_2C_2O_4$ f) $Th(NO_3)_4$ g) $Na_2UO_4$ h) $CaWO_4$ i) $K_2PtCl_6$ j) $(NH_4)_2MoO_4$

5. Indicate the gram equivalent weights for the following compounds. Thus, *GEW* of $H_2SO_4$ is $\frac{H_2SO_4}{2}$, etc.

a) $Al_2(SO_4)_3$
b) $SrSO_3$
c) $MnSO_4 \cdot H_2O$
d) $H_3PO_4$
e) $CuSO_4 \cdot 5H_2O$
f) $Y_2(SO_4)_3$
g) $NaNO_3$
h) $FePO_4$
i) CsI
j) $CCl_4$
k) $CaSiO_3$
l) BaS
m) $AlF_3$
n) $Ag_2Te$
o) AgCl
p) KNCS
q) $Na_2CrO_4$
r) $Hg(NO_3)_2$
s) $PbI_2$
t) $Co_2O_3$

6. Calculate the gram equivalent weights of the following substances:

a) HCl
b) $CaCO_3$
c) NaCl
d) $Fe_2O_3$
e) NaOH
f) $H_2SO_4$

*Ans.* (a) 36.47; (b) 50.00; (c) 58.45; (d) 26.62; (e) 40.00; (f) 49.04.

7. Indicate the gram equivalent weights for the following acids and bases:

a) $HNO_3$
b) $Ca(OH)_2$
c) $HNO_2$
d) KOH
e) $H_2C_2O_4$
f) $H_3PO_4$
g) HBr
h) $NH_4OH$

## CHAPTER II

# CHEMICAL FACTORS AND THE FUNDAMENTAL CALCULATIONS OF GRAVIMETRIC ANALYSIS

Quantitative analysis may be defined as the exact determination of the composition of a substance, or the determination of one or more of the constituents of a substance. The results of a quantitative analysis may be expressed in a number of ways, among which are parts per million, parts per hundred thousand, grains per gallon, grams per hundred milliliters, percentage by volume, and percentage by weight. Percentage by weight has been most widely adopted, and consequently, most of our calculations will deal with percentage composition.

Percentage is defined as a proportionate amount or quantity in or for each hundred. Expressed in the form of an equation or formula, this is

$$\text{Percentage of substance} = \frac{(\text{weight of substance found}) \times 100}{\text{weight of sample}}.$$

An example will serve to show the method of this type of calculation.

*Example* 1. A mixture of pure quartz sand ($SiO_2$) and sodium chloride was analyzed to determine the percentage of $SiO_2$. When 2.500 grams of the mixture were extracted with water, an insoluble residue of pure $SiO_2$ was obtained which weighed 0.9850 gram. What was the percentage of $SiO_2$ in the mixture?

*Solution:*

$$\text{Percentage of } SiO_2 = \frac{(\text{weight of } SiO_2 \text{ found}) \times 100}{\text{weight of sample}}.$$

Substituting,

$$\text{Percentage of } SiO_2 = \frac{0.9850 \times 100}{2.500} = 39.40.$$