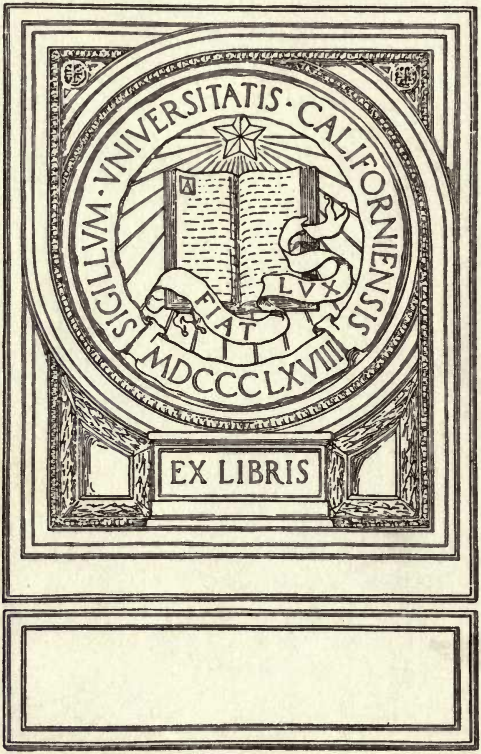
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THE CALCULATIONS
OF
GENERAL CHEMISTRY

WITH
DEFINITIONS, EXPLANATIONS, AND PROBLEMS

BY
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THIRD EDITION, REVISED

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To the Memory of

Henry Barker Hill

LATE PROFESSOR OF ORGANIC CHEMISTRY IN
HARVARD UNIVERSITY

IN APPRECIATION OF HIS MOST INSPIRING INFLUENCE
THIS BOOK
IS GRATEFULLY DEDICATED

PREFACE TO THE FIRST EDITION

THE justification for a book of this character is to be found in the realization that many of the mathematical applications of our fundamental conceptions in chemistry, even upon the most elementary points, remain uncomprehended by students several years advanced in the study of the science. The great attention given to the study of Physical Chemistry, and the far-reaching importance attached to the interpretation of chemical phenomena in the light of modern theories, make it absolutely essential that more time be given in the college courses on General Chemistry to these mathematical demonstrations.

Unless a clear and concise exposition of the methods of calculation is presented in the very first course of college work, the progress of the student is greatly hindered. On the other hand, too great a mass of mathematical data may impede rather than promote this progress. The aim, therefore, has been to limit these calculations to those subjects generally regarded as fundamental, and in which the student should receive the most complete and thorough drill. Such may rightfully constitute our "Arithmetic of Chemistry." Of the many important subjects omitted, the greater number possess a theoretical bearing which brings them more properly into those courses following General and Analytical Chemistry or into the study of Physical Chemistry itself.

The absence of mathematical training as a basis for the study of chemistry constitutes a widely prevailing defect in the education of chemists at the present day. The appearance of works on General Chemistry from the standpoint of Physical Chemistry, with their extensive adoption in our American colleges and universities, is strongly indicative of the mathematical trend in modern chemical instruction. Under this influence the presentation of the methods of chemical calculations in their simplest possible form should facilitate and extend the use of these modern texts and at the same time operate favorably in the eradication of former defects. Primarily, however, this elementary presentation is intended to accompany the laboratory work in General Chemistry and to help the student to a better understanding of the many possible conditions that may arise in the course of experimental work. The ideal plan, therefore, should be to associate these problems and their solutions with the actual laboratory practice. In the study of the last two, and possibly three, chapters only a very few correlated experiments may be found to fit properly into the laboratory courses on General Chemistry; but the important bearing of the topics here outlined upon the thorough grounding of the student's ideas of chemical reactions will make it imperative that a number of the more simple illustrations be given by way of lecture experiments. Especially is this true of those reactions relating to combinations between gases by volume.

For the greater part of material presented no originality is claimed, but gratitude is freely expressed to the authors of the many valuable and admirable treatises on Stoichiometry. In the manner of presentation a somewhat different plan has been followed from that usually found in books of this nature. This consists in a gradual introduction of each new condition properly falling under the consideration of some one subject, and the final development of the subject in its entirety from all the conditions thus considered. By this method it is thought to obviate the dogmatic manner of presenting mathematical facts and to make the student realize immediately the connection between all of our fundamental laws of energy and matter. With this train of thought connecting each and every point to that preceding, it is believed that the student will gain a better and firmer hold upon the entire subject-matter rather than upon the isolated points.

This book in itself comprises no more than is presented by the author to students in their first year of chemistry at the university. The problems at the end of each chapter serve as a guide and basis of selection for examinations throughout the course. Great emphasis, in fact, is laid upon this side of the student's development as the highest and most beneficial for his future advancement.

In general the field of use for a book of this type will be among colleges and universities. It is, however, sincerely hoped that at least the first portion of the book may have a helpful and profitable bearing upon the instruction of chemistry in the high schools.

For the many valuable suggestions and the interest with which criticism has been freely extended in the revision of the manuscript, the author expresses his sincere appreciation and lasting indebtedness to Professor Charles Loring Jackson of Harvard University, Professor Alexander Smith of the University of Chicago, and Professor S. Lawrence Bigelow of the University of Michigan.

WILLIAM J. HALE.

ANN ARBOR, May, 1909.

PREFACE TO THE SECOND AND THIRD EDITIONS

WITH a new and larger edition it has seemed best to make all possible minor changes in both text and problems. The work of revision has been greatly facilitated through the kind suggestions of those who have found the book helpful, and of others who have shown especial interest in this exposition of the subject. For all of which grateful appreciation is heartily expressed.

THE AUTHOR.

ANN ARBOR, January, 1910.
October, 1911.

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CHEMICAL CALCULATIONS.

CHAPTER I.

UNITS OF MEASUREMENT.

The fundamental units employed in chemical calculations will be defined at the outset to insure their clear and consistent use.

Time. — As the unit of time we have adopted the second, $\frac{1}{86400}$ part of the mean solar day, or that period elapsing between the successive daily transits of the sun across a meridian.

Distance or Length. — The meter as the standard of length is fixed as that distance between two marks on a platinum-iridium bar preserved in Paris when this bar is at the temperature of 0° C. It is approximately one forty-millionth of a meridian, or one ten-millionth of the earth's quadrant from pole to equator. Larger values in multiples of the meter by ten, one hundred and one thousand are named by use of the Greek prefixes, — decameter, hectometer and kilometer (km.), — while submultiples by the same values receive names from the Latin prefixes, — decimeter (dcm.), centimeter (cm.) and millimeter (mm.). The one one-hundredth part of the meter, the centimeter, is usually defined as the unit of length. As still smaller values we employ the micron (μ), the one one-thousandth of a millimeter, and the millimicron ($\mu\mu$), the one one-thousandth of a micron.

Volume and Mass. — The cubic decimeter or liter is the standard of volume. The standard of mass is the kilogram, or a mass of platinum-iridium in block form, preserved in Paris, and originally intended to have the same mass as a cubic decimeter of water at its greatest density, 4° C. It is, however, slightly less than a cubic decimeter of water which at 4° C. weighs 1.000013 kilograms. Both the liter and kilogram are somewhat large for general scientific purposes. It is customary, therefore, to use the one one-thousandth part of each, — the cubic centimeter ($cm.^3$ or c.c.) as the unit of volume and the gram (g.) as the unit of mass. The mass of 1 c.c. of water at 4° C. is considered as 1 gram. The slight discrepancy between this value and the true one need be considered only in the most exact calculations.

Through a combination of the fundamental units just mentioned we arrive at a standard system in terms of which so many of our important units of measurement may be defined. This system of units, known as the centimeter-gram-second (C.G.S.) system, has met with universal adoption throughout the scientific world. Its applications may be noted in the following paragraph.

Force and Energy. — When a body moves at a uniform rate through a unit of distance, the centimeter, in a unit of time, the second, it is said to have a unit of velocity (abbreviated cm./sec.). When the change in velocity during one second is one centimeter per second we have a unit of acceleration. That force which will give to unit mass unit acceleration is called the unit of force or *dyne*. Now the same force operating upon different bodies does not produce in each the same acceleration. When, however, the same acceleration is attained in the several cases the bodies must have equal masses. The work done by the force of one dyne in producing a displacement in its own direction of one centimeter is called the unit of work or *erg*. When a body gains or loses energy the amount of energy may be measured in units of work, and when the work done upon a body imparts to it a certain velocity, the body, by virtue of this, is said to possess kinetic energy. The amount of energy so possessed may be expressed by the formula, $E = \frac{MV^2}{2}$, in which E represents the energy, M the mass and V the velocity. Mass, then, is in itself but a "measure of the kinetic energy which a body possesses when it has a definite velocity." — Ostwald.

Standards of Temperature and Pressure.

The accuracy with which measurements are conducted requires certain definite and constant conditions of temperature and pressure, the effect of changes in which will be studied in a later chapter. The standards adopted with these factors will receive only brief mention at this point.

Temperature. — The freezing-point of pure water is taken as the normal temperature and made 0° upon the Celsius or centigrade thermometer. The boiling-point of pure water at 760 mm. pressure is registered at 100° on this scale, and the intervening range of temperature between the freezing- and boiling-points of water is divided into one hundred equal parts or degrees centigrade. As pressure exerts a considerable influence upon the boiling-points of liquids, all temperatures are referred to the normal condition of pressure.

Pressure. — The standard condition of pressure, the normal pressure, is taken as that pressure which the atmosphere exerts at sea level in a latitude of 45°. This pressure is sufficient to sustain a column of mercury, at 0° C., 76 cm. (760 mm.) in height. In a column of this height and 1 sq. cm. cross section there are exactly 76 c.c. of mercury, and since, volume for volume, mercury is 13.596 times as heavy as water and 1 c.c. of it therefore weighs this number of grams, we have at once the value $76 \times 13.596 = 1033.2$ grams as the weight of the atmosphere per square centimeter. By reference to a barometer the actual weight of the atmosphere in millimeters of mercury is observed under the various conditions. These barometric readings are usually made at other temperatures than 0° C.; the correct readings, therefore, for millimeters of mercury at 0° C. must be calculated by use of a proper table showing the expansion of mercury with temperature (Appendix I). Gases measured in vessels inverted over a liquid will of course have the same pressure as the atmosphere (recorded by the barometer) when the levels of the liquid in the vessel and outside of it are equal. The temperature of the gases and liquid should of course be alike.

CHAPTER II.

DENSITY AND SPECIFIC GRAVITY.

THE term density is used to designate the mass in unit of volume. As this is a constant for any substance under given conditions of temperature and pressure, we may call it the *absolute density*. It is expressed simply as $D = M/V$, where D, M and V represent respectively density, mass and volume. When the absolute density of one substance is referred to that of another, *i.e.*, a relation between these two densities determined upon the basis of one of them as a standard, we have a value known as the specific or *relative density*, or what has been more commonly called the *specific gravity*. The relative density of a substance is not affected by the force of gravity, since any change in this force will operate equally upon the absolute densities of all substances as well as upon the standard. The relative density or specific gravity may be defined simply as the ratio between the weight of any substance and that of an equal volume of the standard substance when this latter is considered as unity. As a standard for the specific gravity of liquids and solids, the most natural choice is distilled water, which is considered at the point of its greatest density, namely 4° C. Determinations made at other than this temperature (*e.g.* 15°) are usually referred to the density of water at 4° C., and expressed thus: sp. gr. at 15°/4°.

In the case of gases, the values obtained for the absolute densities, the number of units of mass per unit of volume, are exceedingly small. By reason of this it is more customary to multiply these values by 1000 or, what is the same thing, to determine the number of units of mass in 1 liter instead of 1 c.c. Though the densities of gases referred to some standard such as air are known as *relative densities*, the term *vapor density* meets with constant use when the relative density is determined for a liquid or solid in the state of vapor. Since the composition of the atmosphere is somewhat variable, the relative densities upon this standard cannot possess much accuracy. The employment of a pure gaseous substance, such as hydrogen, gives much better results. As the lightest gas, all other densities referred to it assume values greater than unity. The absolute density of hydrogen, the weight in grams of 1 liter at 0° and 760 mm., is 0.08987. The weight of an equal volume, 1 liter, of oxygen under the same conditions is 1.429 grams; hence with reference to hydrogen as unity, oxygen will be found to have a relative density of 15.90, *i.e.*, 1.429 is 15.90 times 0.08987, or, by simple proportion:

$$0.08987 : 1.429 = 1 : x, \quad \text{or } x = 15.90.$$

The Oxygen Standard. — The intimate relation (to be noted later) between the molecular weight of a substance and the volume which this weight occupies in the state of vapor has led us to refer all densities of gaseous substances to the density of that substance which is to serve as the basis for molecular weights. Formerly hydrogen, as the lightest substance, served this purpose, and consequently the close relationship between densities and molecular weights was apparent.

In recent times oxygen, with the value 32, has been adopted as the basis of molecular weights by reason of the great importance of this element in its numerous combinations with other elements and for reasons that will be made clear after further considerations. The absolute density of oxygen, therefore, is now taken as the standard of gas densities and made equal to unity. Upon this basis the close relationship between the densities of gases and their corresponding molecular weights will be as well attained as originally, when hydrogen was the standard. The relative densities of a number of substances, however, will fall below unity. Thus the relative density of hydrogen becomes on this scale 0.0629, a value easily derived from the simple proportion:

$$1.429 : 0.08987 = 1 : x.$$

In order to avoid these small values some chemists prefer to assign to oxygen the absolute density of 16 instead of unity. From the relations already noted between oxygen on the one hand and hydrogen, as the lightest substance, on the other, we readily see that the relative densities of all other substances are thus brought to values greater than unity. By the adoption of 32 instead of 16, as this basis of densities, the relative densities may be made to coincide at once with the molecular weights.*

Under all conditions the measure of the volumes of gases is conducted at definite temperatures and pressures. The influence of change in these factors will be discussed in the succeeding chapters. Whatever the volume of a gas may be, its relative density will be determined from the ratio of the observed weight per volume to the weight

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* Strictly speaking, an exact agreement on this basis between relative densities and molecular weights is found true only in the case of perfect gases (*cf.* footnote, p. 34). In the study of actual weights of equal volumes of gases it seems preferable, therefore, to base the comparison upon the weight of the standard as unity. The significance of the theoretical or calculated values, upon the basis of 32 as the chemical unit, will be noted in succeeding chapters.

of an equal volume of oxygen under like conditions, when this ratio is brought over to the basis of oxygen as unity.

Example 1.—The actual weight of 1 liter of carbon dioxide, at standard conditions, is 1.977 grams. One liter of oxygen weighs 1.429 grams. What is the relative density of carbon dioxide?

The ratio between these two densities is now to be referred to the density of oxygen as unity. That is, the ratio $\frac{1.429}{1.977}$ is to be made equal to the ratio $\frac{1}{x}$, where x is the relative density of carbon dioxide. We thus have $\frac{1.429}{1.977} = \frac{1}{x}$, or, as more commonly expressed,

$$1.429 : 1.977 = 1 : x.$$

From which x is found to be 1.384.

PROBLEMS.

1. A piece of metal weighing 30 grams displaced 20 c.c. of water (*i.e.*, its own volume). What is the relative density of this metal referred to water? *Ans.* 1.5.

2. A vessel weighing 6.448 grams weighed 7.963 grams when filled with water and 8.266 grams when filled with a salt solution. What is the relative density of this solution referred to water? (The temperature constant throughout.)
Ans. 1.2.

3. The weight of 1 liter of aqueous vapor at 0° and 760 mm. is 0.8045 gram. What is its relative density? *Ans.* 0.5630.

4. Calculate the relative density of mercury vapor, 1 liter of which at standard conditions (0° and 760 mm.) weighs 8.87 grams. *Ans.* 6.207.

5. Calculate the relative density of hydrogen chloride, 5 liters of which under standard conditions weigh 8.205 grams.
Ans. 1.148.

6. Calculate the relative density of chlorine, 100 c.c. of which at standard conditions weigh 0.322 gram. *Ans.* 2.253.

CHAPTER III.

THE EFFECT OF PRESSURE UPON GASES. THE LAW OF BOYLE.

The Relation of Volume to Pressure. — When a gas is subjected to increase of pressure the volume decreases. On release of the pressure the volume increases, regaining its former volume only at the original pressure. The Law of Boyle states this as follows: At constant temperature the product of the volume of a gas (V) by its pressure (P) is a constant, or $P \times V = K$. Thus a volume of gas (1) at a pressure of one atmosphere (1) will be reduced when under a pressure of two atmospheres to one-half of its original volume, or, in the equation $P \times V = K$, the values $1 \times 1 = 1$ will become $2 \times \frac{1}{2} = 1$. This constancy, however, applies to all gases, and hence the product PV in one case will be equal to the product $P'V'$ for any other case when either P or V or both change, the temperature considered constant throughout; hence the equation $PV = P'V'$.

In dividing this equation, $PV = P'V'$, through by the quantity PV' and canceling like terms in numerator and denominator, we obtain $\frac{PV}{PV'} = \frac{P'V'}{PV'}$ or $\frac{V}{V'} = \frac{P'}{P}$. The two fractional quantities may be expressed also by the proportion $V : V' = P' : P$. This is exactly what is indicated above, where a volume of gas under a definite pressure will have its volume halved under double this pressure, etc., or at constant temperature the volume of a gas is inversely proportional to its pressure (a general form for the statement of Boyle's Law). Strictly speaking, the Law of Boyle holds true only for a perfect gas. For practical purposes the law gives a sufficiently accurate means of studying volume and pressure relations.

In order to ascertain what a given volume of gas may become at some new pressure, the temperature constant throughout, we have only to apply the formula $PV = P'V'$, in which we may designate the new values by the prime marks.

Example 2. — 200 c.c. of hydrogen measured at 750 mm. pressure will occupy what volume at the standard pressure (760 mm.), temperature a constant?

$PV = P'V'$, or $V' = V\ (P/P')$. Substituting here the respective values $P' = 760$, $P = 750$ and $V = 200$, we obtain the expression $V' = 200 \times 750/760$, which is easily solved to a value of 197.3.

In general terms, we shall say that a change in the volume of any gas by change in pressure is readily calculated from the values given, by multiplying the volume by the fraction formed from the original pressure as numerator and new pressure as denominator. If this new pressure is greater than the original, then the fraction will have a value less than unity and the new volume (the product of fraction by original volume) will be proportionately less; conversely, if the new pressure is smaller than the original pressure, the fraction (formed from the pressures) becomes larger than unity in value, and the new volume must increase over that of the original. It comes, therefore, to the same end if one ask himself the question: "Is the new pressure greater or less than the original?" If greater, then the fraction formed from the pressures must be so arranged that the new volume of the gas will be smaller, *i.e.*, the fraction must have as its numerator the smaller of the two pressure values, and as its denominator the larger. This fraction less than unity in value will, as was just shown, reduce the volume which it multiplies in the correct proportion. If the new pressure is smaller than the original, the diminution in pressure must be accompanied by an expansion in volume, and, accordingly, the fraction formed from the pressures, which we may conveniently call the *pressure-fraction*, takes the larger value in the numerator and smaller value in the denominator. From the product of this fraction, greater than unity, by the original volume we obtain the new and correspondingly increased volume.

The Relation of Pressure to Volume. — Just as change in pressure produces a change in volume, so also a change in volume will produce a change in the pressure of a gas. The effect of this change in volume upon the pressure is readily determined from the equation $PV = P'V'$, and takes the form of expression:

$$P' = P\,(V/V').$$

As the new volume V' increases or decreases with reference to the original, the *volume-fraction* becomes respectively less or greater than unity in value.

Example 3. — A volume of gas measuring 100 c.c. at 750 mm. was expanded to 500 c.c. at constant temperature. What was the pressure of the gas at this final volume?

In order to arrange the fraction (formed from the volumes) in such a way as to give a value less than unity and one that will reduce the given pressure in the ratio indicated by Boyle's Law, it is necessary here to place the smaller number in the numerator. The product of this *volume-fraction* by the original pressure P, or 750 mm., gives the new pressure sought: $750 \times 100/500 = 150$.

The Relation of Density to Pressure. — The absolute density of a gas, the mass per liter, may be seen now to vary with the pressure to which the gas is subjected. With reference to the formula $D = M/V$, we are aware that the weight or mass is unaffected by any changes in temperature or pressure. The volume (V), however, is altered by either or both of these influences. Thus with an increase of pressure it decreases and hence the absolute density must increase. In other words, both the absolute density and the pressure of a definite quantity of gas vary inversely with the volume when the temperature is constant, and hence are directly proportional to each other. Therefore, in the equation $PV = P'V'$ we may substitute D for P throughout and obtain

$$DV = D'V', \text{ or } D' = D\,(V/V').$$

Example 4. — 100 c.c. of hydrogen, the absolute density of which (the weight of 1 liter) is 0.08987, will have what density when expanded to 200 c.c. in volume at a constant temperature?

Here the increase in volume means a decrease in the pressure and hence in the density. The fraction formed from the volumes, the volume-fraction, must be arranged so as to produce this decrease corresponding to Boyle's Law and, therefore, the numerator must contain the smaller of the two values. When this quantity 100/200 is multiplied by the density 0.08987, we obtain the new density 0.0449.

This is identical with saying that at this new and larger volume the actual weight of the gas has not changed, or the original weight of the 100 c.c., 0.008987 gram, has remained a constant. The mass per volume, however, has been changed, in that this weight of gas is now spread out over twice the original volume. The actual weight of 100 c.c. of the rarefied gas is just one-half of the weight of the total volume, 200 c.c., or 0.00449 gram. As a basis for calculations of this nature, that general property of homogeneous substances is of course understood: The weight of any fractional part of a volume bears the same ratio to the total weight as this fractional volume itself does to the total volume.

It should be remembered in this connection that the relative density of a solid or liquid may vary with the temperature or pressure (p. 5), since the effect of change in these factors upon the volume of a substance and upon that of the standard chosen may not be the same. The relative density of a gas, however, is constant, since changes in these factors affect all gases alike.

PROBLEMS.

7. 512 c.c. of hydrogen at a pressure of 744 mm. will occupy what volume at a pressure of 790.5 mm., the temperature constant? *Ans.* 481 c.c.

8. 240 c.c. of gas at a pressure of 740 mm. were admitted into an empty vessel of 800 c.c. capacity. What was the pressure of the gas at this new volume, temperature constant?

Ans. 222 mm.

9. 500 c.c. of oxygen, absolute density 1.429, were compressed to a volume of 125 c.c. at constant temperature. What was the density of the gas at this final volume? What would be the weight of 50 c.c. of the compressed gas?

Ans. 5.716; 0.2858 gram.

10. A volume of gas measuring 600 c.c. at 760 mm. pressure was expanded to a volume of 1000 c.c. at constant temperature. What was the final pressure of the gas, and what fractional change in its absolute density must have followed this expansion? *Ans.* 456 mm.

Density $\frac{3}{5}$ of former value.

11. 500 c.c. of a gas, the absolute density of which is 6, must be reduced to a density of 0.75 at constant temperature. What will be the volume of this rarefied gas? Calculate also the weight of 400 c.c. of the rarefied gas.

Ans. 4000 c.c.; 0.3 gram.

12. A volume of gas weighing 5 grams was expanded, at a constant temperature, till the pressure was reduced to one-half of its former value. 500 c.c. of the rarefied gas weighed 1.25 grams. What was the original volume of the gas? Calculate also the original density assuming the original observations made at standard conditions. *Ans.* 1000 c.c.

Density 5.

CHAPTER IV.

THE EFFECT OF TEMPERATURE UPON GASES. THE LAW OF CHARLES.

WITH pressure constant the volume of a gas is found to vary with the temperature. The Law of Charles (known also as Gay-Lussac's Law), states this as follows: Under constant pressure the volume of a gas varies directly with the temperature upon the absolute scale.

The Determination of the Coefficient of Expansion. — The standard condition of temperature, 0° C., becomes on the absolute scale 273°. This is calculated from the fact that, given any volume of gas at 0° C., the effect of cooling upon this gas will bring about a diminution in its volume by 1/273 for each degree centigrade below the centigrade zero, consequently at − 273° C. the volume will have been diminished by 273/273 of itself, or by its entirety. This point, therefore, is regarded as the zero point or lowest point at which a gas may possibly come under consideration. At or below this point no gas could exist as such. Though this temperature has not as yet been reached, it follows that all gases will be liquefied above it. A volume of gas measuring 273 c.c. at 0° C. would lose per degree of cooling 1/273 of itself, or a single unit of volume. At one degree of temperature above the absolute zero (designated as 1° A.) the gas, having cooled through 272° and lost 272/273 of its volume at 0° C., would consequently occupy but 1 c.c. At 2° A. its volume would be 2 c.c., having lost here 271/273 of its volume at 0° C. At 273° A. its volume would be again 273 c.c.; in fact throughout the entire range, 0° A. to 273° A., a unit of volume corresponds to a unit of temperature, and the one is therefore directly proportional to the other, *i.e.*, the volume varies directly with the temperature. Upon passing the point 273° A. the same principle holds. For each degree of temperature there is an expansion in volume corresponding to 1/273 of the volume at 273° A. or 0° C. At 283° A. the volume of a gas measuring 273 c.c. at 273° A. will have increased by 10/273 of this volume and measure 283 c.c. The rate of expansion above 0° C. is identical with that of cooling below this temperature. This ratio between the increase in volume per degree and the total volume of a gas at 0° C. — called the coefficient of expansion and often expressed decimally as 0.00367 in place of the fraction 1/273 — was determined by measuring the expansion of gases from 0° C. upward and this upon the centigrade scale; consequently the determination of the zero point on the absolute scale is made in centigrade units, and each degree of temperature centigrade must be equivalent to one degree on the absolute scale. If 273° A. is the zero of centigrade, then 283° A. is equal to 10° C. and so on. In order to preserve this direct proportionality between volume and temperature we have only to convert the centigrade temperatures into their corresponding values upon the absolute scale. By reason of the equivalence in the units we add 273° to the readings above 0° C. and subtract readings below 0° C. from 273°; the results represent absolute temperatures (designated by T in contradistinction to t for the centigrade temperatures).

With this one volume, 273 c.c. as above chosen, the absolute temperature coincides numerically throughout with the volume in cubic centimeters, and simplifies the calculations to adding or subtracting single units. Had any other volume of gas at 0° C. been considered, the same ratio between volume and temperature would be found—a direct proportionality—but the variations would not be in single units. The equation which represents this change in volume V under a definite change in temperature t (centigrade) may be simply expressed as $V' = V(1 + \alpha t)$, where α is the coefficient of expansion per degree (1/273) and t the number of degrees centigrade through which it operates. Thus for a definite rise in temperature, t, the total expansion will be equal to that fractional part of the original volume as is indicated by the quantity αt, *i.e.*, $(1/273 \times t)\,V$; and any new volume V' must be equal to the original volume V plus the total expansion:

$$V' = V + (1/273 \times t)\,V \text{ or}$$
$$V' = V\,(1 + t/273) \text{ or}$$
$$V' = V\,(1 + \alpha t).$$

It is regarded as more helpful in this work to arrange the original and new values as members of a simple proportion, in which, of course, only the absolute temperatures are considered: $V' : V = T' : T$. The application of the Law of Charles to various cases may be illustrated now by examples.

The Relation of Volume to Temperature.

Example 5. — A volume of gas measuring 200 c.c. at 20° C. will have what volume at the standard condition, 0° C.

From the direct proportionality between volume and absolute temperature we have

$$V : V' = T : T', \text{ or } V' = V\,(T'/T),$$

where T and T′ represent, respectively, the original and new temperatures expressed in absolute units. In the example above, $T = 20° + 273° = 293°$; the new temperature is 273°. The change in volume of this gas must follow according to the proportion:

$$200 : x = 293 : 273, \text{ or } x = 200\ (273/293), \text{ or } x = 186.35$$

Here we see the original volume is to be multiplied by a fraction formed from the two temperatures, the *temperature-fraction*, and again we may apply the question as in the consideration of Boyle's Law: "Is the new volume to be smaller or greater than the original volume?" If greater, then the larger number (the degrees in absolute units) must be set over the smaller in order that the fractional quantity, when multiplied by the original volume, may increase that volume in the proportion indicated by these temperature values. If the new volume is to be smaller, then the numerator must contain the smaller of the two numbers and the product accordingly will be proportionately less.

The Relation of Temperature to Volume.

Example 6. — A volume of gas measuring 100 c.c. at 17° C. was expanded by warming to a volume of 250 c.c. at constant pressure. To what temperature must the gas have been heated to bring about this expansion?

From the Law of Charles we draw up the equation $T' = T\ (V'/V)$. In conformity with the direct proportionality between volume and absolute temperature, the new temperature (T') must be greater than the original temperature. The volume-fraction thus arranged to bring about this proportional increase when multiplied by the original temperature ($T = 273° + 17° = 290°$) becomes 250/100, and the final temperature accordingly is $T' = 290\ (250/100)$ or 725°. 725° A. is equal to 452° C.

The Relation of Density to Temperature. — In consideration of the change in absolute density under change of temperature, with pressure a constant, we see from the formula $D = M/V$ that, as the volume increases, the fraction M/V (the expression for the density) must become less and less. With the volume of a gas — the denominator of this fractional quantity — becoming less, we obtain a larger quotient or a larger value for the density. Now as this change in volume is directly proportional to a change in absolute temperature, the density of a gas will decrease with an increase in its absolute temperature and increase with a decrease in this factor, — that is, under constant pressure the absolute density of a definite quantity of gas is inversely proportional to its absolute temperature or $D : D' = T' : T$.

Example 7. — A volume of hydrogen at 0° C., with the absolute density 0.08987, will have what density when expanded by heating to 10° C. at constant pressure?

From the equation above we have $D' = D\,(T/T')$. This signifies that the density given must be multiplied by a fraction formed from the two temperatures (the temperature-fraction). We should now ask the question whether, from the inverse proportionality just mentioned, the new density (D') will be greater or less than the original density (D). Here the new temperature is higher, consequently the new density will be lower, therefore the smaller number must be placed in the numerator and the value for D' can be readily calculated:

$$D' = D\,(273/283), \text{ or } 0.08987\,(273/283), \text{ or } 0.0867.$$

PROBLEMS.

13. What will be the volume of 250 c.c. of hydrogen measured at 30° when cooled to – 10° at constant pressure?
Ans. 217 c.c.

14. A rubber balloon containing 400 c.c. of oxygen measured at – 20° is subjected to a temperature of 120°. What is the increase in volume of the balloon, the atmospheric pressure constant throughout? *Ans.* 221.3 c.c.

15. A volume of gas measuring 500 c.c. at 0° was expanded by heating to 600 c.c., at constant atmospheric pressure. What was the temperature which the gas attained? *Ans.* 54.6°.

16. The absolute density of oxygen is 1.429. What would be the weight of one liter of oxygen collected at 40° and 760 mm. pressure? *Ans.* 1.246.

17. A volume of gas with the absolute density 4 and measuring 250 c.c. at 0° was expanded by warming, under constant pressure, to a volume of 600 c.c. What increase in temperature was required, and what would be the weight of 300 c.c. of the rarefied gas? *Ans.* 382.2°; 0.5 gram.

CHAPTER V.

THE COMBINED EFFECT OF TEMPERATURE AND PRESSURE UPON GASES. PARTIAL PRESSURES.

When a volume of gas is subjected to change in both temperature and pressure the relation of the original volume to the new volume must be in accordance with the two principles already enunciated:

$$V' : V = P : P' \quad \text{and} \quad V' : V = T' : T$$

or $$V'/V = P/P' \quad \text{and} \quad V'/V = T'/T$$

or $$V' = V\,(P/P') \quad \text{and} \quad V' = V\,(T'/T).$$

Considered separately, we know that the original volume under change in pressure must adjust itself in accordance with the ratio denoted by Boyle's Law and attain that value which is expressed by the product of the pressure-fraction by the original volume, — $V\,(P/P')$. The operation of a change in temperature will modify the original volume in accordance with the Law of Charles, and the resulting value will be expressed, as the formula above indicates, by the product of the original volume by the temperature-fraction, — $V\,(T'/T)$.

If the original volume, already modified to accord with a change in pressure, is to come *in turn* under the influence of a change in temperature, which is separate and independent of the pressure, we shall be able to express the result by substituting this already modified value of the original volume, $V\,(P/P')$, for that volume denoted by V in the equation, $V' = V\,(T'/T)$, representing the effect of an alteration in temperature. In other words, the volume V in the equation $V' = V\ (T'/T)$ may be regarded as already affected by some change in pressure, — a change which can have altered it only in accordance with the Law of Boyle and brought it to its new value through the expression $V\ (P/P')$. It follows, therefore, that by substituting $V\ (P/P')$ for V in the equation $V' = V\ (T'/T)$ we shall obtain the value which results from the action of both these agencies, pressure and temperature, upon the gas. Whether we consider the action of pressure before or after that of temperature, the final product will be the same. Thus, when the expression $V' = V\ (T'/T)$ is made to include the effect of a change in pressure upon the original volume V, we have the form

$$V' = V(P/P')\ (T'/T), \text{or } V' = V\left(\frac{P}{P'} \cdot \frac{T'}{T}\right);$$

whereas the expression denoting the influence of pressure alone, $V' = V\ (P/P')$, when made to include the effect of a change in temperature upon the volume V, gives the same form

$$V' = V\ (T'/T)\ (P/P'), \text{ or } V' = V\left(\frac{P}{P'} \cdot \frac{T'}{T}\right).$$

Though the Law of Boyle holds only when temperature is a constant and the Law of Charles only when pressure is a constant, the simultaneous validity of the two laws is here assumed. This is more clearly understood when variations in temperature and pressure are studied under constant volume. Thus a volume of gas V, at temperature T, and under a constant pressure P, when warmed to the temperature T′, gives a new volume V′, according to the equation $V' = V\ (T'/T)$. In order to bring back this increased volume to its original volume V, under constant temperature, a pressure P′ must be now applied. This pressure will be derivable from the original pressure in accordance with the Law of Boyle; and from the new volume V′, or V (T′/T), we can only obtain the original or smaller volume V at the condition of this greater pressure P′; hence the equation $P'V = V(T'/T)P$, or that equation which denotes the inverse proportionality between volume and pressure. With the volume V′, thus brought back to volume V, through this increase in pressure, the variations between temperature and pressure at this constant volume can be derived. The elimination of the common factor V from the equation above gives us

$$P' = P(T'/T), \text{ or } P'/P = T'/T.$$

This signifies that at constant volume the change in pressure is directly proportional to the change in temperature expressed upon the absolute scale, and is therefore exactly analogous to the change in volume by change in temperature at constant pressure; the two thereby stand in harmony with the Law of Charles. The influence of temperature may be as well considered along with alterations in pressure as with volume, since the alterations are exactly analogous and are derived from identical expressions. Consequently the variations in the two factors, pressure and volume, may simultaneously include the effect of temperature and take that form which indicates the direct proportionality of each of these factors to the absolute temperatures:

$$T'/T = P'/P \times V'/V.$$

As more generally expressed, the equation is

$$V'/V = P/P' \times T'/T, \text{ or}$$

$$V' = V\left(\frac{P}{P'} \cdot \frac{T'}{T}\right).$$

This is, as seen, the product of the original volume by both the pressure-fraction and temperature-fraction conjointly. Hence we may consider the original volume as having come under the action of two forces simultaneously; the new volume, therefore, is that volume produced by the resultant of these two forces.*

The Relation of Volume to Temperature and Pressure.

Example 8. — Given 100 c.c. of a gas at 10° and 750 mm. pressure, what will be its volume at standard conditions (0° and 760 mm.)?

The change from the original to the new values may be indicated thus: 283° → 273°, and 750 mm. → 760 mm. With respect to these alterations in temperature and pressure the questions may now be asked in regard to the magnitude of the new volume brought about by each of these influences. From the change in temperature the new volume must be smaller, as the gas in cooling undergoes a contraction (direct proportionality), hence 273/283 will represent the temperature-fraction. From the change in pressure the new volume must be smaller, since the new pressure is larger and the volume therefore will be diminished (inverse proportionality), hence 750/760 will represent the pressure-fraction. Bringing these two influences together, the product of the two by the original volume will give the combined effect of the two changes upon this volume:

$$V' = 100\ (273/283) \times (750/760), \text{ or } V' = 95.2 \text{ c.c.}$$

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* If in this connection the form of equation $V' = V(1 + \alpha t)$ is used, we shall arrive at a similar expression for change in pressure at constant volume: $P' = P(1 + \alpha t)$. The combined effect of a change in volume and change in pressure is then represented by $P'V' = PV(1 + \alpha t)$. By substituting here for t its value on the absolute scale, $T - 273$, we obtain

$$P'V' = PV\left(\frac{273}{273} + \frac{T - 273}{273}\right), \text{ or } P'V' = \frac{PV}{273} \cdot T$$

The expression PV/273 is found to be a constant for a given quantity of gas under all values of temperature, pressure and volume, and is usually expressed by R; hence the general gas equation, $PV = RT$, which signifies "that the pressure-volume product of a definite quantity of any definite gas is proportional to its absolute temperature." — A. A. NOYES.

With these two fractions each less than unity in value, the original volume is materially diminished under the new conditions.

The Relation of Temperature to Volume and Pressure.

Example 9.—At what temperature will a gas 200 c.c. in volume, at 20° and 750 mm., occupy a volume of 300 c.c. when the pressure is 740 mm.?

Here the volumes and pressures are known, and the undetermined quantity is one of temperature. The general formula must be arranged so that the undetermined quantity is on one side of the equation:

$$V'/V = P/P' \times T'/T$$

when divided through by P/P' gives

$$T'/T = V'/V \times P'/P,$$

hence the new temperature T' is expressed by the equation

$$T' = T\left(\frac{V'}{V} \cdot \frac{P'}{P}\right).$$

The entire matter may be simplified and made more apparent if we recall the reasoning advanced in the preceding cases; namely, the unknown quantity is derivable from the known quantity by multiplying this latter by the fractions formed from the related terms, when these terms are arranged so as to give a quotient that will express the magnitude of the term sought (the unknown quantity) over that of the one already existent.

At 20° C., or 293° A., the volume of gas in the problem above was 200 c.c. At the new temperature it is to be 300 c.c., hence this temperature must be larger, else no expansion could occur (direct proportionality); therefore $T' = 293\ (300/200)$. Again, the pressure-fraction must be arranged so that its quotient will acquire a value less than unity, *i.e.*, 740/750, since the effect of a lower pressure must necessarily decrease the temperature here required (direct proportionality) (*cf.* p. 23). The combined influence will be expressed by the product of the two fractions by the original temperature:

$$T' = 293\ (300/200) \times (740/750)$$

or

$$T' = 433.6°\ A. = 160.6°\ C.$$

The Relation of Pressure to Volume and Temperature.

Example 10.— 100 c.c. of a gas at 20° and 740 mm. will exert what pressure when occupying 120 c.c. at 40°?

Arrange the related terms in fractions in accordance with the questions as to whether the new pressure is to be greater or less than the original, 740 mm., and multiply both by this value. The temperature-fraction becomes 313/293, since at higher temperature the pressure must be greater (direct proportionality); the volume-fraction becomes 100/120, since at increased volume the pressure must be less (inverse proportionality), therefore by arranging all these factors we have:

$$P' = 740\ (100/120) \times (313/293), \text{ or } P' = 658.7 \text{ mm.}$$

This is in accord with the general equation which may be drawn up for changes in both volume and temperature upon the pressure of a gas:

$$P' = P\left(\frac{V}{V'} \cdot \frac{T'}{T}\right).$$

When the volume is a constant the equation takes the form indicated on p. 23:

$$P' = P\left(\frac{T'}{T}\right).$$

The Relation of Density to Temperature and Pressure.—The variation in the absolute density of a gas through the simultaneous variations in temperature and pressure follows readily from what has been stated in regard to variation in volume under these same influences. In the study of absolute density, $D = M/V$, the inverse proportionality between the absolute density and the volume of a gas permits, in the general equation denoting the influence of temperature and pressure changes in this connection, of the substitution of the term D' (the new density) and D (the original density) for V and V' respectively. The general equation $V'/V = P/P' \times T'/T$ then becomes $D/D' = P/P' \times T'/T$ or, as transposed to indicate the alteration in temperature and pressure upon the original density:

$$D' = D\left(\frac{P'}{P} \cdot \frac{T}{T'}\right).$$

This is in keeping with what has been already observed, *i.e.*, the absolute density of a definite quantity of gas varies directly with the pressure and indirectly with the absolute temperature.

Example 11. — A volume of oxygen at 20° and 750 mm. pressure has what absolute density under these conditions?

The absolute density of oxygen at 0° and 760 mm. pressure is 1.429. The new density will be less under the conditions named, since both the pressure-fraction 750/760, and temperature-fraction 273/293, will reduce the original value according to the equation:

$$D' = 1.429\ (273/293)\ (750/760), \text{ or } D' = 1.314.$$

PARTIAL PRESSURES.

Whether we have to deal with a simple gas or a mixture of several gaseous components, the Law of Boyle is equally applicable. Each component of a gaseous mixture exerts a definite individual pressure, the same that it would exert were it alone present in this volume. According to the Law of Dalton, the sum of these individual pressures, *partial pressures,* of the several components is equal to the total pressure of the mixture. When two gases of equal volume at the same conditions are brought together and communication made between the two vessels, we find that the gas from each vessel diffuses into the other vessel and becomes uniformly distributed throughout this double volume (the two vessels). In other words, each gas behaves as if it alone were present in the total space included in the two vessels. Under double the original volume each gas can exert but one-half of its original pressure. The sum of the pressures of the two gases, however, must be again equal to unity or that pressure which each originally exerted. Consequently the total pressure of a gaseous mixture may be regarded as the sum of the individual or partial pressures of the several components.

When aqueous vapor is present in a volume of gas we have again the consideration of gaseous mixtures. Water gives off a varying amount of its vapor, independent of any other gaseous substance that may be present in the space about it, but always dependent upon the temperature. At any one temperature we assume an equilibrium between the two tendencies, — that of the molecules of the vapor to condense as liquid, and that of the molecules of the latter to fly off as vapor; in other words, we have a condition of saturation with aqueous vapor.

The density or concentration of aqueous vapor (the *aqueous tension*) as attained at each condition of equilibrium is definite for that temperature at which the equilibrium exists. This density of the vapor is determined most easily by measuring the pressure which it exerts, — the vapor pressure. If a little water is admitted into the vacuum at the top of a barometric column of mercury, the vapor evolved will exert a pressure which increases with a rise in the temperature of the surrounding medium. At 100° the pressure of this vapor will have just sufficed to displace all of the mercury (sustained by the atmosphere at sea level), and consequently will have reached a pressure exactly balancing one atmosphere. This temperature is the *boiling-point* of the liquid or that point at which bubbles of vapor form in the liquid itself. At higher elevations than sea level, *i.e.*, under reduced atmospheric pressures, this attainment of the external pressure by the vapor of the liquid (the boiling-point) will take place at lower temperatures. As the temperature falls the aqueous vapor above the mercury in the barometric tube just mentioned will decrease in concentration and exert less pressure; consequently mercury will be forced into the tube by the pressure of atmosphere from without. The difference in height of the mercury in this tube and that in a barometer, where no moisture is present, will give the height of mercury, or pressure, corresponding to that of the aqueous vapor at the recorded temperature.

When any gas is measured over water at atmospheric pressure, and a temperature constant for both gas and liquid, we obtain the partial pressure of the dry gas in the mixture by subtracting from this barometric reading the pressure which aqueous vapor exerts at the observed temperature. (The values for a range of temperatures are found in Appendix II.)

Example 12. — 100 c.c. of a gas at 10° and 750 mm., measured over water, will have what volume under standard conditions?

At 10° the pressure of aqueous vapor is 9.2 mm. (see Appendix II), therefore the barometric reading, 750 mm., represents the sum of the pressures of the aqueous vapor and that of the dry gas, and, as standard conditions are desired, the volume of the gas should be determined in the dry state. Accordingly 750 mm. − 9.2 mm. = 740.8 mm., the pressure of the dry gas. The problem then resolves itself into one exactly as in Ex. 8, page 24. The volume of a gas at 740.8 mm., when calculated at a pressure of 760 mm., or a greater pressure, must be necessarily diminished; therefore 740.8/760 is the pressure-fraction. The temperature-fraction is 273/283, consequently the new volume will be derived from the equation

$$V' = 100 \times 740.8/760 \times 273/283, \text{ or } V' = 94.03 \text{ c.c.}$$

PROBLEMS.

18. 500 c.c. of hydrogen at 25° and 745 mm. pressure will have what volume at 15° and 755 mm. pressure? *Ans.* 476.8 c.c.

19. A vessel of 2000 c.c. capacity held 5 grams of a vapor at the standard conditions of temperature and pressure. What weight of this vapor at 10° and 750 mm. pressure can be held in this vessel, the capacity considered constant?

Ans. 4.76 grams.

Note. — This volume of vapor (x), at 0° and 760 mm., with the weight (w), when raised to the new volume (y), will still have the same weight. Consequently the vessel can be made to contain only that part of the original weight which is denoted by the fraction x/y.

20. 10 liters of a gas measured at 20° and 750 mm. pressure weighed 14 grams. What weight of this gas could be contained in a smaller vessel holding 4 liters at 10° and 760 mm. pressure?

Ans. 5.87 grams.

21. What volume will 1000 c.c. of gas at 30° and 740 mm. pressure occupy when reduced to standard conditions?

Ans. 877.3 c.c.

22. 1000 c.c. of a gas measured at 10° and 750 mm. pressure was increased to 1120 c.c. by warming. The final pressure read 740 mm. What was the final temperature of the gas?

Ans. 39.7°.

23. A volume of gas measured at 10° and 750 mm. pressure will have what pressure at 20°, the volume a constant?

Ans. 776.5 mm.

24. A volume of gas measuring 1000 c.c. at 15° and 745 mm. pressure was warmed to 32°. What increase in the pressure of the gas would be recorded, the volume a constant?

Ans. 44 mm.

25. What decrease in temperature will be necessary to reduce 400 c.c. of a gas, at 20° and 765 mm., to a volume of 300 c.c. at 750 mm.? *Ans.* 77.56°.

26. What increase in temperature will be necessary to bring a volume of gas, measuring 560 c.c. at 10° and 745 mm. pressure, to a volume of 600 c.c. at this same pressure? *Ans.* 20.2°.

27. A volume of hydrogen measuring 500 c.c. at 25° and 730 mm. was reduced in volume to 400 c.c. at 0°. What was the final pressure of the gas? *Ans.* 836 mm.

28. What increase in pressure is necessary to force 100 c.c. of hydrogen, at 10° and 740 mm., into a vessel of 80 c.c. capacity, when the temperature of this vessel is constant at 0°? *Ans.* 152.3 mm.

29. What is the absolute density of hydrogen at 20° and 740 mm. pressure? *Ans.* 0.08153.

30. What is the absolute density of air at 10° and 750 mm. pressure? The absolute density at the standard conditions is 1.293. *Ans.* 1.231.

31. 400 c.c. of gas, with the absolute density 6 and measured at 25° and 750 mm. pressure, is to be brought to a temperature of 10° and a pressure of 760 mm. What weight of this final gas can be contained in a vessel of 100 c.c. capacity? *Ans.* 0.64 gram.

32. 10 grams of a gas, measured at − 48° and 600 mm. pressure, was expanded by heating to 177° and reducing the pressure to 480 mm. Of this rarefied gas 250 c.c. weighed 0.5 gram. What was the original volume of gas and what was the density of the gas at its original and final volume?

Ans. 2000 c.c.
Original density = 5.
Final density = 2.

33. 150 c.c. of air measured over water at 18° and 746 mm. pressure will have what volume at standard conditions? *Ans.* 135.3 c.c.

34. 1 liter of oxygen at standard conditions weighs 1.429 grams. 440 c.c. of this gas measured over water at 24° and 742 mm. pressure will contain what weight of the dry gas? *Ans.* 0.547 gram.

35. 545 c.c. of nitrogen as measured over water at 22° and 748 mm. pressure contain what weight of the dry gas (density = 1.2507)? *Ans.* 0.6045 gram.

36. 2.2 grams of oxygen will occupy what volume at 20° and 770 mm. pressure when transferred to a vessel inverted over water? *Ans.* 1667 c.c.

37. 1 gram of hydrogen (density = 0.08987) measured at standard conditions will occupy what volume when transferred to a vessel over water at 0° and 760 mm. pressure? *Ans.* 11,195 c.c.

38. 400 c.c. of oxygen at standard conditions will have what volume when measured over water at 20° and 755 mm. pressure? *Ans.* 442.3 c.c.

39. 100 c.c. of a gas, measured over water at 25° and 745 mm. pressure, will have what volume when deprived of moisture? The atmospheric conditions constant. *Ans.* 96.8 c.c.

40. 1000 c.c. of oxygen, measured over water at 10° and 750 mm. pressure, will have what volume at − 10° and 770 mm. pressure when deprived of its moisture? *Ans.* 894.1 c.c.

41. 500 c.c. of a gas contained in a tube inverted over water, and measured at 10° and 765 mm. pressure, will have what volume under a change in the atmospheric conditions to 20° and 745 mm. pressure? *Ans.* 537.7 c.c.

42. What decrease in pressure will be necessary to raise a volume of gas measuring over water 400 c.c., at 22.5° and 748 mm. pressure, to a volume of 440 c.c. under the same conditions? *Ans.* 66.2 mm.

Note. —The actual atmospheric pressure of the moist gas required for the new conditions will be obtained by adding the tension of aqueous vapor to the value for P′.

43. What increase in atmospheric pressure will be necessary to reduce 200 c.c. of a gas, measured in a tube over water at 10° and 720 mm., to a volume of 100 c.c. at 20° in this same tube? *Ans.* 769.2 mm.

Note. —The calculated pressure for the dry gas must be increased by the tension of aqueous vapor at the new conditions in order to obtain the actual pressure that would be recorded (*cf.* Prob. 42).

CHAPTER VI.

AVOGADRO'S HYPOTHESIS AND SOME OF ITS APPLICATIONS.

THE hypothesis of Avogadro is the outcome of the Law of Combining Volumes (Gay-Lussac), and assumes that, if the Laws of Boyle and Charles are strictly true, there must be a uniform distribution of molecules in all volumes of gases at the same conditions of temperature and pressure. More generally the hypothesis takes the following form: Under the same conditions of temperature and pressure equal volumes of all substances in the state of vapor contain an equal number of molecules. By molecules are meant the smallest parts in which a substance maintains its identity. The complete chemical combination between the molecules of equal or multiple volumes of gases to form definitely related volumes of gaseous products, with no molecules of either constituent remaining free or uncombined, presupposes this even distribution of molecules.

Now the weight of a given volume of gas when compared with the weight of an equal volume of another gas, under the same conditions, will represent not alone the ratio between the sum of the weights of all the molecules in one volume and that of the other, but also the ratio between the weight of an individual molecule of one gas and that of the other. This follows, of course, from the fact that the numerical ratio between the weights of each equal volume is not altered through division by a common factor, — the unknown yet equal number of molecules in both volumes. In determining the relative weights of molecules it is therefore of no importance as to what particular volume of gas is weighed, so long as the weight is to be compared with the weight of an exactly equal volume of some other gas at the same conditions of temperature and pressure. Any known volumes of gases upon which accurate data are at hand may serve for this purpose when they are reduced to the same conditions (*cf.* Chap. V) and comparison made between equal volumes of each.

The Relation of Density to Molecular Weight. — This comparison in the weights of equal volumes of gases is, after all, nothing more or less than the comparison in gas densities. Thus the absolute density of hydrogen, 0.08987, when compared with that of oxygen, 1.429, is found to be about 1/16 of the latter, or, if the density of hydrogen is considered as unity, the density of oxygen becomes 15.90:

$$0.08987 : 1.429 = 1 : 15.90.$$

The relative weight of a molecule of oxygen, — its molecular weight, — would be, accordingly, 15.90 times the molecular weight of hydrogen. But from accurate determinations of the atomic weights of these elements the molecular weight of oxygen is found to be only 15.88 times that of hydrogen.*

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* The determination of the atomic weights of all the elements gives us the most accurate means of obtaining the true molecular weights. Density determinations involve numerous complications, and are therefore liable to errors, but nevertheless they give us a very fair approach to the true values. The various degrees of cohesion between the molecules of gases bring into existence a greater or less deviation from the uniform packing of these molecules as assumed by Avogadro's hypothesis for a perfect gas. Thus with oxygen we have a slightly greater packing than with hydrogen, as is shown by the increase of the relative density 15.90 over the calculated value 15.88. In order that our calculations may be free of these slight discrepancies, densities may be given as calculated back from the correct molecular weights,

The relation in the absolute densities applies equally well to the relative densities of gases providing, of course, that they are referred to the same standard. Thus the relative densities of hydrogen and oxygen upon air as a standard are 0.0696 and 1.105 respectively. The comparison of these values gives the same relative weights of the molecules of hydrogen and oxygen as shown above.

We have several cases which show that a volume of hydrogen may enter into combination with an exactly equal volume of another gas, and the resulting gaseous compound occupy the volume originally held by the two gases severally, *i.e.*, the sum of the two gaseous volumes now makes up the volume of the compound. Since temperature and pressure remain the same throughout, the number of molecules in the volume of the resulting compound must be twice the number of molecules in either volume of gaseous constituent. As each of the molecules in the compound contains hydrogen in chemical combination, we clearly see that there are now twice as many hydrogen parts present as there were in the original volume of hydrogen. Since weight for weight there can be no change in the amount of hydrogen present in the two cases, we naturally infer that the original molecule of hydrogen contained two smaller parts or units, — *atoms*, — and that it was these atoms which were concerned in the chemical combination. Never have we been able to get the element hydrogen to spread out over more than twice its original volume when entering into chemical combination, therefore we assume that the hydrogen as we know it contains at least two atoms to its molecule.

and consequently the value for oxygen will henceforth be taken as 15.88 instead of 15.90, when referred to hydrogen as unity.

Unless otherwise stated, the densities hereafter considered are the calculated weights of 1 liter of gas at standard conditions.

We have a number of elements the molecules of which under certain conditions are shown in like manner to possess two atoms (*i.e.*, diatomic), *e.g.*, oxygen (O_2), chlorine (Cl_2), bromine (Br_2), iodine (I_2), and nitrogen (N_2), whereas the molecule of mercury in the vapor state is monatomic (Hg).

As already stated, from the comparison in the weights of equal volumes of gases, we may derive the relative weights of the several kinds of molecules. With the hypothesis now that the molecules themselves are composed of atoms, we must interpret these relative values as those which stand for the ratios between the sums of the weights of the atoms in the molecules, *i.e.*, the molecular weights. A comparison between the relative weight of a molecule of hydrogen and a molecule of oxygen gives us the ratio 1 : 15.88. Since both hydrogen and oxygen molecules contain two atoms each, this same ratio stands likewise for that between the weights of the hydrogen and oxygen atoms. In order, therefore, to include the relative weights of the atoms in the molecular weights and thus be able to compare the relative weights of the molecules upon their smallest units as a basis, it is only natural that we regard the ratio 1 : 15.88 as the ratio between the relative weights of the hydrogen and oxygen atoms. The molecular weights of hydrogen and oxygen then become 2 and 31.76 respectively, values which indicate, of course, that they are made up of the sums of the respective atomic weights in each molecule. All of this presupposes that hydrogen, with the smallest atomic weight, should be regarded as unity for the convenience of these comparisons.

The importance of the element oxygen with its great number of well-defined compounds and the comparative ease with which these compounds may be utilized, through analyses, for the determination of the relative weights of molecules of other elements, has led to its universal adoption as the standard of molecular weights. In order that the values upon this scale may not depart far from those already determined upon the basis of hydrogen as unity, the former value for oxygen, 31.76, was increased to 32, a whole number, and thus the atomic weights of all the elements allowed to retain a value greater than unity. With oxygen changed from 31.76 to 32, we may readily derive the corresponding value for the molecular weight of hydrogen from the simple proportion:

$$31.76 : 2 = 32 : x,$$

which gives the value 2.016. From the molecular weight of oxygen (32) the relative weight of the atom must become 16, while the relative weight of the hydrogen atom will be 1.008. An imaginary gas with the atomic weight 1/16 of the atomic weight of oxygen (16) may be regarded, therefore, as the basis or unit weight of these values. These numerical values refer to no particular standard of weights, but when expressed in grams it is customary to call them *gram-molecular weights;* thus 32 grams is the G.M.W. of oxygen.

As already stated, the comparison of the densities of all substances in the state of vapor gives at once the relative weights of their molecules. In order, then, to obtain the molecular weight of any substance upon the basis of oxygen as 32 it becomes necessary to effect a comparison between its absolute density and that of oxygen on this basis. The calculated absolute density of chlorine is 3.166 (actual value = 3.22). The absolute density of oxygen, 1.429, will bear the same relation to this value for chlorine as the weight 32 bears to the molecular weight of chlorine, 70.92:

$$1.429 : 3.166 = 32 : x, \text{ or } x = 70.92.$$

When the relative density of a gaseous substance is given, *i.e.*, the value obtained by referring the absolute density to that of oxygen as unity, the proportion above will of course take the form:

$$1 : \text{Rel. density of gas} = 32 : x.$$

This proportion shows that the molecular weight (x) is merely the product of the relative density by 32. This is the logical outcome of making oxygen the standard both of gas densities and molecular weights. Since as the basis of relative densities the weight of a unit volume of oxygen is considered unity and as the basis of molecular weights it is considered 32, we naturally need only multiply any particular relative density by 32 in order to obtain the molecular weight of this substance.

If, on the other hand, the relative density of a gas is given in terms of some other density besides oxygen as a standard, the molecular weight of this standard substance must of course replace 32 in the proportion above. Formerly the relative densities were determined upon the basis of hydrogen as unity. The proportion indicating the molecular weight upon this basis is as follows:

$$1 : \text{Rel. density } (H = 1) = 2.016 : x.$$

Consequently the molecular weight may be derived from the relative density ($H = 1$) by multiplying this value by 2.016.

The Calculation of Relative Densities upon Different Standards. — To convert the relative density of a gas upon the hydrogen standard over to the standard of oxygen, or vice versa, we shall need to refer this value to the ratio between the absolute densities of the two standards, namely 0.08987 and 1.429, in an inverse order. As the means and extremes of the proportion we must have the product of the relative density of a substance by the absolute density of the corresponding standard, a product always equal to the absolute density of the substance in question; and hence a constant for the proportion. Thus:

$$\left\{\begin{matrix}\text{Abs. density}\\ \text{oxygen}\\ (1.429)\end{matrix}\right\} : \left\{\begin{matrix}\text{Abs. density}\\ \text{hydrogen}\\ (0.08987)\end{matrix}\right\} = \left\{\begin{matrix}\text{Rel. density}\\ \text{substance}\\ (\mathrm{H}=1)\end{matrix}\right\} : \left\{\begin{matrix}\text{Rel. density}\\ \text{substance}\\ (\mathrm{O}=1).\end{matrix}\right\}$$

Example 13. — The calculated relative density of chlorine (H = 1) is 35.23. What is the relative density of this gas referred to oxygen?

According to the proportion: $1.429 : 0.08987 = 35.23 : x$, the value of x, or relative density, (O = 1), is calculated as 2.216. When this is multiplied by 32 we obtain the molecular weight of chlorine, 70.92.

Quite often the vapor density of a substance is determined upon air as a standard. The ratio 1.429 : 1.293 is the ratio between the absolute densities of oxygen and air respectively, hence the calculated molecular weight of air referred to oxygen as 32 will be derived from the proportion: $1.429 : 1.293 = 32 : x$. From this the value 28.955 is found; a value which signifies that if air were a compound its molecular weight would be 28.955.

The molecular weight of a substance may be calculated, therefore, from its vapor density referred to air if we substitute this value, 28.955, for 32 in the proportion on page 38, and the relative vapor densities are made one member of the proportion.

Example 14. — The calculated vapor density of mercury is 6.908 referred to air. What is its molecular weight?

The proportion $1 : 6.908 = 28.955 : x$ gives 200 as the molecular weight of mercury. The conversion of any vapor density (air = 1) to the basis (O = 1) is exactly analogous to the case of hydrogen and oxygen above. The absolute density of air is 1.293.

The Gram-Molecular Volume. — If the actual weight of 1 c.c. of a gas is known in grams and this value is divided into the molecular weight also expressed in grams, the quotient will indicate the exact number of cubic centimeters of the gas in question that will be required to give this weight or the gram-molecular weight (G.M.W.). In other words, the quotient expresses the volume in cubic centimeters which contains the gram-molecular weight.

For example, 32 = G.M.W. of oxygen; 0.001429 gram is the weight of 1 c.c. of oxygen, therefore

$$\frac{32}{0.001429} = 22{,}390 \text{ (approximately)},$$

the number of cubic centimeters of oxygen, at 0° and 760 mm., necessary to give its G.M.W.

Again, the G.M.W. of hydrogen is 2.016 and the weight of 1 c.c. is 0.00008987 gram, therefore

$$\frac{2.016}{0.00008987} = 22{,}400 \text{ (approximately)},$$

the number of cubic centimeters of hydrogen at 0° and 760 mm. necessary to give its G.M.W.

This volume occupied by the G.M.W. of a substance is known as the *gram-molecular volume* (G.M.V.). Its calculation from the density of a gas gives values which diverge slightly from the average obtained for the more nearly perfect gases (*i.e.*, 22,400 c.c.) according as the degree of packing of the molecules in each diverges from that in the latter. We deduce, therefore, the simple statement that the weight of 22,400 c.c. of a gaseous substance, at 0° and 760 mm., will give, when expressed in grams, the gram-molecular weight of that substance. From the weight of any given volume of a gas the weight of 22,400 c.c. may be calculated by simple proportion;

hence a ready means is given for determining molecular weights in general.

Example 15. — What is the molecular weight of a gas, 5600 c.c. of which at standard conditions weigh 5 grams?

The value 22,400 is a standard, and the volume here to be compared with it (5600) must form the same ratio thereto as the relative weights of the two volumes:

$$5600 : 22{,}400 = 5 : x, \text{ or } \frac{5600}{22{,}400} = \frac{5}{x}.$$

From which the molecular weight of this gas (x) is found to be 20.

With this definite relation established between the volume 22,400 c.c., calculated at 0° and 760 mm., and that weight in grams which stands for the molecular weight of an element or compound, we may derive the fractional volume of this G.M.V. which any corresponding fractional part of the G.M.W. of a substance may occupy, and, vice versa, any fractional weight of the G.M.W. which any fractional part of this G.M.V. of the substance in state of vapor may have. In other words, the same fractional parts of the G.M.V. and the G.M.W. are directly proportional to each other.

Example 16. — 16 grams of oxygen will occupy what volume at 0° and 760 mm. pressure?

Since 32 grams occupy 22,400 c.c. at these conditions, the volume occupied by 16 grams will be 16/32 of 22,400 or 11,200 c.c., or, by simple proportion, $32 : 16 = 22{,}400 : x$, or $x = 11{,}200$ c.c.

To apply the effect of temperature and pressure changes let it be desired to find the volume which 2 grams of nitrogen will occupy at 20° and 750 mm. The molecular weight of nitrogen is 28. $22{,}400 : x = 28 : 2$, or $x = 1600$ c.c. This volume corrected for temperature and pressure becomes increased at 20° by 293/273 of itself, and, at 750 mm., by 760/750 of itself, and hence the corrected volume will be $1600\left(\frac{293}{273} \times \frac{760}{750}\right)$, or 1739.2 c.c.

Vice versa, the weight of any volume of a substance in the state of vapor may be determined if the gram-molecular weight of the compound is known.

Example 17. — What is the weight of 5600 c.c. of hydrogen chloride measured at 0° and 760 mm.?

The molecular weight of hydrogen chloride is 35.46 + 1.01, or 36.47. Therefore

$$22{,}400 : 5600 = 36.47 : x, \text{ or } x = 9.118 \text{ grams.}$$

Calculation of Densities of Gases from the Molecular Weights. — From these relations the determination of the density of any volume of vapor is reduced to the simple task of ascertaining from the molecular weight of the substance and this volume 22,400 c.c., what the weight of a unit volume (1 liter for gases) will be at standard conditions. The determination of the relative density of one gaseous substance upon any other as a standard resolves itself, therefore, into a comparison of the gram-molecular weights of the two gases, *i.e.*, the comparison of the weights of these equal volumes, — the G.M.V. With air, the weight of 22,400 c.c. has been given as 28.955 grams (this may be construed as the hypothetical gram-molecular weight of air).

Example 18. — What is the relative density of chlorine referred to (*a*) air? to (*b*) oxygen?

(*a*) The gram-molecular weight of chlorine is 70.92, the weight of 22,400 c.c. The weight of 22,400 c.c. of air is 28.955 grams. Therefore the ratio 70.92/28.955 when made equal to the ratio $x/1$ (where the weight of an equal volume of air is unity) gives us the proportion: $70.92 : 28.955 = x : 1$, or the relative density of chlorine as 2.449 (air = 1).

(*b*) When referred to oxygen the relative density of chlorine is determined in an exactly similar manner. The G.M.W. of oxygen, 32, replaces the weight of 22,400 c.c. of air in the example above. The process is of course the reverse of that in which the molecular weight of a substance is derived by multiplying its relative density ($O = 1$) by the value 32, the basis of molecular weights ($O = 32$) (*cf.* p. 38).

PROBLEMS.

44. The relative density of carbon dioxide ($H = 1$) is 21.83. What is the relative density of this gas upon the oxygen standard? *Ans.* 1.373.

45. The relative density of chlorine (air = 1) is 2.449. What is its relative density upon the oxygen standard? *Ans.* 2.216.

46. The vapor density of phosphorus trichloride (air = 1) is 4.745. What is its molecular weight? *Ans.* 137.38.

Note. — Though Ex. 14 may be followed it is much more simple to calculate the weight of 1 liter of the vapor, which is 4.745 times the weight of 1 liter of air (1.293 grams), and with this weight of 1 liter to apply Ex. 15.

47. What is the molecular weight of mercuric chloride, the vapor density of which is 9.354 referred to air? *Ans.* 270.84.

48. The vapor density of water is 0.622 (air = 1). What is its molecular weight? *Ans.* 18.016.

49. What is the molecular weight of sulphur dioxide, the relative density of which is 2.002 ($O = 1$)? *Ans.* 64.07.

50. What is the molecular weight of a gas, 2 liters of which at standard conditions weigh 12 grams? *Ans.* 134.4.

51. The weight of 3840 c.c. of a certain vapor, at standard conditions, is 24 grams. What is the molecular weight of the substance? *Ans.* 140.

52. 3180 c.c. of a gas measured at 24° and 750.2 mm. pressure weighed 6 grams. What is the molecular weight? *Ans.* 48.

53. 8019 c.c. of a gas measured over water at 20° and 742.4 mm. pressure weighed 14 grams when deprived of aqueous vapor. Calculate the molecular weight. *Ans.* 44.

54. 5647 c.c. of a gas measured over water at 24° and 754.2 mm. pressure weighed 6.254 grams when deprived of aqueous vapor. Calculate its molecular weight. *Ans.* 28.02.

55. What volume will 49.63 grams of chlorine (mol. wt. = 70.92) occupy at standard conditions? *Ans.* 15,680 c.c.

56. What is the volume occupied by 8.8 grams of carbon dioxide (mol. wt. = 44) at 12° and 752 mm. pressure? *Ans.* 4726 c.c.

57. 10 grams of carbon dioxide (mol. wt. = 44) will occupy what volume when contained in a vessel over water at 20° and 742.4 mm. pressure? *Ans.* 5728 c.c.

58. 1 gram of oxygen will occupy what volume over water at 30° and 756.5 mm. pressure? *Ans.* 814.3 c.c.

59. 8 grams of hydrogen (mol. wt. = 2.016) are to be admitted into a balloon at a temperature of 20° and a pressure of 740 mm. What must be the capacity of the balloon? *Ans.* 97,980 c.c.

60. Of what capacity is that vessel which contains 4 grams of oxygen (mol. wt. = 32) at the temperature of 18° and pressure of 748.4 mm.? *Ans.* 3031 c.c.

61. 10.08 grams of hydrogen (mol. wt. = 2.016) at 0° and 760 mm. pressure are to be forced into a vessel of 11.2 liters capacity. Under what pressure will the hydrogen be at this same temperature? *Ans.* 10 atmospheres.

62. At what temperature will 8 grams of oxygen (mol. wt. = 32) under a pressure of 760 mm. occupy a volume of 11.2 liters at this same pressure? *Ans.* 273°.

63. A vessel holding 30.8 grams of carbon dioxide (mol. wt. = 44) at 10° and 740 mm. pressure is to be brought to a temperature of 50° and a pressure of 750 mm. What weight and volume of carbon dioxide will be lost?

Ans. 2105 c.c. gas at latter conditions; 3.449 grams.

64. What is the weight of 6.594 liters of oxygen (mol. wt. = 32) at 40° and 740 mm. pressure? *Ans.* 8 grams.

65. What is the absolute density of hydrogen sulphide (mol. wt. = 34.09). *Ans.* 1.52.

66. What is the relative density of hydrogen sulphide (mol. wt. = 34.09) referred to air and also to oxygen?

Ans. 1.177 (air = 1).
1.065 (O = 1).

67. What is the relative density of hydrogen chloride (mol. wt. = 36.47) referred to hydrogen, air, oxygen and chlorine?

Ans. 18.05 (H = 1).
1.259 (air = 1).
1.139 (O = 1).
0.514 (Cl = 1).

68. 8 grams of oxygen were mixed with 10.08 grams of hydrogen (mol. wt. = 2.016). Both gases were measured at the standard conditions. What was the relative density of this mixture (O = 1)? *Ans.* 0.1076.

69. A gas with the relative density 1.5 (O = 1) was reduced from standard conditions to 20° and 740 mm. pressure so that it might have a volume measuring 6172.3 c.c. What is the weight of this volume of the gas? *Ans.* 12 grams.

70. A volume of gas, with the relative density 0.8757 (O = 1), was found to measure 1560 c.c. when transferred to a vessel over water at 18° and 742.4 mm. What is the weight of the dry gas here concerned? *Ans.* 1.75 grams.

CHAPTER VII.

THE LAW OF DEFINITE PROPORTIONS.

When two or more elements unite in chemical combination, a definite ratio is found to exist between the quantities of each element present and also between each of these several quantities and that of the molecular weight of the compound itself. In other words, upon the basis of 100 as the molecular weight, the amount by weight, here the percentage, of each element in the compound is constant and must bear a constant and unalterable ratio to the percentage by weight of any other element present.

The molecular weight of a compound represents the sum of the atomic weights that go to form it. The atomic or unit weight, *i.e.*, the symbol weight, is regarded as the smallest weight in which an element can be present in a molecular weight of any of its volatile compounds. A formula, therefore, is merely the expression in symbols which, under the existing conditions, denotes the number of atomic weights of the several elements in one molecular weight; this is better called the *molecular formula* (*cf.* Chap. VIII). The multiples of these atomic weights which occur in the molecular weight of a compound are always expressed by integers which are usually small.

The Percentage Composition of a Compound. — The percentage composition of a compound may be determined by analytical or synthetical means. Thus, for example, 10 grams of magnesium unite with 6.58 grams of oxygen (when heated in an atmosphere of oxygen), and the resulting magnesium oxide weighs 16.58 grams.

Of the 16.58 grams magnesium oxide, 10 grams are of course magnesium, or the fractional quantity 10/16.58 represents the weight of magnesium in magnesium oxide; the fraction 6.58/16.58 will represent, then, the proportional amount of oxygen present in the compound. These same definite ratios hold for all quantities of magnesium oxide; hence, if 100 grams are taken as a basis, 10/16.58 of 100, or 60.3, will give the amount of magnesium in the 100 grams, *i.e.*, the percentage of this element in the compound. Similarly, 6.58/16.58 of 100, or 39.7, is the percentage of oxygen present. By reference to simple proportion upon the basis of 100 as the total weight, these same percentage amounts are readily determined:

$$\begin{aligned}
\mathrm{MgO} : \mathrm{Mg} &= 100 : x \\
16.58 : 10 &= 100 : x, \text{ or } 60.3 \text{ per cent} \\
\mathrm{MgO} : \mathrm{O} &= 100 : x \\
16.58 : 6.58 &= 100 : x, \text{ or } 39.7 \text{ per cent.}
\end{aligned}$$

Now the formula of magnesium oxide is MgO, in which one atomic weight of magnesium (24.32) is combined with one atomic weight of oxygen (16). From the Law of Definite Proportions we know the ratios Mg/MgO and O/MgO are constant and, when expressed in numerical values of the several atomic weights concerned, become respectively:

$$\frac{\mathrm{Mg}}{\mathrm{MgO}} \quad \text{or} \quad \frac{24.32}{24.32 + 16} \quad \text{or} \quad \frac{24.32}{40.32}$$

and

$$\frac{\mathrm{O}}{\mathrm{MgO}} \quad \text{or} \quad \frac{16}{24.32 + 16} \quad \text{or} \quad \frac{16}{40.32}.$$

The constant ratio 24.32/40.32 stands for the amount of magnesium in magnesium oxide in all amounts of the latter, and upon a percentage basis will be represented by this same fractional part of 100, *i.e.*, 24.32/40.32 of 100, or 60.3 per cent. Similarly, for the amount of oxygen in magnesium oxide when expressed on a percentage basis, 16/40.32 of 100, or 39.7 per cent, will be obtained. These values are identical (*cf.* preceding paragraph) with those obtained in the synthesis of this compound where a definite weight of magnesium was converted into the oxide. In accordance with the Law of Definite Proportions, the same relations must hold for all determinations in this compound.

The general expression for problems of this type when the relative molecular weights are referred through simple proportion to a basis of 100 is as follows:

$$\begin{aligned} MgO : Mg &= 100 : x \\ 40.32 : 24.32 &= 100 : (60.3) \end{aligned}$$

and

$$\begin{aligned} MgO : O &= 100 : x \\ 40.32 : 16 &= 100 : (39.7). \end{aligned}$$

In the simple compound water, with the formula H_2O, the quantity of hydrogen in one molecular weight is represented by two atomic weights of this element. This aggregate of atomic weights, which represents the quantity in which any element, or group of elements, is present in a molecular weight of some compound, may be regarded as the *formula-quantity* for the particular element, or elements, concerned in the total molecular weight. Thus 2 H stands for the formula-quantity of hydrogen (2) in water (18), and the ratio $2\,H/H_2O$ or 2/18 or 1/9 represents this constant proportion between the formula-quantity of hydrogen and the molecular weight of water when concerned, of course, in this compound.* As there is but one

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* The molecular weight of a substance is, after all, a formula-quantity for that particular group of elements when associated in this compound. The ratio between the two is always expressed by unity. Thus 18 is the formula-quantity of water in its molecular weight as steam, whereas in the form of ice the formula-quantity, just as the molecular weight, must be increased to 3 (?) times this number if the molecule is to be regarded as $(H_2O)_3$.

atomic weight of oxygen in the molecular weight of water, the second ratio is simply O/H_2O or 16/18 or 8/9. Hence in water 1 part by weight of hydrogen (1/9) is combined with 8 parts by weight of oxygen (8/9). Expressed in percentage composition we have:

$$H_2O : 2\,H = 100 : x$$
$$18.02 : 2.02 = 100 : 11.2 \text{ per cent hydrogen}$$

and

$$H_2O : O = 100 : 88.8 \text{ per cent oxygen,}$$

the same ratio, 1 : 8, holding true, of course, for the percentages.

In the compound sodium sulphate, Na_2SO_4, we may express the constant ratios: $2\,Na/Na_2SO_4$, S/Na_2SO_4, and $4O/Na_2SO_4$, by percentages of the molecular weight, 142.07, or (46.0 + 32.07 + 64), as follows:

$$Na_2SO_4 : 2\,Na = 100 : x$$
$$142.07 : 46.0 = 100 : 32.38 \text{ per cent}$$

$$Na_2SO_4 : S = 100 : x$$
$$142.07 : 32.07 = 100 : 22.57 \text{ per cent}$$

$$Na_2SO_4 : 4\,O = 100 : x$$
$$142.07 : 64 = 100 : 45.05 \text{ per cent}$$

The sum of these = 100 per cent.

The Relation of Formula-Quantity to Molecular Weight. — Whatever the weight of a substance under consideration may be, the ratio between any one formula-quantity and the total molecular weight of the compound is always equal to the ratio between the actual weights which here correspond to these respective quantities.

Example 19. — Calculate the weight of chlorine present in 50 grams of sodium chloride.

The formula of sodium chloride, $NaCl$, indicates that 1 atomic weight of sodium (23.00) is combined with 1 atomic weight of chlorine (35.46) to give a molecular weight of 58.46. The ratio $Cl/NaCl$ or 35.46/58.46 expresses the relation between the formula-quantity of chlorine and the molecular weight of the salt, and all weights of these substances when jointly involved in the compound salt must be in accord with this ratio. When this ratio is converted to a percentage basis we obtain the value 60.6 as the percentage of chlorine in all amounts of salt: $58.46 : 35.46 = 100 : 60.6$. If, then, 60.6 per cent of any weight of salt is chlorine, 50 grams × 60.6 per cent or 30.3 grams is the amount of chlorine present in the known weight of salt.

Without resort to the percentage composition of a compound the constant ratio between the formula-quantity of any element present and the total molecular weight may be used directly for the determination of the amount of this element in any weight of compound. In the example just given, 35.46/58.46 represents the proportional amount of chlorine in salt. Without reference, then, to 100 as a basis, this same proportional part of the weight of salt taken must give the required value for chlorine; thus $50 \text{ grams} \times 35.46/58.46 = 30.3$ grams or weight of chlorine present; or, as is more customary, we may express the same by simple proportion: Since 58.46 grams of salt contain 35.46 grams of chlorine, 50 grams of salt can contain only that proportional part of its own weight which 35.46 is of 58.46; the ratio $58.46 : 35.46$ at once becomes equal to the ratio $50 : x$; thus

$$58.46 : 35.46 = 50 : x, \text{ or } x = 30.3 \text{ grams.}$$

These proportions are most easily formed when we bear in mind that only one set of related terms, *e.g.*, the formula-quantities, constitute one member of the proportion, whereas the other set of related terms, the actual weights (here with one unknown factor), constitute the other member.

Example 20. — Calculate the weight of sodium chloride that can be prepared from 30.3 grams of chlorine.

The amount of salt that can be prepared from this definite weight of chlorine (30.3 grams) will be represented by the same ratio, Cl/NaCl, as under the preceding example (Ex. 19); but, for the purposes of multiplication into known values, it is necessary to use the inverted form NaCl/Cl or 58.46/35.46, with the large value in the numerator so that a proportional increase in the values affected by this ratio may be obtained. The same end may be reached by the use of simple proportion, where the unknown term increases over the known in direct ratio to the corresponding formula-quantities:

$$35.46 : 58.46 = 30.3 : x, \text{ or } x = 50 \text{ grams.}$$

The Relation of Formula-Quantities to Each Other. — The ratio between any two formula-quantities occurring in one molecular weight may be used, of course, independently of the molecular weight, and when the ratio between certain groups of elements in a formula is to be determined the same principle will be found to apply as between single elements. The symbols representing these groups serve as usual for the calculation of the correct formula-quantities. In analyses of minerals the determination of these formula-quantities for various groups of oxides, etc., aids materially in the general classification; thus in the mineral feldspar, $AlK(Si_3O_8)$, or $Al_2K_2(Si_3O_8)_2$, when intended for resolution into the constituent groups, becomes $Al_2O_3 . K_2O . 6\,SiO_2$, from which the percentage of any one of the oxides present may be calculated from the corresponding formula-quantity.

Example 21. — What weight of aluminium is present in a sample of pure cryolite, $Al_2F_6 . 6 NaF$, which analyzed for 10 grams of sodium?

The ratio between the formula-quantity of each of the two substances concerned is $2 Al/6 Na$, or $2 (27.1)/6 (23)$, or $54.2/138$. As this is a constant we need only refer the ratio directly to the equivalent ratio when based upon sodium as 10 grams, — $54.2/138 = x/10$, — or, as has been the practice, $138 : 54.2 = 10 : x$, from which we obtain the value 3.93 grams for x, the weight of aluminium present.

The Relation of Formula-Quantities to Percentage Composition. — When data are given in percentages and it is desired to ascertain the percentage amount of some other element or group of elements present in the same compound, the calculations are made directly upon these percentages. They occupy, of course, the identical relation to each other as do the actual weights themselves, but with the condition that a constant value of 100 serves as a basis for the entire molecular weight.

Example 22. — What percentage of potassium oxide, K_2O, is present in a sample of feldspar, $AlK(Si_3O_8)$, which analyzed for 12.2 per cent potassium?

The ratio between the potassium and its corresponding amount of potassium oxide possible of existence in this same molecule is expressed by $2 K/K_2O$. With this definite quantity of oxygen in the molecule now to be associated with the potassium, there naturally will be an increase in the percentage amount of the group K_2O over that of the potassium alone. The ratio between these percentage amounts must be in accordance with the corresponding formula-quantities, 2 K and K_2O, upon which their weight and consequent percentage is dependent; therefore the ratio 2 K/K_2O must be equal to the ratio $12.2\%/x\%$. From the equation 2 K/K_2O or $78.2/94.2 = 12.2/x$ we obtain, as the value of x, 14.7 per cent, *i.e.*, 14.7 per cent of a compound of the composition noted, and analyzing for 12.2 per cent potassium, may be considered as potassium oxide.

Percentage Composition as a Basis for Percentage Purity. — Upon this method of comparison it is a very simple task to calculate the percentage purity or percentage amount of some compound in one of its samples submitted to an analysis; and this too upon the data secured in the determination of only one of its constituent elements.

Example 23. — A sample of salt analyzed for 50 per cent chlorine. Assuming all of the chlorine to have been present as sodium chloride, what was the percentage of salt in the sample?

The ratio Cl/NaCl must be equal to the ratio between the corresponding percentage amounts of these quantities, — $50\%/x\%$. $Cl/NaCl = 35.46 : 58.46 = 50/x$ or, by simple proportion, $35.46 : 58.46 = 50 : x$. From this, x is found to be 82.4 in place of the theoretical 100. This is, therefore, the percentage purity of the sample. When analytical data are not given in percentages, the weight of both sample and final product must be known in order to determine the percentage amount of any constituent present.

The percentage purity of a compound may be determined also by calculating the weight of substance theoretically possible from the results at hand (*cf.* Ex. 20) and then determining what percentage the weight of sample bears to this calculated value.

The Interrelationship of two Formula-Quantities through a Common Quantity. — When the results of an analysis are given in terms of some compound other than that involved in the investigation it is necessary to calculate these results through the element common to both compounds.

Example 24. — A sample of feldspar, $KAlSi_3O_8$, weighing 0.2507 gram gave upon analysis 0.0658 gram of potassium sulphate, K_2SO_4. What was the percentage of potassium oxide present in the sample?

We have here two distinct ratios: $K_2SO_4/2\ K$, which answers for the definite quantity of potassium present in this weight of potassium sulphate, and also $2\ K/K_2O$ for the quantity of oxide possible from a definite weight of potassium (*cf.* Ex. 22). Since the ratios involve the same definite quantities of potassium throughout, they may be considered as equivalent in respect to this element, and when brought together may be cleared of this common term, 2 K, as indicated when $K_2SO_4/2\ K$ is involved with $2\ K/K_2O$. By multiplication we should have K_2SO_4/K_2O, or that ratio with which the corresponding ratio between the actual weights of these substances, involving the same weight of potassium, must accord. From the known weight of potassium sulphate, the actual weight of potassium oxide is easily calculated: K_2SO_4/K_2O or $174.27/94.27 = 0.0658/x$, *i.e.*, $174.27 : 94.27 = 0.0658 : x$, or x, the weight of potassium oxide in the sample, is equal to 0.0356 gram. From this weight of oxide and the original weight of the sample the percentage amount of potassium oxide in the compound may be calculated: $0.2507 : 0.0356 = 100 : x$, or $x = 14.2$ per cent. Without the simplification noted it would have been necessary first to determine the actual weight of potassium present in the potassium sulphate, and second, from the weight of potassium, the consequent weight of oxide.

This cancellation or elimination of a common term between two ratios may be illustrated by a second example somewhat more complicated.

Example 25. — What percentage of potassium chloride can be regarded as present in a sample of potassium chlorplatinate, K_2PtCl_6, which analyzed for 43.6 per cent chlorine?

The ratio of the formula-quantity of chlorine to that of potassium is $6\ Cl/2\ K$. Now the ratio between potassium and potassium chloride in one molecular weight of potassium chloride is K/KCl. By examination of the formula of potassium chlorplatinate it is seen that two molecules of potassium chloride are involved in each molecule of chlorplatinate. This latter ratio then becomes $2\ K/2\ KCl$ when considered in the molecule of chlorplatinate. By this manner the same formula-quantity of potassium is considered in both ratios ($6\ Cl/2\ K$ and $2\ K/2\ KCl$); consequently this equivalent quantity may be eliminated from each (*cf.* Ex. 24), and the final ratio $6\ Cl/2\ KCl$ obtained for the corresponding weights of chlorine and potassium chloride possible in a molecule of chlorplatinate. Though a fractional quantity of the total chlorine is brought into consideration as potassium chloride, this in no way disturbs the definite relation between the total chlorine and the total potassium even when considered as chloride. The ratio may be simplified, if desired, to $3\ Cl/KCl$, and is equal to the ratio between the corresponding percentage amounts of these substances, $43.6\%/x\%$. From the equation

$$3\ Cl/KCl = 106.38 : 74.56 = 43.6/x$$

we obtain 30.56 as the percentage amount of potassium chloride possible in the sample.

PROBLEMS.

71. Determine the percentage composition of calcium carbonate, $CaCO_3$. *Ans.* Ca, 40.05%; C, 11.99%; O, 47.96%.

72. Determine the percentage composition of sodium nitrite, $NaNO_2$. *Ans.* Na, 33.33%; N, 20.30%; O, 46.37%.

73. Determine the percentage composition of potassium chlorate, $KClO_3$. *Ans.* K, 31.90%; Cl, 28.93%; O, 39.17%.

74. Determine the percentage composition of crystallized sodium sulphate, $Na_2SO_4 . 10\ H_2O$.
Ans. Na, 14.28%; S, 9.95%; O, 69.51%; H, 6.26%.

75. Determine the percentage composition of sulphuric acid, H_2SO_4. *Ans.* H, 2.05%; S, 32.70%; O, 65.25%.

76. Determine the percentage of sulphur trioxide, SO_3, in sulphuric acid. *Ans.* 81.64 per cent.

77. Determine the percentage of water in crystallized sodium carbonate, $Na_2CO_3 . 10\ H_2O$. *Ans.* 62.95 per cent.

78. Determine the percentage composition of ordinary alum, $K_2Al_2(SO_4)_4 . 24\ H_2O$.
Ans. K, 8.24%; Al, 5.71%; S, 13.52%; O, 67.43%; H, 5.10%.

79. What weight of sodium is present in 50 grams of sodium nitrate, $NaNO_3$? *Ans.* 13.53 grams.

80. What weight of sodium is present in 100 grams of sodium hydrogen carbonate, $NaHCO_3$? *Ans.* 27.38 grams.

81. What weight of oxygen is present in 200 grams of potassium chlorate, $KClO_3$? *Ans.* 78.34 grams.

82. What weight of oxygen is present in 200 grams of mercuric oxide, HgO? *Ans.* 14.815 grams.

83. What weight of mercuric oxide, HgO, will contain 30 grams of oxygen? *Ans.* 405 grams.

84. What weight of potassium chlorate will contain 30 grams of oxygen? *Ans.* 76.6 grams.

85. What weight of sulphuric acid can be prepared from 100 grams of sulphur? *Ans.* 305.9 grams.

86. Calculate the weight of potassium in a sample of pure sylvite, KCl, which analyzed for 2.230 grams of chlorine.
Ans. 2.459 grams.

87. What weight of copper is present in a sample of pure copper sulphate, $CuSO_4 . 5 H_2O$, which analyzed for 30.2 grams of sulphur trioxide, SO_3? *Ans.* 23.97 grams.

88. Calculate the percentage purity of a sample of horn-silver, $AgCl$, which analyzed for 74.2 per cent silver.
Ans. 98.61 per cent.

89. Calculate the percentage purity of a sample of marble, $CaCO_3$, which analyzed for 39.6 per cent calcium.
Ans. 98.88 per cent.

90. Calculate the percentage of potassium chloride in a sample of carnallite, $KCl . MgCl_2 . 6 H_2O$, which analyzed for 37.72 per cent chlorine. *Ans.* 26.44 per cent.

Note. — Theory calls for 26.83 per cent KCl. Therefore the deviation, 0.39, between the percentage values means an error of 1.5 per cent from the theory (26.83). Halogen determinations are usually quite accurate. If the analysis is at all good, the salt falls a little short of purity.

91. Calculate the percentage of calcium oxide, CaO, present in a sample of marble, $CaCO_3$, which analyzed for 43.8 per cent carbon dioxide. *Ans.* 55.84 per cent.
Sample practically pure; theory, 56.04 per cent.

92. A sample of sodium chromate, Na_2CrO_4, weighing 1.6780 grams, gave upon analysis 1.4620 grams of sodium sulphate, Na_2SO_4. What was the percentage of sodium oxide, Na_2O, in the sample? *Ans.* 38.01 per cent.
Theory, 38.25 per cent.

93. Calculate the percentage purity of a quantity of potassium ferrocyanide, $K_4Fe(CN)_6$, 0.5793 gram of which gave upon analysis 0.4650 gram of potassium sulphate, K_2SO_4.
Ans. 84.8 per cent.

Note. — From this weight of K_2SO_4 determine the actual weight, and finally the percentage, of potassium in the sample and then apply Ex. 23.

94. What is the percentage of potassium sulphate, K_2SO_4, in a sample of common alum, $K_2SO_4 . Al_2(SO_4)_3 . 24 H_2O$, which analyzed for 33.51 per cent sulphur trioxide, SO_3?
Ans. 18.23 per cent K_2SO_4.
Sample practically pure; theory, 18.36 per cent K_2SO_4.

95. What is the percentage of copper carbonate, $CuCO_3$, in a sample of malachite, $Cu(OH)_2 . CuCO_3$, which analyzed for 57.1 per cent copper? *Ans.* 55.49 per cent $CuCO_3$.

The salt is probably pure; theory, 55.87 per cent $CuCO_3$.

96. A sample of carnallite, $KCl . MgCl_2 . 6 H_2O$, analyzed for 35.34 per cent chlorine. What is the percentage of magnesium chloride present? *Ans.* 31.64 per cent $MgCl_2$.

Note. — Theory: 34.27 per cent $MgCl_2$. Therefore 92.31 per cent pure.

97. A sample of crystallized ferrous-ammonium sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6 H_2O$, analyzed for 8.66 per cent ammonia, NH_3. What is the percentage of ferrous sulphate, $FeSO_4$, present? *Ans.* 38.60 per cent $FeSO_4$.

Theory, 38.74 per cent $FeSO_4$.

98. A sample of gahnite, $Zn(AlO_2)_2$ or $ZnO . Al_2O_3$, weighing 0.1909 gram, gave on analysis 0.1664 gram of zinc sulphate, $ZnSO_4$. What was the percentage of alumina, Al_2O_3, in the sample? *Ans.* 55.18 per cent.

If analysis is correct, the sample is slightly impure.

Theory, 55.67 per cent.

CHAPTER VIII.

THE DERIVATION OF CHEMICAL FORMULÆ.

Molecular Formulæ from Molecular Weight and Percentage Composition. — The formula of a compound, designated by symbols which stand individually for one atomic weight of an element, is derived from data afforded by analysis or synthesis. In reverse to the determination of the percentage composition, as described in the preceding chapter, we can derive the true molecular formula when given the correct molecular weight of a compound and the percentage amount of each element present. The proportional parts of the molecular weight indicated by the several percentages are of course the quantities (formula-quantities) of the respective elements in one molecular weight of the compound, and necessarily must be multiples of the corresponding atomic weights by unity or a small integer.

Example 26. — The molecular weight of water is 18.016. The amount of hydrogen present is 11.2 per cent and that of oxygen 88.8 per cent. What is the molecular formula?

Molecular weight.	Percentage indicated.	Proportional part of molecular weight corresponding to element.	Unit or atomic weight of element.	Number of units.
18.016	H = 11.2%	2.016	1.008	2
18.016	O = 88.8%	16.00	16.00	1

The values 2.016 and 16 represent respectively the sum of the atomic weights of hydrogen and oxygen which are present in the molecular weight of water. They are, therefore, the formula-quantities of these elements in this compound. With 1.008 and 16 as the atomic weights of hydrogen and oxygen respectively, it is only a simple step to determine the number of hydrogen units (2) and oxygen units (1) which are necessary to make up the formula-quantity of each element in this molecule and consequently, together, the molecular weight of water; hence the formula H_2O.

The correct molecular weight of a compound is rarely ever at hand for the determination of chemical formulæ. The usual procedure lies, then, in the determination of the formulæ from the percentage composition or other data, and in the final adjustment of these to accord with the molecular weights which may have been determined only with approximate exactness.

Empirical Formulæ from Percentage Composition.— Upon the percentage basis the molecular weight is regarded as brought over to the value 100; this number, however, gives in itself no clue to the probable molecular weight. In Example 26 we were given the correct molecular weight; consequently, the proportional parts of this total weight, as indicated by the percentage amounts, agree always with the exact quantity of each element present in one molecular weight of the compound. Now, upon the adoption of 100 as the molecular weight, each percentage amount becomes the accepted value for the formula-quantity of that particular element in the molecular weight. In dividing each of these values through by the atomic weight of the corresponding element, we obtain not whole numbers, indicating the number of atomic weights of the respective elements present, but fractions or factors of these whole numbers, all of which are related to the true numbers in the same ratio as the adopted value, 100, is related to the true molecular weight.

Since a chemical formula calls for simple multiples of the atomic weights concerned, we need only raise the entire range of factors by some term which will bring each and all into whole numbers. When the smallest factor is made the divisor, then all of the other factors divided through by it must necessarily give quotients which are equal to or greater than this smallest factor as unity. In bringing the correct molecular weight over to 100 as a basis, this smallest factor was of course reduced from unity, or a multiple of it, in the same proportion as were all of the other factors. The quotients, then, upon the basis of this small factor as unity, will possess values close to their former and correct numbers. If the smallest factor had been reduced from unity itself, then the quotients will represent the correct formula, — a *molecular formula,* — of the compound. If, however, the original value of this smallest factor was a simple multiple of unity (*e.g.*, 3), then the quotients will vary from their true values in a molecular formula by just this same fractional amount that unity is of the simple multiple. (If 3 were the multiple, then the quotients would stand at one-third of their original values.) This simplest expression of a formula in symbols is known as an *empirical formula,* and the sum of the atomic weights therein represented, though a formula weight, is not necessarily the molecular weight.

From the empirical formula the true percentage composition of a compound is always derivable. Its formula weight, however, may not be coincident with the molecular weight, and, if so, the correct molecular formula can be derived only when the molecular weight, or at least a fair approach to this, is known. The molecular formula, therefore, is always a multiple of the empirical formula by some small integer.

Example 27. — A substance by analysis was found to contain 32.32 per cent sodium, 22.44 per cent sulphur, and 45.24 per cent oxygen. What is the formula of the compound?

The method of solution will be made most apparent when we set down the percentages and refer these to the respective atomic weights of the elements present, as indicated below:

Substance.	Percentage.	Percentage referred to corresponding at. wt. as basis	Factor.		Factor to unit value.
Sodium..	32.32	32.32/23.00	1.406	Divide through by 0.699	2.01
Sulphur..	22.44	22.44/32.07	0.699		1.00
Oxygen..	45.24	45.24/16	2.827		4.04
	100.00				

These unit values approach very closely to the integers 2, 1 and 4, and designate the number of unit or atomic weights of sodium, sulphur and oxygen, respectively, in their corresponding formula-quantities in a formula weight of the compound, Na_2SO_4.

In Chapter VII we have noted the means for calculating the theoretical percentage composition of a compound. In the case of a derived formula it is always well to calculate from it the percentage amount of each element present and note whether or not these values check with those derived by analysis. The derived formula Na_2SO_4 presents the following percentage composition:

$$\left.\begin{array}{ll}Na_2SO_4 & : 2\,Na\\ 142.07 & : 46\end{array}\right\} = 100 : x, \text{ or } 32.38 \text{ per cent sodium.}$$

$$\left.\begin{array}{ll}Na_2SO_4 & : S\\ 142.07 & : 32.07\end{array}\right\} = 100 : x, \text{ or } 22.57 \text{ per cent sulphur.}$$

$$\left.\begin{array}{ll}Na_2SO_4 & : 4\,O\\ 142.07 & : 64\end{array}\right\} = 100 : x, \text{ or } \begin{array}{l}\underline{45.05} \text{ per cent oxygen.}\\ 100 \quad \text{ per cent.}\end{array}$$

The percentage amounts actually found by analysis approach very closely to these theoretical values based upon the formula Na_2SO_4; consequently we may conclude that this formula represents the constitution of the compound. The molecular weight of sodium sulphate is found to be close to 142; hence the formula Na_2SO_4 (with the formula weight 2 (23) + 32.07 + 4 (16) or 142.07) satisfies also the requirements for a molecular formula.

Accuracy in analytical data is dependent upon purity of material and method of operation. In all of our results we may expect a certain degree of variation from the theoretical values, but the limits of error in the determination of chemical formulæ should not greatly exceed two-tenths of 1 per cent. Much depends, however, upon the particular element considered. For example, in the case of hydrogen the error often may be as much as four-tenths of 1 per cent above the theoretical, due to insufficient removal of moisture from the sample or to a faulty combustion. In the case of oxygen the data are rarely ever determined directly, but by difference; thus in Example 27 the sum of the percentage amounts for sodium and sulphur was subtracted from the total 100 per cent, and the difference considered as the value for oxygen, a value altogether dependent upon the accuracy of the other data. From these considerations the chemist finds it greatly expedient, in problems of this nature, to consider each analysis separately and to determine what one is likely to be most free of error. The factor, therefore, which corresponds to the percentage amount of this one element is the best to select as a basis for the reduction of all the other factors to unit values. Let us suppose, in Example 27, that the value for sodium was known to be more accurately determined. The factor here is 1.406, and, if we base all the other data upon this one, *i.e.*, by dividing each factor by 1.406, we shall obtain the values, 1, 0.498 and 2.010, for sodium, sulphur and oxygen respectively. These may be brought to unit values by multiplication by a small integer, — here by 2, — and we obtain finally 2, 0.996 and 4.02, — values which approach the respective integers 2, 1 and 4 somewhat more closely than in the previous calculation. This, of course, is due to the close agreement between the theoretical and found percentage values for sodium. It is now seen why the factor for oxygen is rarely selected as a basis for formula determinations.

Example 28. — Determine the formula for that substance which presented, by analysis, the following percentage composition: carbon, 39.78 per cent, hydrogen, 6.97 per cent and oxygen, 53.25 per cent. Above 230° the vapor of this substance gave a constant relative density, 2.09 (air = 1), calculated to standard conditions.

From the relative density it is only a simple step to calculate the molecular weight (*cf.* Ex. 14):

$$1 : 2.09 = 28.955 : x,$$

where x, the molecular weight, is found to be 60.52.

The following table of percentages and corresponding atomic weights is easily constructed as under Example 27:

Substance.	Percentage.	Percentage referred to corresponding at. wt. as basis.	Factor.		Unit value.
Carbon....	39.78	39.78/12	3.315	Divide through by 3.315	1.00
Hydrogen .	6.97	6.97/1.01	6.90		2.08
Oxygen....	53.25	53.25/16	3.33		1.01

These unit values approach well the integers 1, 2 and 1, which represent now the number of atomic weights of these respective elements in a formula weight of the compound, CH_2O. The sum of the formula-quantities thus represented in the formula weight is 30.02 (*i.e.*, $12+2.02+16$), a value which does not coincide with the molecular weight calculated from the vapor-density determination above (60.52). The molecular formula as previously stated is always a multiple of this simplest or empirical formula, and by just that integer which brings the empirical formula weight up to the molecular weight or an approximation to the same. The integer in the present case is 60.52/30.02 or 2.02. This is well within the limits of error, which in some cases may exceed a variation of 0.2 from an integral value. The empirical formula CH_2O must be multiplied now by the integer 2, when we shall obtain $C_2H_4O_2$, the correct molecular formula, or that formula in which the sum of the atomic weights involved gives the molecular weight. The calculation of the theoretical percentage composition for this substance, acetic acid, gives the following: carbon, 39.97 per cent, hydrogen, 6.73 per cent and oxygen, 53.50 per cent. The analytical data, therefore, are closely in accord with the theoretical.

Formulæ from Percentage Composition involving Radicals. — As a more complex example it will be well to examine the analytical data upon some mineral on which the results are given in percentage amounts of the several groups present. Feldspar belongs to this class of substances, and in its analyses certain values will be found for silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and potassium oxide (K_2O); but associated with these there may occur other oxides which are isormorphous with one or more of the above. Consequently the factor for these isomorphous substances, found, of course, as heretofore described, by the relation of percentage composition to atomic weight or groups of atomic weights representing the substance, must be reckoned together as one factor and hence as one group, in order to determine the extent to which this particular group of isomorphous substances may be present in the complete formula. If, perchance, a portion of the data were not given in terms of the proper isomorphous compound, but in some part of it, for instance, the percentage of potassium instead of potassium oxide, we should require only a single calculation to convert the data into the correct form (*cf.* Ex. 22):

$$2\,K : K_2O = -\text{ per cent given} : -\text{ per cent sought.}$$

Example 29. — A sample of the mineral orthoclase (a feldspar) gave by analysis the following percentage composition: SiO_2, 65.69 per cent, Al_2O_3, 17.97 per cent, (CaO, 1.34 per cent, K_2O, 13.99 per cent, Na_2O, 1.01 per cent, — isomorphous). What is its formula?

By drawing up a table of these percentages and referring each to the formula weight of the respective groups, we may expect to obtain factors which in this case do not refer to the simplest relation between the elements, but rather between the groups of elements.

The factors for K_2O, Na_2O and CaO, since these oxides are isomorphous and mutually may replace each other in the molecule, must be added together and considered as some generic formula such as R_2O, when in the final adjustment of the number of each group present in the formula they will figure as an individual group of uniform composition.

Substance.	Percentage.	Percentage re-referred to formula wt. of group as basis.	Factor.	Factor of isomorphous groups.		Unit value.
SiO_2..	65.69	65.69/60.3	1.0894	1.0894	Divide through by 0.1741	6.258
Al_2O_3.	17.79	17.79/102.2	0.1741	0.1741		1.000
CaO..	1.34	1.34/56.09	0.0239	0.1887		1.084
K_2O..	13.99	13.99/94.2	0.1485			
Na_2O.	1.01	1.01/62.2	0.0163			

As has been already noted in selecting the factor of those equally small, for division into the entire range of factors, it is always better to select that one which is likely to have been based upon more accurate analytical results, — in this case the aluminium oxide and not the composite oxide (into the determination of which three analyses must have entered). The resulting integers are here found to be 6, 1 and 1, and consequently the formula for the feldspar is $(K_2O \cdot CaO \cdot Na_2O)$ (Al_2O_3) 6 (SiO_2), in which the oxides of the metals K, Na and Ca make up one single group of the general formula of a feldspar, — $(K_2O) \cdot (Al_2O_3) \cdot 6\ (SiO_2)$, or $KAlSi_3O_8$. The extent of these isomorphous replacements within any group may vary considerably. This empirical formula is accepted as the true formula in the absence of any conflicting statements in regard to the true molecular weight.

Formulæ from the Relation of Formula-Quantities to Each Other. — Without recourse to percentage composition, the actual weight of any element found by analysis to be present in a known weight of compound may be referred directly to the formula-quantity of this element in the total molecular weight of that compound. Since these analytical data are dependent upon the number of atomic weights of each element present in one molecular weight, the ratio between the weight of each element in a known weight of compound containing, for example, two constituents, must be equal to the ratio between a certain unknown number of atomic weights of the one element and that of the other, *i.e.*, to the ratio between the corresponding formula-quantities.

Example 30. — Determine the formula of an iron oxide produced in the oxidation of 22.4 grams of iron to a final weight of 32 grams.

Here $32 - 22.4 = 9.6$ grams of oxygen taken up. The ratio between the weight of each of these two constituents in this sample of oxide, *i.e.*, $22.4/9.6$, must be equal to the ratio between the formula-quantity of each corresponding element in the molecular weight.

Since the number of atomic weights of each element, grouped in its formula-quantity, is here unknown, only the algebraic expression Fe_xO_y can be written for the complete formula; x and y representing, of course, these unknown integers. Given, then, the atomic weights of these two elements, iron (55.85) and oxygen (16), we may easily draw up the ratio between the formula-quantity of each in the compound. This ratio involves an unknown factor (an integer) in each term, but as a ratio it must be always equal to any other ratio that can be drawn up from data on the weights of these same particular substances in a definite weight of the compound. Thus the ratio Fe_x/O_y, as determined in the analysis of the oxide given above, is represented by $22.4/9.6$, and consequently, if the analyses are correct, these two ratios must be identical:

$$\frac{Fe_x}{O_y} = \frac{22.4}{9.6}, \text{ or } \frac{55.85\,x}{16\,y} = \frac{22.4}{9.6}.$$

The exact numerical relation between x and y may be readily calculated by bringing the numerical values to one side of the equation (*i.e.*, by multiplying the equation through by 16/55.85), when we obtain

$$\frac{x}{y} = \frac{22.4 \times 16}{9.6 \times 55.85} = \frac{358.4}{536.4},$$

a result likewise obtained through the simple proportion:

$$55.85\,x : 16\,y = 22.4 : 9.6$$
$$(55.85 \times 9.6)\,x = (16 \times 22.4)\,y$$
$$x/y = 358.4/536.2.$$

In one equation involving two unknown terms we can only expect to determine the simplest ratio between them. The ratio 358.4/536.4 when reduced by division of each term by the smaller (358.4), gives us 1/1.49, and this in turn, through multiplication of each term by 2, is brought very close to 2/3, which, as the ratio between the smallest integers, indicates the value of x and y respectively; hence the formula of the compound, Fe_2O_3.

Whether the molecular formula calls for this simplest form or some multiple of it by a simple integer cannot be determined without knowledge of the molecular weight of the compound.

The application of this method to compounds containing three or more elements introduces, of course, this corresponding number of unknown terms (the number of atomic weights of each element present), and lends itself less readily to a simple solution. When, however, two or more groups of elements, as radicals, etc., are present, the method may be applied to the determination of the number of each of the two groups in the molecule.

Example 31. — What is the formula of that oxy-halogen salt of potassium, $(KCl)_yO_x$, 13.9 grams of which lost 6.4 grams of oxygen upon heating, and gave a residue of 7.5 grams $(13.9-6.4)$ of potassium chloride, KCl?

The ratio between the weight of oxygen driven off and the residue of potassium chloride left is $6.4/7.5$, which, of course, is equal to the ratio between the formula-quantity of each:

$$\frac{O_x}{(KCl)_y}=\frac{6.4}{7.5}, \quad \text{or} \quad \frac{(16)\,x}{(39.1+35.46)\,y}=\frac{6.4}{7.5},$$

or

$$\frac{x}{y}=\frac{(6.4)\,(74.56)}{(7.5)\,(16)}=\frac{476.2}{120}.$$

From this we obtain $x/y = 3.97/1$ or, by simplest integers, $x=4$ and $y=1$. The formula of the compound $(KCl)_yO_x$ now becomes $(KCl)_1O_4$, *i.e.*, $KClO_4$.

Formulæ Containing Water of Crystallization. — Again we have a good illustration of examples of this kind in the consideration of those salts which contain water of crystallization, — definite in amount under certain definite and fixed conditions.

Example 32. — 7.15 grams of crystallized sodium carbonate, $Na_2CO_3 . x\,H_2O$, lost all of its water of crystallization when gently heated. The weight of the residue was 2.655 grams. What is the formula of the crystallized salt?

Here $7.15 - 2.655 = 4.495$ grams, or the weight of water in this weight of salt. The ratio between the weight of water actually associated with the weight of anhydrous salt (that portion of the crystallized salt left after the elimination of the water) is $4.495/2.655$. This ratio therefore must be equal to the ratio between the formula-quantity of water and the formula-quantity of the anhydrous salt in the molecular weight of the crystallized salt. In that the water of crystallization is usually determined with reference to one molecule of the anhydrous salt, one of the unknown terms in the ratio between the formula-quantities drops out (*i.e.*, equals unity) and we have only the determination of the unknown number of molecular weights (x) of water present. Thus:

$$\frac{x\,(H_2O)}{Na_2CO_3} = \frac{4.495}{2.655}.$$

By substituting the atomic weights indicated, we obtain

$$\frac{x\,(18.02)}{106} = \frac{4.495}{2.655},$$

which, when solved for x, gives the value 10 as the number of molecules of water associated with one molecule of the anhydrous salt to form a molecule of crystallized sodium carbonate, $Na_2CO_3 \cdot 10\,H_2O$.

The calculation may be conducted by simple proportion as follows:

$$\begin{array}{rcl} Na_2CO_3 : x\,(H_2O) & = & \text{wt. anhydrous salt} : \text{wt. } H_2O. \\ 106 : x\,(18.02) & = & 2.655 \qquad : 4.495. \end{array}$$

The expression x (18.02) is found equal to 179.5, hence the integral value for x will be 10 and accord with the formula above.

Formulæ from the Relation between Formula-Quantities and Their Corresponding Weights. — This constancy in the ratios between the quantities of all the elements either singly or collectively in a chemical compound was comprehended, of course, in the Law of Definite Proportions; and the proportions in which the elements enter into chemical combination are seen, accordingly, to be functions of the corresponding atomic weights. In any known amount of substance there is always a definite ratio between the actual weight of some one element, or group of elements, present and the corresponding formula-quantity. Furthermore, this ratio is always identical with every other ratio between the weight of any other element in this same sample and its corresponding formula-quantity.* The ratio can be unity only when we are dealing with a gram-molecular weight of the substance. Thus, in 18 grams of water, the weight of oxygen (16 grams) bears the ratio of unity to the formula-quantity of this element in the molecular weight, and also the same ratio, unity, exists between the weight of hydrogen (2 grams) and its formula-quantity.

As is often the case, no one correct formula-quantity is at hand. Under such circumstances it is only possible to refer any and all of the known weights of the elements in a given sample of compound directly to their corresponding atomic weights. In order to maintain throughout the same constant ratio between these values — actual weights and atomic weights — it is necessary to select the ratio between the actual weight of some one element in the sample and the atomic weight corresponding thereto as the standard ratio. By means of this ratio the actual weight of any other element present in the sample may be brought over immediately (simple proportion) to a value which holds the same relation to its true formula-quantity as the single atomic weight of the first element will be found to have toward its formula-

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* The equivalence in the ratios between any two formula-quantities, as x and y, and the corresponding weights, as w_1 and w_2, which represent them respectively in any given sample, is usually expressed as $x/y = w_1/w_2$. By multiplying through by y/w_1 we immediately obtain the expression $x/w_1 = y/w_2$ for this equivalence in the ratios between each formula-quantity and the weight representing it in some sample. The two expressions take the following forms through simple proportion: $x : y = w_1 : w_2$ and $x : w_1 = y : w_1$, each of which follows algebraically from the other, *i.e.*, the ratio between the first and second terms of a proportion, when equal to the ratio between the third and fourth terms, signifies also this equivalence in the ratios between the first and third terms and the second and fourth terms.

quantity. In this latter case, with the formula-quantity always a multiple of the atomic weight by a small integer, the process of determining the true formula-quantity is comparatively a simple one. The integer selected, however, must also bring each and all of the other values, similarly found, to multiples of their individual atomic weights. In other words, we determine the least common multiple for the entire range of values, such that each in order will be raised to a multiple, by unity or a small integer, of its atomic weight. Finally, the quotients of these so derived formula-quantities by the corresponding atomic weights will give the units of each element necessary in the simplest formula; one which can be raised later to any desired multiple, depending, of course, upon the molecular weight in question.

Example 33. — Derive the formula of iron oxide from the data in Example 30 : 22.4 grams of iron gave 32 grams of oxide.

The weight of oxygen entering into the compound is 9.6 grams. Accordingly, the ratio 9.6/16, between weight of oxygen present in the sample and the atomic weight of this element, may be taken as the standard ratio. By means of this ratio the weight of iron present is now brought over to a value always equivalent to oxygen as 16 in this compound.* Thus, $9.6 : 16 = 22.4 : x$, where

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* In the combinations between hydrogen and oxygen no compound has been found to contain more than two atomic weights of hydrogen with one of oxygen in a single molecular weight. Consequently the lowest weight of oxygen corresponding to the lowest weight of hydrogen (1.008, its atomic weight) will be one-half of 16, or 8. This weight of oxygen, the smallest equivalent to one atomic weight of hydrogen, is often used as a basis for the conversion of known weights or percentages of other elements (associated with oxygen) to the scale of atomic weights. Though it brings into the calculations numbers somewhat smaller (by one-half) than otherwise obtained through the use of the actual atomic weight, 16, the process of determining the least common multiple is in no way simplified.

this value for iron is found to be 37.2. By referring these values now to the respective atomic weights we have:

Substance.	Relative amount in known weight of compound.	Value constructed upon oxygen as 16.	Multiple	Value raised to multiple of corresponding at. wt.	Atomic weight.	Unit value.
Iron...	22.4	37.2	3	111.6	55.85	2
Oxygen	9.6	16		48	16	3

From this the formula of the compound is found to be Fe_2O_3.

Formulæ from the Relation between Formula-Quantity and Percentage Composition. — In extending this method to compounds which contain a number of elements, it serves equally well if we employ, in place of actual weights, the percentage amounts of the elements, or groups of elements, present. These values, of course, are as definitely related to each other as any other fractions of the total weight of a substance. The ratio between the percentage of any one element and its atomic weight suffices, through simple proportion, to bring over each of the other percentages to the corresponding values for these elements in the compound.

Example 34. — Derive the formula of sodium sulphate from the data given in Example 27.

Substance.	Percentage.	Value constructed upon oxygen as 16.	Multiple	Value raised to multiple of corresponding at. wt.	Atomic weight.	Unit value.
Sodium...	32.32	11.43	4	45.72	23	1.99
Sulphur...	22.44	7.94		31.76	32.07	0.99
Oxygen...	45.24	16		64	16	4
	100.00					

The value of oxygen is made equal to the atomic weight of this element, and the ratio 45.06 : 16 is used to reduce all of the other values proportionately, *e.g.*:

with sulphur $45.24 : 16 = 22.44 : x$, or $x = 7.94$ and
with sodium $45.24 : 16 = 32.32 : x$, or $x = 11.43$.

These final values represent correctly the relative amounts of each element. One, oxygen, was made to coincide with its corresponding atomic weight, hence each of the other values will represent a weight of that respective element in this compound equivalent to oxygen as 16; and, as this is the unit value for oxygen, the entire range of values can be raised only through multiplication by simple integers until the lowest possible formula-quantity for each is obtained. The integer 4, found by trial, here raises all to values that are multiples of the corresponding atomic weights. These formula-quantities when divided by the respective atomic weights give at once the number of atomic weights of each element in the molecule, hence the formula Na_2SO_4.

The Derivation of Formulæ of a Known Type from a Single Analytical Value. — If it is known to what general class (oxides, chlorides, sulphates, etc.) a particular substance of simple type (not involving replacements) belongs, its complete analysis is not necessary for the determination of the formula. For instance, the percentage of copper in a sample known to be a copper chloride will be sufficient to this end. This follows by reason of the fact that the percentage amount of any element found comes from the ratio between its formula-quantity in the molecule and the total molecular weight, — a ratio represented, we shall say, by the expression, — mol. wt./x (at. wt.). Upon analysis certain definite numerical values fall to this ratio; in percentages, for example, we have the ratio 100/per cent element found. We thus form the equation:

$$\frac{100}{\%\ \text{element found}} = \frac{\text{mol. wt.}}{x\ (\text{at. wt. element})}.$$

Example 35. — A sample of a chloride of copper gave upon analysis 47.9 per cent copper. What is the formula of the compound?

The ratio between the known and theoretical values now becomes

$$100/47.9 = \text{mol. wt.}/x\ (63.57),$$

or

$$100 : 47.9 = \text{mol. wt.} : x\ (63.57).$$

As x is always a small integer it may be neglected for the first calculation: 100 : 47.9 = mol. wt. : 63.57. From this we obtain a value 132.71, as the molecular weight, in which one atomic weight of copper must be present to the extent of 47.9 per cent. The difference, therefore, or 69.14 (*i.e.*, 132.71 − 63.57 = 69.14), must represent the atomic weights of chlorine associated with this one atomic weight of copper. The quotient of 69.14 by 35.46, the atomic weight of chlorine, gives 1.95, or practically 2, and we at once draw up the formula $CuCl_2$ (63.57 + 2 (35.46) = 134.49), with the molecular weight of which the analytical data are well in agreement; hence the correct formula.

If there had been obtained some fractional quantity as a quotient (in place of 2 above), this quantity, together with the value for copper as unity, may be raised by multiplication to integral values which indicate the probable formula. This, of course, is identical with multiplying the molecular weight found by x (the smallest integrals in their order) until a value is obtained that can be made up of atomic weights without fractional parts. This try-out of a formula is nothing more than the reverse of the method outlined in Example 23, wherein was shown the means of determining the amount of any salt present in any one of its samples when given the percentage of some one element in the salt. In place of the molecular weight there given we have here only to set down, in order, the trial values for this molecular weight which correspond to the possible formula. Thus:

$$\left\{\begin{matrix}\text{Percentage amount}\\ \text{of copper}\end{matrix}\right\} : \left\{100\right\} = \left\{\begin{matrix}\text{Formula-quantity}\\ \text{copper}\end{matrix}\right\} : \left\{\begin{matrix}\text{Molecular weight}\\ \text{calculated.}\end{matrix}\right\}$$

$$47.9 \quad : \quad x \quad = \quad 63.57 \quad : \quad ....$$

When the value calculated for x, from any trial molecular weight, approaches closely to 100 we are assured of the correct value for this molecular weight and consequently of the correct formula.

PROBLEMS.

99. What is the formula of that substance which gave, by analysis, 26.9 per cent sodium, 16.58 per cent nitrogen, 56.52 per cent oxygen? *Ans.* $NaNO_3$.

100. What is the formula of that substance which gave, by analysis, 26.6 per cent potassium, 35.22 per cent chromium, 38.18 per cent oxygen? *Ans.* $K_2Cr_2O_7$.

101. What is the formula of that substance which gave, by analysis, 24.65 per cent potassium, 34.85 per cent manganese, 40.5 per cent oxygen? *Ans.* $KMnO_4$.

102. Derive the formula of that substance with the observed relative density 0.8853($O = 1$) and, by analysis, the composition: 85.41 per cent carbon and 14.64 per cent hydrogen. *Ans.* C_2H_4.

103. Derive the formula of that substance with the observed density 1.189 and, by analysis, the composition: 92.1 per cent carbon, 7.85 per cent hydrogen. *Ans.* C_2H_2.

104. Derive the formula of that compound of hydrogen and oxygen which gave, by analysis, 5.93 per cent hydrogen. A determination of its molecular weight gave the value 31.8.

Ans. H_2O_2.

105. Derive the formulæ of that oxide of nitrogen which gave, by analysis, 30.4 per cent nitrogen. In the solid state it was found to have a molecular weight of 92.4, whereas the actual density of its vapor above 140° was only 2.013.

Ans. $\begin{cases} \text{Solid, } N_2O_4. \\ \text{Gas, } NO_2. \end{cases}$

106. Derive the formula of that acid which gave, by analysis, 26.5 per cent carbon, 2.2 per cent hydrogen and the rest oxygen. The molecular weight was determined approximately as 90.4.

Ans. $H_2C_2O_4$.

107. Derive the formula of the mineral chalcopyrite, a specimen of which gave, by analysis, the following percentage composition: 34.40 per cent copper, 30.47 per cent iron and 35.87 per cent sulphur.

Ans. $CuFeS_2$.

108. Derive the formula of the mineral dolomite which gave, by analysis, the following percentage composition:

CaO	31.37 per cent	isomorphous
MgO	21.23 per cent	
CO_2	47.67 per cent	
	100.27	

Ans. $(CaO,MgO)(CO_2)$
or $(Ca,Mg)\ CO_3$.

109. By analysis a specimen of melanterite gave the following:

FeO	20.37 per cent	isomorphous
MgO	4.60 per cent	
SO_3	29.80 per cent	
H_2O	45.07 per cent	
	99.84	

Derive the formula.

Ans. $(FeO,MgO)(SO_3)\ .\ 7\ H_2O$
or $(Fe,Mg)SO_4\ .\ 7\ H_2O$.

110. By analysis a specimen of xenotime gave the following:

P_2O_5	32.45 per cent	
Y_2O_3	54.13 per cent	isomorphous
Ce_2O_3	11.03 per cent	
Fe_2O_3	2.06 per cent	
	99.67	

Derive the formula.

Ans. $(Y_2O_3,Ce_2O_3,Fe_2O_3) \,.\, (P_2O_5)$
or $([Y,Ce,Fe]_2O_3)\ (P_2O_5)$

111. By analysis a specimen of columbite gave the following:

Nb_2O_5	47.05 per cent	isomorphous
Ta_2O_5	34.04 per cent	
SnO_2	0.30 per cent	isomorphous
FeO	11.15 per cent	
MnO	7.80 per cent	
	100.34	

Derive the formula.

Ans. $([Fe,Mn,Sn]O) \,.\, ([Nb,Ta]_2O_5)$.

112. By analysis a specimen of garnet gave the following:

SiO_2	39.09 per cent	
Al_2O_3	23.05 per cent	isomorphous
Fe_2O_3	0.53 per cent	
FeO	0.11 per cent	isomorphous
MnO	0.35 per cent	
MgO	1.01 per cent	
CaO	35.75 per cent	
H_2O	0.15 per cent	(neglected)
	100.04	

Derive the formula.

Ans. $3\,([Ca,Mg,Mn,Fe]O) \,.\, ([Fe,Al]_2O_3) \,.\, 3\,(SiO_2)$
General type, $3\,RO \,.\, R_2O_3 \,.\, 3\,SiO_2$
or $R''_3R'''_2(SiO_4)_3$.

113. Derive the formula of the oxide produced when 6.87 grams of barium unite with 1.6 grams of oxygen.

Ans. BaO_2.

114. Derive the formula of the oxide formed in the combustion of 2.61 grams of aluminium with oxygen to a final weight of 5.01 grams. *Ans.* Al_2O_3.

115. Derive the formula of the oxide produced by the combustion of 43.45 grams of lead with 4.48 grams of oxygen. *Ans.* Pb_3O_4.

116. Derive the formula of the oxide produced by the burning of 2.5 grams of phosphorus in oxygen to a final weight of 5.7 grams. *Ans.* P_2O_5.

117. Derive the formula of the nitrate, 19.7 grams of which were prepared from 10.4 grams of bismuth. *Ans.* $Bi(NO_3)_3$.

118. Derive the formula of the nitrate, 17 grams of which gave a residue of 13.8 grams of sodium nitrite, $NaNO_2$, upon heating. *Ans.* $NaNO_3$.

119. Derive the formula of that chlorate, 4.165 grams of which lost 1.3 grams of oxygen upon heating and gave a residue of barium chloride, $BaCl_2$. *Ans.* $Ba(ClO_3)_2$.

120. Derive the formula of mercuric cyanide, 5.4 grams of which lost 1.1 grams of cyanogen upon heating. *Ans.* HgC_2N_2.

121. Derive the formula of the double salt of ammonium sulphate and copper sulphate, 4.12 grams of which lost 1.81 grams of ammonium sulphate upon heating. *Ans.* $(NH_4)_2SO_4 . CuSO_4$.

122. Derive the formula of crystallized sodium sulphate, 8.16 grams of which lost 4.51 grams of water upon dehydration. *Ans.* $Na_2SO_4 . 10\,H_2O$.

123. Derive the formula of crystallized copper sulphate, 7.84 grams of which lost 2.79 grams of water upon dehydration. *Ans.* $CuSO_4 . 5\,H_2O$.

124. Derive the formula of crystallized aluminium sulphate, 9.54 grams of which lost 4.61 grams of water upon dehydration. *Ans.* $Al_2(SO_4)_3 . 18\,H_2O$.

125. Derive the formula of aluminium hydroxide, 4.75 grams of which lost 1.64 grams of water and left a residue of Al_2O_3. *Ans.* $Al(OH)_3$.

126. Derive the formula of that nitrate which gave, by analysis, 62.45 per cent lead, 8.68 per cent nitrogen, 28.85 per cent oxygen. *Ans.* $Pb(NO_3)_2$.

127. Derive the formula of that substance which gave, by analysis, 52.02 per cent carbon, 13.2 per cent hydrogen, 34.68 per cent oxygen. *Ans.* C_2H_6O.

128. Derive the formula of that acetate which gave, by analysis, 63.61 per cent lead, 14.62 per cent carbon, 1.98 per cent hydrogen, 19.79 per cent oxygen. *Ans.* $Pb(C_2H_3O_2)_2$.

129. A salt of mercury known to be a chloride analyzed for 26.15 per cent chlorine. What is the formula? *Ans.* $HgCl_2$.

130. A salt known to be a nitrate analyzed for 62.4 per cent lead. What is the formula? *Ans.* $Pb(NO_3)_2$.

131. An oxide of iron gave, by analysis, 69.80 per cent iron. What is the formula? *Ans.* Fe_2O_3.

132. An oxide of barium gave, by analysis, 81 per cent barium. What is the formula? *Ans.* BaO_2.

133. Derive the formula of the crystallized salt which, by analysis, gave the percentage composition: 19.98 per cent iron, 11.47 per cent sulphur, 5.24 per cent hydrogen, 63.31 per cent oxygen. 10 grams of this crystallized salt lost 4.5 grams of water upon dehydration. *Ans.* $FeSO_4 . 7\,H_2O$.

134. The percentage composition of a certain salt is: 15.6 per cent chromium, 14.41 per cent sulphur, 4.79 per cent hydrogen, 65.2 per cent oxygen. 10 grams of the crystallized salt lost 4 grams of water upon dehydration and gave a residue of $Cr_2(SO_4)_3$. What is the formula? *Ans.* $Cr_2(SO_4)_3 . 15\,H_2O$

135. The percentage composition of a certain salt is: 27.51 per cent calcium, 22.15 per cent sulphur, 1.02 per cent hydrogen, 49.32 per cent oxygen. 10 grams of this crystallized salt lost 0.6 gram of water upon dehydration. What is the formula? *Ans.* $(CaSO_4)_2 . H_2O$.

136. 2.5 grams of a crystallized salt known to be a sulphate of iron, and containing 20 per cent of iron, lost 1.13 grams of water upon dehydration. What is the formula? *Ans.* $FeSO_4 . 7\,H_2O$.

CHAPTER IX.

CALCULATIONS DEPENDING UPON CHEMICAL EQUATIONS.

In calculations which depend upon chemical reactions, the equations representing these reactions must first be constructed. In all chemical equations the number of atomic weights of any one element concerned remains a constant; the relative amount of each element, therefore, will be alike for both sides of the equation. Naturally the valence of each element in the reaction under consideration must be known, as upon these factors the balancing of equations is dependent. This valence or measure by which each atom of any element can enter into combination determines, accordingly, the number of other atoms or groups of atoms necessary for consideration in any reaction. When, however, an element undergoes a change of valence the arrangement of these atom groupings must be made to accord with this change (*cf.* Chap. XII). The representation of all substances in the molecular form — constituting here a molecular equation — has the great advantage of indicating the corresponding volume relations between the gaseous substances by reason of the like molecular volumes of all substances in the state of vapor.

Reaction-Quantities. — The action of metallic sodium upon water is shown in the following equation:

$$
\begin{array}{ll}
 & \begin{array}{llll} 2\,\mathrm{Na} & +\,2\,\mathrm{H_2O} & =\,2\,\mathrm{NaOH} & +\,\mathrm{H_2} \\ 2\text{ mol.} & +\,2\text{ mol.} & =\,2\text{ mol.} & +\,1\text{ mol.} \end{array} \\
\begin{array}{l}\text{Relative}\\ \text{parts}\\ \text{by weight.}\end{array} & \left\{\begin{array}{llll} 2\,(23.00) & +\,2\,(18.02) & =\,2\,(40.01) & +\,2.02 \\ 46.00 & +\,36.04 & =\,80.02 & +\,2.02 \end{array}\right. \\
 & \begin{array}{llll} & 82.04 & =\,82.04 & \end{array}
\end{array}
$$

In this simple equation each of the quantities represented is definite and bears that relation to every other quantity as is indicated by the corresponding group of atomic weights present in each. These quantities may be considered as the *reaction-quantities,* — atomic or molecular quantities definite for any given reaction and always proportional to each other, such that, when involved together, the ratio between them will be exactly equal to the ratio between the actual weights, of whatever denomination, which may represent them. This proportionality, relative, of course, to the construction of the equation itself, follows naturally from the Law of Definite Proportions. The reaction equation only indicates the apportionment of the various atomic or molecular groupings for the several compounds possible under the observed conditions. The formula-quantities going to make up any number of molecules of a compound indicated, still bear a definite ratio to every other formula-quantity, with the result, of course, that the weight which represents any of these reaction-quantities in a given equation must also bear a similar and definite proportion to each other, no matter whether they are upon the same or opposite sides of the equation. The reaction-quantity of sodium in the equation above is represented by two molecular weights; the reaction-quantity of sodium hydroxide, corresponding to this value for sodium, is also represented by two molecular weights. As both involve the same quantity of sodium they may be regarded also as equivalent quantities. The ratio between them, $2\,Na/2\,NaOH$, is more simply expressed in the unimolecular form, $Na/NaOH$.

The reaction-quantity of hydrogen directly proportional to the reaction-quantity of sodium in this equation is represented by one molecular weight, or H_2. The ratio

$2\ Na/H_2$ is definite, therefore, for all possible values for these substances in this reaction.

Example 36. — What weight of sodium hydroxide and of hydrogen can be procured by the action of 50 grams of sodium upon water?

From the equation just studied, the ratio $2\ Na/2\ NaOH$, or $Na/NaOH$, *i.e.*, 23/40.01, is constant for all proportional amounts of these two substances. Therefore the ratio $50/x$, between this known weight of the metal (50 grams) and its proportional value in hydroxide (x), must be equal to the ratio above (the related terms in these ratios are of course placed similarly), and we shall have

$$23/40.01 = 50/x.$$

By simple proportion this may be expressed as

$$23 : 40.01 = 50 : x.$$

From these expressions the value of x (the weight of sodium hydroxide) is found to be 86.98 grams.

In an exactly similar manner the ratio between the reaction-quantities of sodium and hydrogen, $2\ Na/H_2$, or Na/H, or 23/1.01 may be made equal to the ratio between the known or unknown weights of these substances concerned in the reaction. Between the weight of sodium (50 grams) and its unknown proportional weight of hydrogen (x) we have the ratio $50/x$; this is therefore immediately referred to the ratio between the corresponding proportional quantities above, Na/H or 23/1.01. Thus, $23/1.01 = 50/x$, or $23 : 1.01 = 50 : x$, from which the value for x is found to be 2.2 grams.

In general we may state that when any substance is concerned in a chemical reaction, the amount of any other substance, resulting directly or indirectly through this reaction, bears to the former a definite ratio and one always equal to the ratio between the corresponding reaction-quantities of the substances in the equation.

Example 37. — What weight of magnesium will be required for the liberation of 10 grams of hydrogen from water or an acid?

We may first consider the decomposition of water by magnesium as shown in the following:

$$\begin{array}{lllll} & \mathrm{Mg} & + \mathrm{H_2O} & = \mathrm{MgO} & + \mathrm{H_2} \\ & 1\text{ mol.} & + 1\text{ mol.} & = 1\text{ mol.} & + 1\text{ mol.} \\ \text{Parts by weight.}\ \{ & 24.32 & + 18.02 & = 40.32 & + 2.02 \end{array}$$

and again, the reaction of magnesium upon an acid such as hydrochloric acid:

$$\begin{array}{lllll} & \mathrm{Mg} & + 2\,\mathrm{HCl} & = \mathrm{MgCl_2} & + \mathrm{H_2} \\ & 1\text{ mol.} & + 2\text{ mol.} & = 1\text{ mol.} & + 1\text{ mol.} \\ \text{Parts by weight.}\ \{ & 24.32 & + 2\,(36.47) & = 95.24 & + 2.02 \end{array}$$

In each case we find that the molecule of magnesium — containing one atomic weight — displaces, and is equivalent to, one molecule of hydrogen — containing two atomic weights. The quantities Mg and H_2 are therefore directly proportional to each other in both equations, and the constant ratio Mg/H_2, or 24.32/2.02, must be equal to the ratio between the corresponding weights of these elements here concerned, *i.e.*, $x/10$. From the equation $24.32/2.02 = x/10$, or the simple proportion $24.32 : 2.02 = x : 10$, we calculate the value of x to be 120.4 grams (magnesium).

In the more complicated reactions the relations between the several quantities on the two sides of an equation are often difficult to ascertain. To say nothing of reversible actions and the possibilities for dependent or secondary reactions to take place between certain of the quantities, we have assumed and must continue to assume that the reaction in question takes place along the lines indicated in that equation best substantiated by the facts under the observed conditions.

Example 38. — What weight of sulphur dioxide, SO_2, can be obtained by the action of 10 grams of copper upon concentrated sulphuric acid?

Copper acts upon sulphuric acid (conc.), to give sulphur dioxide, water and copper sulphate. Notwithstanding the slight amount of cuprous sulphide formed here through a secondary reaction, we shall represent the action by a single equation:

$$\begin{array}{lcccccccc} \mathrm{Cu} & + & 2\,\mathrm{H_2SO_4} & = & \mathrm{CuSO_4} & + & 2\,\mathrm{H_2O} & + & \mathrm{SO_2} \\ 63.57 & & & & & & & & 64.07 \end{array}$$

The reaction-quantities, Cu and SO_2, are directly proportional; the ratio between them, Cu/SO_2, or $63.57/64.07$, is constant for all amounts here involved, and consequently equal to the ratio, $10/x$, representing these substances respectively in this example. From the equation $63.57/64.07 = 10/x$ the value of x is calculated as 10.08, the weight in grams of sulphur dioxide.

Calculation of Volume Relations Introduced by Chemical Equations. — In the consideration of gaseous substances formed in these reactions, their gram-molecular quantities may be referred at once to the gram-molecular volumes as a basis (*cf.* Ex. 16). For example, to recall the illustrations at the beginning of this chapter, two gram-molecular weights of sodium displace one gram-molecular weight of hydrogen, which under standard conditions occupies 22,400 c.c. Whatever be the weight of hydrogen evolved, the ratio between the G.M.W. and this weight will be identical with that between the G.M.V. and the volume of hydrogen corresponding to the known weight above (*cf.* Ex. 15).

Example 39. — Calculate the volume of hydrogen, at 10° and 750 mm., that will be evolved by the action of 100 grams of zinc upon an acid.

The nature or strength of the acid here is of no concern, for, so long as the zinc is used up, the proportional amount of hydrogen must be displaced, and from this weight of hydrogen displaced its volume may be easily calculated. With sulphuric acid the reaction may be represented as follows:

$$\begin{array}{lcl} Zn + H_2SO_4 & = & ZnSO_4 + H_2 \\ 65.37 + 98.09 & = & 161.44 + 2.02. \end{array}$$

The reaction-quantities Zn and H_2 establish the ratio Zn/H_2, or 65.37/2.02, as constant for all proportional amounts of these elements; hence the equation $65.37/2.02 = 100/x$. From this the value of x is calculated as 3.09 grams.

A gram-molecular weight of hydrogen, 2.02, occupies 22,400 c.c. at standard conditions. As previously stated the volume occupied by any other weight of the gas will stand in the same proportion to this gram-molecular volume as does its weight to the gram-molecular weight. Thus the ratio 2.02/3.09, between the known weights, will be exactly equal to the ratio between the corresponding volumes, — $2.02/3.09 = 22{,}400/x$. By simple proportion we should have $2.02 : 3.09 = 22{,}400 : x$; or, with reference to the fractional part of the volume occupied by 2.02 grams of the gas, we know that 3.09 grams must occupy 3.09/2.02 times this known volume, *i.e.*, $\frac{3.09 \times 22{,}400}{2.02}$ or 34 261 c.c. The value of x, as here calculated, must be adjusted now to the observed conditions of temperature and pressure. For this we need but a moment's glance to see that the corrected volume, x', will be expressed by the equation

$$x' = (34\,261)\frac{(760)\ (283)}{(750)\ (273)}, \text{ or } x' = 35\,980 \text{ c.c.}$$

The reverse process — that of determining the amount of any substance which will give a definite volume of gas measured at certain definite conditions — is made clear when the weight of this gas is ascertained (*cf.* Ex. 17). So also the consideration of aqueous vapor, when present, brings into these calculations only those methods already outlined in previous examples.

Calculations with Reference to Degree of Purity. — Oftentimes the purity of materials employed in chemical operations does not come up to the standard or 100 per cent. In such cases, where the deviation from the theoretical is known, the results found must be recalculated with reference to the standard purity. For instance, if the magnesium considered in Example 37 had been of only 80 per cent purity (contaminated, we shall say, with 20 per cent of inert or extraneous matter), then our results, wrongly based upon a valuation of 100 instead of the actual 80, must be raised in accordance with the ratio existing between the actual and theoretical value, *i.e.*, according to the ratio 80/100. The result in the example cited would be changed through the simple proportion: $120.4 : x = 80 : 100$; or 150.5 grams would be the weight of magnesium (80 per cent) necessary to give 10 grams of hydrogen.

Conversely, if it were desired to ascertain what weight of hydrogen could be obtained from this weight (150.5 grams) of magnesium (80 per cent pure), then the result upon the basis of 150.5 grams of pure magnesium would need to be lowered in the same proportion: 100 : 80. The same end is attained by bringing into the original calculation just 80 per cent of the weight of magnesium (80 per cent pure), *i.e.*, 120.4 grams in this example.

These calculations afford, therefore, a simple means for estimating the degree of purity of a definite weight of a substance when the amount of some constituent concerned in one of its reactions is referred to the corresponding theoretical value.

Example 40. — A specimen of marble weighing 5 grams evolved 2.1 grams of carbon dioxide (corresponding to a theoretical volume of 1162.5 c.c. at 20° and 750 mm.) when acted upon by an acid. Estimate the degree of purity, assuming that all of the carbonate was present as calcium carbonate.

The reaction with hydrochloric acid is here given:

$$\underset{100.09}{CaCO_3} + 2\,HCl = CaCl_2 + H_2O + \underset{44}{CO_2}.$$

From this equation the proportionality between the reaction-quantities $CaCO_3$ (100.09) and CO_2 (44) leads to the equation $\frac{100.09}{44} = \frac{5}{x}$, where x, 2.2 grams, is the weight of carbon dioxide theoretically possible from this weight of pure calcium carbonate. The specimen is accordingly only $\frac{21}{22}$, or 95.45 per cent, pure ($2.2 : 2.1 = 100 : x$). Calculating from the standpoint of the carbon dioxide, we naturally reach the same value: $\frac{44}{100.09} = \frac{2.1}{x}$; or x, 4.772 grams, is the theoretical amount of calcium carbonate required for the production of 2.1 grams of carbon dioxide. This weight is $\frac{4772}{5000}$, or 95.45 per cent, of the weight of the specimen; consequently, just this fraction of the specimen can be considered calcium carbonate, *i.e.*, its degree of purity is 95.45 per cent.

Calculation of Products Resulting from Mixtures. — The definite weights of various substances brought together for chemical combination are rarely ever present in the exact proportions indicated by the equation representing the particular reaction.

Thus, in the interaction between a metal and an acid, as already noted, the acid is taken in excess of the theoretical amount proportional to the definite weight of metal concerned. Such an excess is easily removed from the final product by volatilization. In cases where this cannot be accomplished without decomposition of some product sought, other means (crystallization, etc.) are employed. In order to ascertain the exact amount of any substance formed through one of these interactions it is necessary first to determine what particular component or components can be acted upon to completion by the others present. This, of course, presupposes the tendency for the reaction to run to completeness in some one direction, and implies the elimination of those products which may lead to a reversal of these conditions.

Example 41 — What weight of sodium sulphate may be expected to result from the interaction of 10 grams of sodium, 11 grams of sulphur and 40 grams of oxygen?

The equation representing the possible combination of these elements to this end is as follows:

$$\begin{array}{rllll}
 & 2\ \mathrm{Na} & + \mathrm{S} & + 2\ \mathrm{O}_2 & = \mathrm{Na}_2\mathrm{SO}_4 \\
 & 46 & + 32.07 & + 64 & = 142.07 \\
\text{Weights given.}\ \{ & 10 & 11 & 40. &
\end{array}$$

The actual weights of the several substances here entering into combination as sodium sulphate must stand in the same relation to each other as do the corresponding reaction-quantities. There is then an equivalence in the ratios between each reaction-quantity and the corresponding weight that represents it in the reaction (see footnote, page 72).

If these conditions are fulfilled in the example, we shall have an equality in the ratios, 46/10, 32.07/11 and 64/40. A single glance, however, disproves this point. It then becomes necessary to determine by trial which one of these ratios, between a reaction-quantity and its corresponding weight as given in the example, is the correct ratio to select as the basis of calculation. For example, upon the basis of 64/40, we must have: $\frac{64}{40} = \frac{46}{x} = \frac{32.07}{y}$, where x, (28.7), and y, (20), as the respective values for sodium and sulphur, actually exceed the amounts at hand. Upon the basis 32.07/11, we have: $\frac{32.07}{11} = \frac{46}{x} = \frac{64}{y}$, where x, (15.7), and y, (22), are the respective values for sodium and oxygen. In this latter case only the sodium is higher than the weight stipulated. Finally, upon the basis 46/10, we have the equation $\frac{46}{10} = \frac{32.07}{x} = \frac{64}{y}$, and from this both x, (6.97), the weight of sulphur, and y, (13.9), the weight of oxygen, fall below the amounts given; hence 46/10 is the proper ratio upon which to base the calculation. The sum of the respective weights thus obtained, 30.87 grams, (10 + 6.97 + 13.97), gives the highest weight of sodium sulphate possible from the data in the problem.

In general we select as the basis of calculation for any given reaction only that ratio which brings into consideration those values for the various substances involved as do not exceed the amounts present. More simply stated, perhaps, we base our calculations upon that weight of a particular substance at hand which gives, with its corresponding reaction-quantity as denominator, the smallest numerical factor. Thus the total weight of this particular substance determines the theoretically proportional weights of the other substances.

Under conditions where reversible reactions are likely, for example the preparation of sodium sulphate by the action of sulphuric acid upon common salt, as shown in the equation:

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl,$$

we determine in similar manner the weight of sodium sulphate possible from any known weight of salt (if the sulphuric acid is in excess) or from the weight of sulphuric acid (if the salt is in excess). The presence of hydrochloric acid as the reversing agent must be removed in either case if we wish to obtain the calculated results.

Calculation of Ratios between Reaction-Quantities in Dependent Equations. — When an element or group of elements enters into a series of successive reactions and the equation for each reaction can be constructed, we may draw up a proportionality between the reaction-quantities in any two of the equations providing that some quantity is common to both. In like manner this proportionality may be extended step by step over any number of dependent equations (*cf.* Ex. 24).

Example 42. — What weight of bromine can be liberated from a concentrated solution of potassium bromide (excess) by the addition of 12 grams of hydrochloric acid (containing 39.1 per cent HCl) and an excess of manganese dioxide?

The two equations representing the action are as follows:

$$\begin{aligned} &(a)\quad MnO_2 + 4\,HCl &&= MnCl_2 + Cl_2 + 2\,H_2O \\ &(b)\quad 2\,KBr + Cl_2 &&= 2\,KCl + Br_2. \end{aligned}$$

It is observed that the reaction-quantity Cl_2 is common to both (*a*) and (*b*), consequently the reaction-quantities directly proportional to this quantity in either equation will be also directly proportional to each other. The ratio $4\,HCl/Cl_2$ from equation (*a*) and the ratio Cl_2/Br_2 from equation (*b*) give us, accordingly, the ratio $4\,HCl/Br_2$ for the proportionality between the reaction-quantities required for this example. From the equivalence between this ratio and the ratio of the weights corresponding thereto, we have 4 HCl/Br_2, or $4(36.47)/2(79.92)$, or $145.88/159.84 = 12/x$, which, solved for x, gives a value of 13.1 grams. This weight of bromine, 13.1 grams, is based upon the hydrochloric acid as 100 per cent hydrogen chloride. The concentrated acid at our command, the acid stated in the example, contained only 39.1 per cent hydrogen chloride. It remains then to calculate the weight of bromine which a 39.1 per cent acid can give. By reference to Example 40, the method is outlined to be simply one of proportion, according to which we shall have

$$100 : 39.1 = 13.1 : x,$$

or $x = 5.13$ grams, the weight of bromine evolved by 12 grams of 39.1 per cent hydrochloric acid. This same result is easily obtained by determining first the weight of hydrogen chloride in the 12 grams of 39.1 per cent acid, (12×39.1 per cent $= 4.69$), and working the example with this value for the hydrogen chloride.

The elimination of a quantity occurring in two dependent equations may necessitate a readjustment of one or both of the equations containing it before the quantity becomes alike in each.

Example 43. — What weight of iron sulphide will be required to furnish sufficient hydrogen sulphide for the reduction of 10 grams of sulphur dioxide to sulphur?

The two equations here required are as follows :

$$(a)\quad FeS + 2\,HCl = FeCl_2 + H_2S$$
$$(b)\quad 2\,H_2S + SO_2 = 2\,H_2O + 3\,S.$$

The reaction in equation (*b*) depends upon the hydrogen sulphide that is evolved in (*a*); consequently this substance must constitute the common reaction-quantity. In order to make this quantity alike for the two equations and thus eliminate it from the calculations, it is only necessary to multiply equation (*a*) by 2, when we obtain (*a*′):

$$(a')\quad 2\,FeS + 4\,HCl = 2\,FeCl_2 + 2\,H_2S.$$

The comparison of any of the reaction-quantities in the two equations (*a*′) and (*b*) with reference to hydrogen sulphide is now made simple. In the example given, iron sulphide and sulphur dioxide are found to be related through the ratios $2\,FeS/2\,H_2S$ and $2\,H_2S/SO_2$, or directly as $2\,FeS/SO_2$. The calculation is conducted, therefore, as follows:

$$2\,FeS/SO_2,\ \text{or}\ 2\,(87.92)/64.07,\ \text{or}\ 175.84/64.07 = x/10.$$

From which x, the weight of iron sulphide, is found to be 27.44 grams.

Without this elimination of the quantity common to both equations, the calculation, of course, can be made directly toward ascertaining the weight representing this quantity in the first equation, and then finally, from this weight, the weight representing any other reaction-quantity proportional to it in the second equation. Such calculations, here involving the weight of hydrogen sulphide, are indeed roundabout and entirely unnecessary.

Calculation of Ratios between Reaction-Quantities in Independent Equations. — In the study of dependent equations the reaction-quantities may be regarded as related to each other, through this common reaction-quantity, as are the members of a single equation. The reaction-quantities of the second equation are, so to speak, brought into existence through the agency of this common quantity. In the study of independent equations, where there is present no one quantity which has a direct bearing upon any other equation, we have simply a further application of this same principle; namely, the comparison of all the possible reaction-quantities in the separate equations so long as some quantity can be made common to each. Quantities so compared will be directly proportional to each other, but only in respect to this common reaction-quantity. As an illustration, the following equations are cited:

$$(a)\quad Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2O + CO_2$$
$$(b)\quad NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

In these independent equations there are a number of substances represented for which the reaction-quantities could be adjusted alike for both; thus the reaction-quantity CO_2 is a common one. Upon this fact we may draw up the ratio $Na_2CO_3/NaHCO_3$ to express the proportionality between the relative amounts of normal carbonate and primary carbonate necessary to give an equal amount of carbon dioxide, *i.e.*, the relation is based upon the carbon-dioxide content. In order to obtain a comparison with reference to the salt, equation (*b*) must be doubled to (*b′*):

$$(b')\quad 2\,NaHCO_3 + 2\,HCl = 2\,NaCl + 2\,H_2O + 2\,CO_2.$$

The ratio $Na_2CO_3/2\,NaHCO_3$ then expresses the relation between the relative amounts of each carbonate necessary to give equal amounts of salt with hydrochloric acid. Or, since sodium is always a constant quantity in salt, we may say that the ratio above is that based upon a like content of sodium in each carbonate.

In addition to the carbonate discussed in the preceding paragraph, we may also compare the reaction-quantities for the carbon dioxide present. Between equations (*a*) and (*b*), where this is a common quantity, we have the ratio $2\,HCl/HCl$ representing the relative amounts of acid necessary in the respective cases to give equal amounts of carbon dioxide. Between equations (*a*) and (*b′*) we have the ratio $CO_2/2\,CO_2$ representing the relative amounts of carbon dioxide evolved from equal amounts of sodium when contained respectively in normal carbonate or primary carbonate, as indicated by the ratio $Na_2CO_3/2\,NaHCO_3$, or the ratio $2\,NaCl/2\,NaCl$, in each of which the sodium content is the same for both terms of the ratio. This latter point may be illustrated by the equation:

$$2\,NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

Here it is shown that two molecules of the primary carbonate break down into one molecule of the normal carbonate with the loss of one molecule of carbon dioxide. The ratio $2\,NaHCO_3/CO_2$ represents the relative amounts of these substances concerned in the action of heat upon the primary carbonate. This, in fact, is a case where the entire quantity of a substance, (CO_2), available in a compound need not be concerned in a ratio for the study of that compound, but only that portion of it separately involved as a reaction-quantity and made directly proportional, therefore, to some other reaction-quantity.

Example 44. — What relative weights of mercuric oxide and barium peroxide are required in the preparation of equal amounts of oxygen?

The molecular equations with oxygen as the common quantity adjusted alike in both are as follows:

$$\begin{aligned}2\,HgO &= 2\,Hg + O_2\\ 2\,BaO_2 &= 2\,BaO + O_2.\end{aligned}$$

The ratio $2\,HgO/2\,BaO_2$, or HgO/BaO_2, or $216/169.37$, determines accordingly the relation between the corresponding weights of these two substances in this problem. If we take one, *e.g.*, the mercuric oxide, as 100 we reduce the second to a comparatively simple value:

$$\frac{216}{169.37} = \frac{100}{x}.$$

This gives 78.4 as the value of x, or that weight in grams of barium peroxide equal to 100 grams of mercuric oxide in the preparation of oxygen.

Calculation of Reaction-Quantities from the Weights of Substances Involved. — The direct proportionality which exists between the reaction-quantities of a given equation requires, as we have seen, the same proportionality between the corresponding weights which represent them in this particular reaction. This permits of an equivalence in the ratios between each reaction-quantity and its corresponding weight (*cf.* Ex. 41 and footnote, page 72).

In the construction of chemical equations from the actual weights of substances therein concerned, we must bear in mind the possibility of deviations in these weights from those demanded in the reactions. These deviations may be due to any number of causes and rapidly increase with the instability of the compounds considered as well as with the tendencies for secondary reactions. Consequently the determination of the correct reaction-quantities for these equations must be made a special study in each individual case.

Example 45. — A solution of 10 grams of crystallized sodium thiosulphate, $Na_2S_2O_3 . 5\,H_2O$ decolorized 5.1 grams of iodine. What molecular quantity of this salt was associated with one molecule of iodine in this reaction?

From the equivalence in ratios between the reaction-quantities and the actual weights involved we have:

$$\frac{x}{10} = \frac{I_2}{5.1}, \text{ or } \frac{x}{10} = \frac{253.84}{5.1}.$$

This gives to x the value 497.7, the reaction-quantity of the thiosulphate associated with one molecular weight of iodine. The molecular weight of sodium thiosulphate, $Na_2S_2O_3 . 5\,H_2O$, is 248.2, consequently we have here 497.7/248.2 or approximately 2 molecules of this salt in its reaction-quantity, *i.e.*, the equation constructed upon the iodine involved as just one molecule will be

$$2\,Na_2S_2O_3 . 5\,H_2O + I_2 = (2\,NaI + Na_2S_4O_6).$$

Complex Reaction-Quantities. — There are a number of equations in which the reaction-quantities upon one side are incorporated into one single reaction-quantity upon the other side. The same principles hold here as in the cases just discussed, but the study of this larger quantity is nothing more or less than the study of the formula-quantities present in it. The consideration of the so-called molecular compounds, as are the double salts and salts containing water of crystallization, illustrates this point.

Example 46. — 100 grams of copper sulphate will give what weight of blue vitriol ($CuSO_4 . 5\,H_2O$)?

From the equation, —

$$\begin{aligned} CuSO_4 + 5\,H_2O &= CuSO_4 . 5\,H_2O \\ 159.64 + 90.1 &= 249.74, \end{aligned}$$

the ratio

$$\frac{CuSO_4}{CuSO_4 . 5\,H_2O}, \text{ or } \frac{159.64}{249.74}$$

is a constant, and denotes the direct proportionality between these two reaction-quantities. The ratio between the actual weights, 100 and x, when put equal to the ratio between the molecular quantities, gives us

$$\frac{159.64}{249.74} = \frac{100}{x},$$

where x, with the value 156.4 grams, is the weight of blue vitriol. As the percentage composition of the anhydrous copper sulphate is a constant, we may just as well calculate what weight of pure copper, Cu, or sulphur, S, or even oxygen, 4 O, is necessary to give any definite weight of anhydrous copper sulphate and finally blue vitriol; or, vice versa, what weight of blue vitriol is obtainable from any definite weight of one of these constituents.

As another illustration of this point we may take the formation of ordinary alum:

$$\begin{array}{ccccc} K_2SO_4 . 6\,H_2O & + & Al_2(SO_4)_3 . 18\,H_2O & = & K_2SO_4 . Al_2(SO_4)_3 . 24\,H_2O \\ 1\text{ mol.} & + & 1\text{ mol.} & = & 1\text{ mol.} \end{array}$$

A molecular quantity of one sulphate unites with one of another to form one molecular quantity of the double sulphate. These quantities are all directly proportional to each other, and from the equation we write the following ratios:

$$(a)\quad \frac{K_2SO_4 . 6\,H_2O}{K_2SO_4 . Al_2(SO_4)_3 . 24\,H_2O}$$

$$(b)\quad \frac{Al_2(SO_4)_3 . 18\,H_2O}{K_2SO_4 . Al_2(SO_4)_3 . 24\,H_2O}$$

$$(c)\quad \frac{K_2SO_4 . 6\,H_2O}{Al_2(SO_4)_3 . 18\,H_2O}.$$

These serve as the ratios for calculating, upon the molecular quantities involved, the amount of alum obtainable from certain known amounts of (*a*) crystallized potassium sulphate; (*b*) crystallized aluminium sulphate; and also (*c*) the amount of crystallized aluminium sulphate necessary for combination with one molecule of the crystallized potassium sulphate, or vice versa. Though somewhat more complicated molecular aggregates may be present, the ratios between the several factors are always constant.

Example 47. — How much alum can be prepared from 100 grams of anhydrous potassium sulphate?

The ratio

$$\frac{K_2SO_4}{K_2SO_4 . Al_2(SO_4)_3 . 24\,H_2O},\ \text{or}\ \frac{174.27}{949.16}$$

is placed equal to the ratio $100/x$, and the equation solved in the usual manner. The value of x, the weight of alum, is found to be 544.6 grams.

PROBLEMS.

137. What weight of potassium hydroxide may be prepared by the action of 100 grams of potassium upon water?
Ans. 143.5 grams.

138. What weight of potassium will be required in the preparation of 20 grams of potassium carbonate, K_2CO_3?
Ans. 11.3 grams.

139. What weight of magnesium chloride, $MgCl_2$, may be obtained by the action of hydrochloric acid upon 10 grams of magnesium carbonate, $MgCO_3$? What weight of carbon dioxide will be liberated?
Ans. 11.3 grams $MgCl_2$.
5.2 grams CO_2.

140. Recalculate Problem 139 on the supposition that the magnesium carbonate contained 10 per cent of insoluble matter.
Ans. 10.16 grams $MgCl_2$.
4.7 grams CO_2.

141. What weight of sulphur dioxide, SO_2, can be obtained by the action of an acid upon 250 grams of sodium sulphite, Na_2SO_3?
Ans. 127 grams.

142. Recalculate Problem 141 on the supposition that 20 per cent of the sulphite had become oxidized to sulphate.
Ans. 101.6 grams.

143. Calculate the volume of carbon dioxide, at 22° and 740 mm. pressure, that will be liberated by the action of acid upon 20 grams of calcium carbonate, $CaCO_3$.
Ans. 4967 c.c.

144. What weight of magnesium will be required for the liberation of 500 c.c. of hydrogen, at 20° and 740 mm. pressure, when acted upon by an acid?
Ans. 0.49 gram.

145. Calculate the volume of hydrogen, measured over water at 17° and 742 mm. pressure, that can be liberated by the action of 10 grams of sodium upon water.
Ans. 5403 c.c.

146. What weight of aluminium will be required for the liberation of 420 c.c. of hydrogen, measured over water at 18°

and 746.4 mm. pressure, when acted upon by hydrochloric acid? *Ans.* 0.306 gram.

147. What weight of ammonium nitrite, NH_4NO_2, will evolve, when heated, 480 c.c. of nitrogen, measured over water at 21° and 747.5 mm. pressure? *Ans.* 1.22 grams.

148. Determine the purity of a sample of anhydrous sodium carbonate, Na_2CO_3, 6 grams of which gave, when acted upon by an acid, 1310 c.c. of carbon dioxide, at 10° and 750 mm. pressure. *Ans.* 98.35 per cent pure.

149. Determine the purity of a sample of anhydrous sodium carbonate, 3 grams of which gave, by treatment with sulphuric acid and final ignition, 3.99 grams of sodium sulphate, Na_2SO_4. *Ans.* 99.25 per cent pure.

150. A sample of iron wire weighing 2.4 grams was found to give, when acted upon by excess of acid, a volume of hydrogen measuring 1015.1 c.c., at 10° and 745 mm. pressure. What was its degree of purity? The presence of any other substance capable of liberating hydrogen from an acid is here disregarded. *Ans.* 99.72 per cent pure.

151. A sample of silver nitrate weighing 2.40 grams was brought into solution and treated with a soluble chloride (excess). The weight of silver chloride, AgCl, precipitated was 2.01 grams. What was the purity of the sample? *Ans.* 99.26 per cent pure.

152. What weight of zinc (98 per cent pure) will be required for the liberation of the hydrogen from 10 grams of hydrochloric acid containing 39.1 per cent HCl? *Ans.* 3.576 grams.

153. What weight of sulphuric acid containing 27.32 per cent H_2SO_4 will be required for interaction with 2.17 grams of iron wire (99 per cent pure)? *Ans.* 13.82 grams.

154. What volume of hydrogen, measured over water at 18° and 746.4 mm. pressure, will be liberated by the action of aluminium upon 20 grams of sulphuric acid containing 41.5 per cent H_2SO_4? *Ans.* 2100 c.c.

155. What weight of sulphuric acid (27.32 per cent H_2SO_4) will be required for interaction with a metal (Zn, Mg, etc.) in order to give a volume of hydrogen measuring over water 1032 c.c., at 16° and 742.5 mm. pressure? *Ans.* 15 grams.

156. What weight of hydrochloric acid (23.82 per cent HCl) will be required for interaction with iron sulphide, FeS, in order to give a volume of hydrogen sulphide, measuring 613.1 c.c., at 20° and 745 mm. pressure?

Calculate also the weight of iron sulphide (98 per cent pure) here consumed. *Ans.* 7.655 grams acid.
2.243 grams FeS (98 per cent).

157. When 100 grams of mercury and 20 grams of sulphur are rubbed together what weight of mercuric sulphide, HgS, may be formed? *Ans.* 116 grams.

Note. — From the reaction-quantities involved it is seen that the sulphur is in excess. This excess is easily removed by solution in carbon disulphide.

158. A mixture of 10 grams of zinc dust and 2 grams of sulphur was gently heated to point of reaction. What weight of zinc sulphide, ZnS, was formed? *Ans.* 6.053 grams.

159. A mixture of 10 grams of iron and 8 grams of sulphur was gently heated to point of reaction. What weight and volume (at standard conditions) of hydrogen sulphide could be obtained from the final product, FeS, by the action of an acid?
Ans. 6.104 grams, or 4010.5 c.c. H_2S.

160. A mixture of 4 grams of sodium oxide, Na_2O, and 6 grams of sulphur trioxide will give what weight of sodium sulphate? *Ans.* 9.166 grams.

161. 3 grams of silver nitrate, $AgNO_3$, and 1 gram of potassium chloride, KCl, were brought together in aqueous solution. What weight of silver chloride, AgCl, was precipitated?
Ans. 1.923 grams.

162. 8.2 grams of crystallized barium chloride, $BaCl_2 . 6 H_2O$, and 7 grams of sulphuric acid (70 per cent H_2SO_4) were brought together in aqueous solution. What weight of barium sulphate, $BaSO_4$, was precipitated? *Ans.* 6.05 grams.

163. 10 grams of a mixture of marble ($CaCO_3$), magnesium, and an inert substance were acted upon by excess of acid. The carbon dioxide evolved (taken up in a solution of potassium hydroxide) was found to weigh 1.318 grams. The volume of the other gas, hydrogen, measured over water at 10° and

750.2 mm. pressure, was 5874 c.c. Calculate the percentage amount of each component in the mixture.

Ans. 30 per cent marble.
60 per cent magnesium.
10 per cent insoluble matter.

164. 15 grams of an alloy of zinc and copper (containing 10 per cent of copper) were placed in a vessel containing 100 grams of sulphuric acid (25 per cent H_2SO_4). What weight of hydrogen was liberated? *Ans.* 0.417 gram.

165. 12 grams of an alloy of aluminium and zinc (containing $33\frac{1}{3}$ per cent of zinc) were placed in a vessel containing 180 grams of hydrochloric acid (35 per cent HCl). What volume of hydrogen, at standard conditions, was liberated?

Ans. 11,290 c.c.

166. A specimen of silver, containing 3 per cent copper, weighed 9.8 grams. After solution in nitric acid an excess of sodium chloride was added to it. Calculate the weight of the silver chloride precipitated. *Ans.* 12.632 grams.

167. 10 grams of phosphorus tribromide, PBr_3, were mixed with an excess of water and an excess of silver nitrate added to this solution. What weight of silver bromide was formed? Calculate also the exact weight of silver nitrate required for this removal of bromide. *Ans.* 20.81 grams AgBr.
18.82 grams $AgNO_3$.

168. What volume of hydrogen sulphide, at standard conditions, would be required for interaction with an excess of iodine, in aqueous suspension, in order to furnish an amount of hydriodic acid sufficient for the precipitation of 10 grams of silver iodide from a solution of silver nitrate? *Ans.* 477 c.c.

169. What weight of fluorspar, CaF_2, would be required to furnish sufficient hydrogen fluoride (by interaction with sulphuric acid) to convert 5 grams of quartz, SiO_2, into silicon fluoride, SiF_4? *Ans.* 12.95 grams.

170. Calculate the volume of chlorine, at standard conditions, necessary to give, by interaction with water, an amount of oxygen which will just suffice for the oxidation of 10 grams of mercury to mercuric oxide, HgO. *Ans.* 1120 c.c.

171. Calculate the volume of chlorine, at standard conditions, necessary to give an amount of potassium chlorate (by interaction with a hot solution of potassium hydroxide) which would just suffice, in its decomposition into oxygen and potassium chloride, for the oxidation of 5 grams of hydrogen to water. *Ans.* 55,446 c.c.

172. 100 grams of iron pyrites, FeS_2, were roasted to ferric oxide, Fe_2O_3, and sulphur dioxide. The sulphur dioxide was then taken up by sodium peroxide, Na_2O_2, to form sodium sulphate, and this product treated with a solution of barium chloride, $BaCl_2$. What weight of barium sulphate was precipitated? *Ans.* 389.1 grams.

173. 20 grams of nitrogen were carried through the following series of reactions. Calculate the resulting volume of nitrous oxide, N_2O, at standard conditions.

$$\begin{aligned} 3\,Mg + N_2 &= Mg_3N_2 \\ Mg_3N_2 + 6\,H_2O &= 3\,Mg\,(OH)_2 + 2\,NH_3 \\ NH_3 + HNO_3 &= NH_4NO_3 \\ NH_4NO_3 &= N_2O + 2\,H_2O \end{aligned}$$

Ans. 50,237 c.c.

174. Calculate the relative weights of sodium chlorate and potassium chlorate necessary to give the same volume of oxygen. *Ans.* 100 ($NaClO_3$) : 115 ($KClO_3$).

175. Calculate the relative weights of potassium chlorate and perchlorate, $KClO_4$, necessary to give the same volume of oxygen. *Ans.* 100 ($KClO_3$) : 84.8 ($KClO_4$).

176. Compare the weights of aluminium and zinc necessary for the production of equal weights of hydrogen by interaction with an acid. *Ans.* 100 (Al) : 361.8 (Zn).

177. Compare the weight of calcium nitride, Ca_3N_2 (in its interaction with water), and the weight of ammonium chloride (in its interaction with a base), necessary to give the same weight of ammonia. *Ans.* 100 (Ca_3N_2) : 72.2 (NH_4Cl).

178. What relative weights of cupric oxide, CuO, and cuprous oxide, Cu_2O, are procurable from the same weight of copper? *Ans.* 100 (CuO) : 89.95 (Cu_2O).

179. In the interaction of methane, CH_4, and chlorine, 2 grams of the former required 17.7 grams of the latter. Calculate the reaction-quantity of chlorine per molecule of methane. *Ans.* 2 Cl_2.

180. 2 grams of hydrogen sulphide, H_2S, decolorized 5.8 grams of potassium dichromate, $K_2Cr_2O_7$ (in acid solution). Calculate the reaction-quantity of the former required per molecule of the latter. *Ans.* 3 H_2S.

181. 2.4 grams of ammonia, NH_3, reduced 17 grams of hot cupric oxide, CuO, to copper. Calculate the reaction-quantity of cupric oxide required per molecule of ammonia. *Ans.* 1½ CuO.

Note. — In order to avoid fractional quantities we may here multiply by two and obtain 3 CuO per 2 NH_3.

182. What weight of chrome-alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24\,H_2O$, may be obtained from 20 grams of crystallized potassium sulphate, $K_2SO_4 . 6\,H_2O$, and an excess of chromium sulphate? *Ans.* 70.76 grams.

183. What weight of ammonium-magnesium phosphate, $NH_4MgPO_4 . 6\,H_2O$, could be formed from a solution containing 50 grams of crystallized magnesium sulphate, $MgSO_4 . 7\,H_2O$, and an excess of ammonia and sodium phosphate? *Ans.* 49.79 grams.

184. What weight of iron-ammonium alum, $(NH_4)_2SO_4 . Fe_2(SO_4)_3 . 24\,H_2O$, may be formed when 12 grams of ammonium sulphate, $(NH_4)_2SO_4$, and 30 grams of ferric sulphate, $Fe_2(SO_4)_3$, are brought together in concentrated aqueous solution? *Ans.* 72.3 grams.

CHAPTER X.

NORMAL SOLUTIONS.

In reactions between substances in solution no attention thus far has been given to the actual amount of substance contained in a definite volume of solvent.

In the action between an acid, furnishing hydrogen-ion, and a base, furnishing hydroxide-ion, the point of neutralization is reached when equal quantities of these two kinds of ions — chemically equivalent — are present, and the complete removal of both in the form of the compound water as a slightly ionized substance is effected. The detection of this point in solution is readily accomplished through the use of an *indicator*, or some substance which shows a change in color by the merest trace of either the one or the other of these two ions. The operation of ascertaining this *end-point* is called *titration*. Naturally it may be applied to the determination of other end-points, or points of completion of definite chemical reactions in solution, as well as to this process of neutralization.

The neutralization of hydrochloric acid by sodium hydroxide is shown by the following equation:

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O$$

$$\underbrace{23 + 17.01}_{40.01} + \underbrace{1.01 + 35.46}_{36.47} = \underbrace{23 + 35.46}_{58.46} + \underbrace{18.02}_{18.02}.$$

A solution which contains 40.01 parts by weight of sodium hydroxide will exactly neutralize one which contains 36.47 parts by weight of hydrogen chloride. This follows from the fact that in the former there are 17.01 parts of ionizable hydroxyl and in the latter 1.01 parts of ionizable hydrogen, — the exact proportions of these two substances necessary for the formation of water. When equal volumes of these solutions neutralize each other, then the concentration of ionizable hydrogen in the acid solution is equal to the concentration of ionizable hydroxyl in the solution of the base; *i.e.*, the relative amounts of each are directly proportional to 1.01 and 17.01 respectively. The liter has been adopted as the standard volume for reactions in solution; when a gram-molecular weight of a substance is contained in this volume we have what is called a gram-molecular solution or more commonly a *Molar Solution.* Some definite temperature, *circa* 20°, is usually understood.

From the reaction between sodium hydroxide and hydrochloric acid, and from the definitions just given, we are aware that one liter of a molar solution of the former will exactly neutralize one liter of a molar solution of the latter; consequently any fractional part of the one solution will neutralize this same fractional part of the second solution.

In the neutralization of this same base by a dibasic acid, such as sulphuric acid, the following equation comes into consideration:

$$2\,Na^{\cdot} + 2\,OH' + 2\,H^{\cdot} + SO_4'' = 2\,Na^{\cdot} + SO_4'' + 2\,H_2O$$
$$2(23) + 2(17.01) + 2(1.01) + 96.07 = 2(23) + 96.07 + 2(18.02)$$

From this it is evident that a molar solution of sulphuric acid, with 98.09 grams of the acid per liter, will contain 2.02 grams of ionizable hydrogen, a quantity that requires 34.02 grams (2 × 17.01) of ionizable hydroxyl for its complete neutralization. This quantity of hydroxyl is furnished, as the equation indicates, through the use of two gram-molecular weights of sodium hydroxide. If we were dealing with molar solutions of these substances, two volumes of the sodium hydroxide solution would be required for the neutralization of one volume of a molar sulphuric acid solution.

By reason of this variation in the number of ionizable hydroxyl and hydrogen groups in the various substances, it is found advisable to base our standard solutions upon the exact number of these univalent groups which they contain, rather than upon the entire molecular weight of the substance itself. A solution which contains in one liter exactly 1.01 grams of ionizable hydrogen is taken as the standard for acids, while that which contains in one liter exactly 17.01 grams of ionizable hydroxyl is taken as the standard for bases. These two solutions are, volume for volume, always equivalent and may be termed *Equivalent Normal Solutions* or, as is more generally the case, *Normal Solutions.*

The molar solution of sodium hydroxide is identical, of course, with its normal solution. The molar solution of sulphuric acid contains twice as much ionizable hydrogen as is required for its normal solution, — a fact indicated by the use of two volumes of the molar sodium hydroxide solution above to neutralize only one volume of this acid. We are therefore required to dissolve one-half of the gram-molecular weight (98.09) of sulphuric acid, or 49.04 grams, in water and bring this to one liter in order to obtain its true normal solution.

In the same manner a base such as barium hydroxide, $Ba(OH)_2$, with a molecular weight of 171.39, will contain in its molar solution 171.39 grams of substance of which 34.02 grams is ionizable hydroxyl. A definite volume of this molar solution would neutralize two volumes of a normal hydrochloric acid solution; consequently to obtain a solution of 17.01 grams of hydroxyl to the liter (a normal solution) we should need to dissolve 171.39/2 grams of the substance in a liter of solution. A solution of this concentration is here unattainable, as the solubility falls below the value required. In such cases various degrees of dilution are used, as will be indicated below.

Solutions that furnish neither hydrogen- nor hydroxide-ion are considered normal when they contain, per liter, an equivalent of 1.01 grams of hydrogen or 17.01 grams of hydroxyl. This signifies that in the reactions in which they are concerned they will have, per liter, the power of combining with or displacing, either directly or indirectly, these proportional amounts of hydrogen or hydroxyl. Thus, in the action of hydrochloric acid upon sodium carbonate:

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2O + CO_2,$$

it is observed that one gram-molecular weight of the carbonate brings into the reaction 2.02 grams of hydrogen; consequently one-half of its gram-molecular weight (106), or 53 grams of sodium carbonate, is required in 1 liter of its normal solution.

Normality Factors. — For chemical purposes it is not necessary to bring every solution to the same standard of concentration, — the normal solution. The variations from the true normality may be readily expressed by fractions, or factors, which designate at once the actual concentration of the solutions in terms of the normal. Thus a molar solution of sulphuric acid contains twice what a normal solution should contain. Its normality, therefore, is 2, and is expressed as 2 N. A solution containing 0.365 gram of hydrogen chloride per 100 c.c. would contain 3.65 grams per liter. This is 1/10 of what a normal solution contains; hence the solution is N/10 or 0.1 N, (deci-normal).

By another method of procedure, this solution, containing 0.365 gram of hydrogen chloride per 100 c.c., may be compared directly with the amount required in a liter of a normal solution, namely, 36.5 grams: — $36.5 : 0.365 = 1 : x$. The factor (x) is here 0.01, hence this weight (0.365 gram) of hydrogen chloride would be contained in 1/100 of 1000 c.c., or 10 c.c. of the normal acid. As it actually occurs in 100 c.c., then the solution in question is 10/100 N or N/10; that is, 100 c.c. of this solution is necessarily equivalent to 10 c.c. of the normal solution.

By reason of the equivalence between equal volumes of normal solutions we can readily calculate the normality of any solution if we are given the normality of that solution which is to be titrated against it.

Example 48. — 100 c.c. of N/2 sodium hydroxide solution were required in the neutralization of 400 c.c. of an unknown acid solution. Calculate the normality of this acid?

Here, of course, 100 c.c. of N/2 solution is the equivalent of 50 c.c. of a normal solution; *i.e.*, in 100 c.c. of N/2 sodium hydroxide solution we have 100/1000 or 1/10 of 17.01/2 grams, or 17.01/20 gram, of hydroxyl, which is exactly the amount contained in 1/20 of a liter (50 c.c.) of a normal solution containing 17.01 grams per liter. In order to find the normality of the unknown solution it will be necessary to get some expression for it in terms of the known or normal solution. For example, 400 c.c. of this unknown solution neutralize 50 c.c. of the normal. By reduction, 1 c.c. neutralizes 1/8 c.c. of the normal. The relative volumes are equivalent; hence 1 liter of the unknown solution must neutralize, and possess an equivalent amount of substance to, that contained in one-eighth of a liter of normal sodium hydroxide solution. It is, therefore, but 1/8 N, a fact indicated at once by the factor obtained for the equivalent of that unit value 1 c.c. above. If we had taken as the unit value 1 c.c. of the known solution, we should have obtained 8 as a factor denoting the number of cubic centimeters of the unknown acid solution equivalent in value to 1 c.c. of the known. This comes to the same end and indicates the strength of 1 c.c. of the unknown solution as 1/8 that of the normal.

Calculation of Normality by Simple Proportion. — A very simple method for calculations of this sort rests upon the consideration of the proportionality which exists between the normality factors and the volumes for these equivalent solutions.

Example 49. — 400 c.c. of N/8 acid solution neutralized 100 c.c. of an unknown alkaline solution. Calculate the normality of the alkali.

(Now the volume of a solution when multiplied by its normality factor gives, as we have seen, the equivalent volume in terms of its normal solution) As all of these solutions are balanced or titrated to an end-point which signifies that equivalent quantities of the various substances are present, we may at once place the two expressions for the two solutions as equal to each other. Thus:

$$400 \times 1/8 = 100 \times x.$$

All of this is in exact accord with our premises which make it necessary for equal volumes to neutralize equal volumes when an equivalent amount of substance is present in each. By separating these terms of the equation into means and extremes of a simple proportion (for example by dividing through by the quantity 100 × 1/8) we obtain

$$\frac{400}{100} = \frac{x}{1/8}.$$

This is synonymous with saying that the normality factors of the two equivalent solutions stand to each other in an inverse proportion to the corresponding volumes required in the titration:

$$100 : 400 = 1/8 : x.$$

By calculation x is found to be 1/2, *i.e.*, the alkaline solution is 0.5 normal.

Calculation of the Weights of Substances Present in Standard Solutions.— When the normality of an unknown solution has been determined it is often desirable to find the exact amount of substance in a given volume of this solution. For example, in the last paragraph the normality of the alkaline solution was found to be N/2. If it is now desired to learn the amount of sodium hydroxide actually present in the 100 c.c. of solution, we need only take the proportional amount of sodium hydroxide in a liter of N/2 solution (20 grams) as is indicated by the fractional part which this volume is of 1000,—100/1000 or 1/10, *i.e.*, 1/10 of 20 grams, or 2 grams. By simple proportion a comparison of the volume relations with the corresponding weights of the substances gives the following:

$$1000 : 100 = 20 : x.$$

Standardization of Solutions by Gravimetric Means.— For our standard solutions, it is usually customary to dissolve a certain calculated amount of substance in water and bring the volume up to the desired mark by the gradual addition of more water. As these solutions may vary slightly from the true values, it is always desirable to standardize them by purely chemical means, such as titration against certain accurately prepared solutions, or if possible by the formation of precipitates in a known volume of their solution. These precipitates when dried and weighed serve as a means for the calculation of the exact normality.

Example 50. — 100 c.c. of a hydrochloric acid solution, made up approximately to 1/5 N, gave, when treated with a slight excess of a silver nitrate solution, 3.22 grams of silver chloride. What is the normality of the acid?

From the equation: 100cc : 3.22

$$AgNO_3 + HCl = AgCl + HNO_3,$$

the proportionality between all amounts of hydrogen chloride and silver chloride are indicated by the ratio:

$$\begin{array}{ccc} AgCl & : & HCl \\ (107.88 + 35.46) & : & 36.47. \end{array}$$

From this ratio the weight of hydrogen chloride, 0.8195 gram, corresponding to the weight of silver chloride, 3.22 grams, is easily calculated:

$$\begin{array}{l} AgCl \ : HCl \ = 3.22 : x \\ 143.34 : 36.47 = 3.22 : 0.8195. \end{array}$$

This weight of hydrogen chloride is found present in 100 c.c. of solution. In one liter we shall have 8.195 grams, whereas we should have 36.47 grams if it were a normal solution. The fraction 8.195/36.47 represents then the normality, expressed decimally as 0.2247 N, and gives to the solution a value somewhat higher than that estimated, (N/5).

Standardization of Solutions by Volumetric Means. — In place of the method of precipitates another very instructive method is applicable in standardization; chiefly with acids. This consists in measuring the volume of a gas evolved by the action of some substance upon a known volume of the acid solution.

Example 51. — 250 c.c. of an acid solution gave, when acted upon by zinc, 560 c.c. of hydrogen (calculated at standard conditions of temperature and pressure). What is the normality of the acid.

560 c.c. of hydrogen from 250 c.c. of solution would mean, of course, 2240 c.c. from one liter of the solution. By definition a normal solution of an acid is one that contains 1.01 grams of ionizable hydrogen per liter. The gram-molecular weight (2.02) of hydrogen occupies a volume of 22,400 c.c. at standard conditions. The volume occupied by 1.01 grams therefore will be just one-half this, or 11,200 c.c. Accordingly every liter of a normal acid solution must contain that weight of hydrogen which when set free will occupy 11,200 c.c. under the standard conditions of temperature and pressure.

It is only a simple step to calculate the volume of hydrogen per liter when we have given the volume for any fraction of a liter. In the problem above, 250 c.c. of solution evolved 560 c.c. of hydrogen; consequently 1 liter will evolve 2240 c.c. of this gas: $250 : 1000 = 560 : x$. As a liter of normal acid should give 11,200 c.c., the solution in question is less than normal, and in accordance with the ratio

$$11{,}200 : 2240 = 1 : x, \text{ or } x = 1/5,$$

i.e., the acid is 0.2 N. In other words, the normality is expressed by the fraction, or factor, which the volume of hydrogen evolved per liter makes with the total volume of hydrogen that can be evolved from a liter of the normal acid.

If the hydrogen is measured at room temperature and pressure, it is only necessary to calculate the volume it would occupy at the standard conditions and thus make possible the comparison between this and the standard volume per liter. If this is not done, then the standard volume per liter (11,200 c.c.) must be calculated to the conditions of the experiment under which the gas is measured.

Similarly, the evolution of other gases by chemical action, from known volumes of solutions, may serve for the estimation of the normalities of these solutions. For example, a solution of sodium carbonate may be treated with an acid and the carbon dioxide set free measured. The following equation is here involved:

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O.$$

The direct proportionality between the reaction-quantities concerned is expressed by the ratio CO_2/Na_2CO_3 or 44/106. This shows that for every gram-molecular weight of carbon dioxide (44) we must estimate the presence of one gram-molecular weight of sodium carbonate (106). Now a normal solution of sodium carbonate contains only one-half of the gram-molecular weight in 1 liter; a fact readily determined by its titration with a normal solution of any acid. This is indicated in the equation above, wherein we note that 2.02 grams of ionizable hydrogen ($2\,H^{\cdot} + SO_4''$) are required for the complete action, and consequently only one-half of the gram-molecular weight of the carbonate, 53 grams, can be equivalent to 1.01 grams of hydrogen. The amount of carbon dioxide evolved from one gram-molecular weight of the carbonate is one gram-molecular weight, or a volume of 22,400 c.c.; hence from a normal solution with one-half the gram-molecular weight of carbonate, we should have, per liter, just 11,200 c.c. of this gas.

When the volume of carbon dioxide evolved from a definite volume of solution is known we need only to calculate the volume of gas evolved, per liter, and compare this volume at standard conditions with the standard volume, 11,200 c.c. The ratio to this value gives the ratio to unit normality.

Example 52. — What is the normality of a sodium carbonate solution, 125 c.c. of which evolved 350 c.c. of carbon dioxide (at standard conditions) when treated with an excess of acid?

Since 125 c.c. of the solution gave 350 c.c. of the gas, 1000 c.c. will give 2800 c.c. as determined from the proportion 125 : 1000 = 350 : x. A normal solution should evolve 11,200 c.c. of this gas; consequently the solution in question is only 2800/11,200 or 1/4 N.

The evolution of carbon dioxide in the equation above may serve equally well in determining the normality of the sulphuric acid used. Each liter of normal sulphuric acid will liberate 11,200 c.c. of the gas. The ratio of comparison, therefore, is carried out just as described in the previous paragraph.

Comparison of Solutions with Standard. — When a solution is once standardized other solutions may be standardized by comparison with it either directly or indirectly. In the case of a second acid solution it is necessary to ascertain what volumes of both this acid and our standard acid are required for the neutralization of equal volumes of some alkaline solution. These two equivalent volumes are then compared just as in the preceding examples.

Example 53. — 10 c.c. of 1.5 N hydrochloric acid neutralized 40 c.c. of an alkaline solution. 50 c.c. of an unknown sulphuric acid solution neutralized 80 c.c. of this same alkaline solution. Calculate the normality of the sulphuric acid.

50 c.c. of the sulphuric acid neutralized 80 c.c. of the alkali; 25 c.c. of the acid would neutralize 40 c.c. of the alkali. This is the same volume of alkali neutralized by 10 c.c. of 1.5 N hydrochloric acid; hence these two volumes of the acid solutions must be equivalent:

$$10 \text{ c.c.} \times 1.5 \text{ N HCl} = 25 \text{ c.c.} \times (x) \text{ N } H_2SO_4.$$

By proportion:

$$25 : 10 = 1.5 : x, \text{ or } x = 3/5.$$

Hence the normality of the sulphuric acid is found to be 3/5, *i.e.*, 0.6 N.

Adjustment of Solutions to a Desired Standard. — When a solution has been standardized and found to vary somewhat from the estimated normality, it is customary to calculate the amount of substance (if too dilute) or water (if too concentrated) that will bring the solution to the desired normality. The latter, which constitutes the more simple case, is illustrated in the following example:

Example 54. — A solution of hydrochloric acid was found to have a normality of 1.05. What volume of water must be added to 400 c.c. of this solution to make it exactly normal?

1 c.c. of 1.05 N hydrochloric acid is equivalent by definition to 1.05 c.c. of a normal hydrochloric acid solution. Therefore, to make this more concentrated acid normal, we need only add water until 1.05 c.c. of the diluted solution will be exactly equivalent to 1.05 c.c. of a normal solution; in other words,

$$1.05 \text{ c.c.} - 1 \text{ c.c.} = 0.05 \text{ c.c.},$$

or that volume of water required per cubic centimeter of the 1.05 N acid. 400 c.c. will require 400 × 0.05 c.c., or 20 c.c. Therefore, when 400 c.c. of this 1.05 N acid are diluted with 20 c.c. of water, the final 420 c.c. will be just normal.

By comparison of the actual weights of hydrogen chloride in equal volumes of these acids and the direct proportionality between these weights and the corresponding volumes which are equivalent, volume for volume, we may calculate the amount of dilution necessary to bring any known solution to a desired normality. Thus in 1 c.c. of normal hydrochloric acid there is 0.0365 gram of hydrogen chloride, and in 1 c.c. of 1.05 N hydrochloric acid there is 1.05×0.0365 gram of hydrogen chloride. Therefore

$$0.0365 : (1.05 \times 0.0365) = 400 : x, \text{ or } x = 420.$$

This gives the volume to which 400 c.c. of 1.05 N acid must be diluted.

When a solution is found too dilute, a similar calculation will give the amount of water that should be removed from the volume in question. Without resorting to this procedure, it is found better to add to the entire volume that weight of substance (usually a well-defined salt) necessary to make with this excess of water a solution of the desired normality. Any change in volume due to process of solution of the salt may be neglected.

The calculation of results through reactions which involve solutions of definite concentration follows the general outlines presented in Chapter IX. The amount of any substance present in a required volume of a standard solution is to be considered, of course, with reference to its corresponding reaction-quantity.

The method of determining the amount of a substance necessary to complete a given reaction with a known amount of some other substance contained in a definite volume of solution is called "Volumetric Analysis." When no reference is made to volume relations, but calculations are made upon the weighed quantities which come under consideration, we have the more common "Gravimetric Analysis." These two form the basis of work in quantitative chemical analysis.

PROBLEMS.

185. 400 c.c. of N/4 potassium hydroxide solution were required for the neutralization of 600 c.c. of an unknown acid solution. Calculate the normality of this acid solution. *Ans.* N/6.

186. 500 c.c. of N/10 acid solution were required for the neutralization of 25 c.c. of a solution of sodium hydroxide. Calculate the normality of this latter solution. *Ans.* 2 N.

187. 220 c.c. of N/20 acid solution were required for titration with 124 c.c. of a solution of barium hydroxide. Calculate the normality factor of the barium hydroxide solution. *Ans.* .0887 N.

188. What volume of N/10 acid solution will be required in the titration of 440 c.c. of N/4 sodium hydroxide solution? *Ans.* 1100 c.c.

NOTE: — The method by simple proportion, with one of the volumes as the unknown term, will be found to serve well in such examples.

189. What volume of N/6 alkaline solution will be required in the titration of 254 c.c. of N/10 acid solution? *Ans.* 152.4 c.c.

190. Calculate the weight of hydrogen chloride present in 400 c.c. of a hydrochloric acid solution which required 320 c.c. of N/4 alkaline solution for titration. *Ans.* 2.918 grams.

191. Calculate the weight of sulphuric acid present in 150 c.c. of a solution which required 48.1 c.c. of 0.78 N alkali for titration. *Ans.* 1.84 grams.

192. An excess of silver nitrate solution was added to 350 c.c. of a solution of hydrochloric acid. The precipitate of silver chloride weighed 7.54 grams. Calculate the normality of the acid. *Ans.* 0.1503 N.

193. A slight excess of barium chloride solution was added to 400 c.c. of a solution of sulphuric acid. From the weight of barium sulphate, $BaSO_4$, precipitated, 4.12 grams, calculate the normality of the acid. *Ans.* 0.0882 N.

194. 600 c.c. of a sulphuric acid solution, when acted upon by an excess of zinc, evolved 1242 c.c. of hydrogen (at standard conditions). Calculate the normality of the acid.
Ans. 0.1848 N.

195. 440 c.c. of an acid solution, when acted upon by an excess of zinc, evolved 2430 c.c. of hydrogen, measured over water at 21° and 747.5 mm. pressure. Calculate the normality of the acid. *Ans.* 0.4408 N.

196. Calculate the normality of an acid solution, 600 c.c. of which, when acted upon by an excess of sodium carbonate, evolved 2100 c.c. of carbon dioxide (calculated to standard conditions). *Ans.* 0.3125 N.

197. Calculate the normality of a solution of potassium carbonate, 200 c.c. of which, when treated with an excess of acid, evolved 4502 c.c. of carbon dioxide (calculated to standard conditions). *Ans.* 2.01 N.

198. An excess of iron sulphide, FeS, was added to 500 c.c. of a solution of sulphuric acid. The volume of hydrogen sulphide set free measured 4640 c.c. (at standard conditions). Calculate the normality of the acid. *Ans.* 0.8285 N.

199. An excess of sodium sulphite, Na_2SO_3, was added to 400 c.c. of a solution of hydrochloric acid. The volume of sulphur dioxide set free measured 5600 c.c. (at standard conditions). Calculate the normality of the acid. *Ans.* 1.25 N.

200. 1400 c.c. of ammonia (calculated to standard conditions) were passed into 500 c.c. of N/2 hydrochloric acid solution. Calculate the normality of the hydrochloric acid still present. *Ans.* 3/8 N.

201. 210 c.c. of carbon dioxide (at standard conditions) were passed into 250 c.c. of N/10 barium hydroxide solution. Calculate the normality of the barium hydroxide solution still present. *Ans.* N/40.

202. 50 c.c. of N/5 hydrochloric acid solution neutralized 40 c.c. of an unknown alkaline solution. 300 c.c. of a sulphuric acid solution neutralized 60 c.c. of this same alkaline solution. Calculate the normality of the sulphuric acid.
Ans. 0.05 N.

203. 200 c.c. of a barium hydroxide solution were required in the titration of 40 c.c. of an acid solution. 100 c.c. of this acid solution exactly neutralized 80 c.c. of N/2 alkaline solution. Calculate the normality of the barium hydroxide solution. *Ans.* 0.08 N.

204. A solution of hydrochloric acid is desired to be made exactly normal. 40 c.c. of the solution neutralized 50 c.c. of 0.84 N sodium hydroxide solution. Calculate the volume of water that must be added per 100 c.c. of the acid solution. *Ans.* 5 c.c.

205. A solution of sodium hydroxide is desired to be made exactly 0.5 N. 32 c.c. of the solution at hand were required for the titration of 28 c.c. of 0.8 N hydrochloric acid. Calculate the volume of water that must be added per 100 c.c. of the alkaline solution. *Ans.* 40 c.c.

206. A solution of sodium carbonate is desired to be made exactly 0.05 N. 24 c.c. of the solution at hand neutralized 9.6 c.c. of 0.12 N hydrochloric acid solution. Calculate the weight of anhydrous salt, Na_2CO_3, that must be added per 100 c.c. of solution. *Ans.* 0.0106 gram.

207. What weight of iron will be required for interaction with 400 c.c. of N/5 hydrochloric acid? *Ans.* 2.234 grams.

208. What weight of sodium carbonate will be required for interaction with 600 c.c. of N/8 sulphuric acid? What volume of carbon dioxide (at standard conditions) will be evolved?

Ans. 3.975 grams.
840 c.c. CO_2.

209. What weight of sodium hydrogen carbonate, $NaHCO_3$, will be required for interaction with 600 c.c. of N/8 sulphuric acid? What volume of carbon dioxide (at standard conditions) will be evolved? *Ans.* 6.3 grams.
1680 c.c. CO_2.

210. Calculate the weight of crystallized oxalic acid, $C_2H_2O_4 . 2\,H_2O$, required for a solution which is to be made up to 500 c.c. in volume at N/2. *Ans.* 15.75 grams.

211. Calculate the volume of nitric oxide, NO (at standard conditions) that could be evolved by the action of copper upon 1000 c.c. of a 7 N nitric acid solution. *Ans.* 39,200 c.c.

CHAPTER XI.

COMBINATIONS BETWEEN GASES BY VOLUME.

When expressed in grams the molecular weights of all substances in the state of vapor occupy a volume of 22,400 c.c. at the standard conditions of temperature and pressure. In Chapter IX it was observed that a molecular equation offered for this reason an insight into the volume relations of the various substances concerned in a given reaction.

Molecular Volumes. — These volumes comply naturally with the laws relating to gases, and, further, are subject to the operation of those properties, characteristic of each substance, which may here be brought into consideration through the conditions of the experiment. Thus the condensation of a gas or vapor to the liquid or solid state, or its solution in, or combination with, various substances which may be present, will remove it completely from further considerations.

As a simple illustration of these facts an excellent example is found in the combination of hydrogen with oxygen:

$$2\,H_2 + O_2 = 2\,H_2O.$$

By molecules: $2 \quad + 1 \quad = 2.$

By gram-molecular volumes:

$$2\,(22{,}400)\text{ c.c.} + 1\,(22{,}400)\text{c.c.} = 2\,(22{,}400)\text{ c.c.} + (22{,}400\text{ c.c. contraction}).$$

Reduced through the
common term, 22,400:

$$2 \text{ vol.} + 1 \text{ vol.} = 2 \text{ vol.} + (1 \text{ vol. contr.}).$$

Each gram-molecular weight may be represented by one volume, *i.e.*, its gram-molecular volume. The coefficients or integers which designate the number of gram-molecular weights will stand likewise for the number of gram-molecular volumes involved in the reaction. The combination of gases by volume expressed thus by simple numbers has been developed experimentally and is comprehended in Gay-Lussac's well-known Law of Combining Volumes.

In the reaction above we observe that 2 volumes of hydrogen and 1 volume of oxygen unite to form 2 volumes of aqueous vapor, the temperature of 100° or above, and the observed pressure, remaining constant throughout. This diminution in the total volume of the gaseous components when transformed into aqueous vapor has been considered in the study of Avogadro's hypothesis.

If the temperature falls below 100° a further contraction in volume occurs. Since this is due to the condensation of aqueous vapor to the liquid state, and increases accordingly with a lowering of temperature, there is left, eventually, no volume of gaseous product. The water formed becomes associated with the liquid over which the gases are measured, and consequently drops out of further consideration through the equalization or adjustment of the levels within and without the vessel to bring all to uniform pressure. Of course a small amount of water remains in the vapor state, even at a low temperature; corrections for this are made by reference to a table of aqueous vapor tensions (Appendix II).

The volume of the dry gaseous product, which in this case is theoretically *nil*, may be expressed in this manner:

$$2\,H_2 + O_2 = 2\,H_2O.$$

Molecular volumes: 2 + 1 = 2 + (1 vol. contr.).

Molecular volumes
below 100°: 2 + 1 = 0 + (3 vol. contr.).

The Relation of Molecular Volume to a Definite Volume-Unit. — In the study of these volume-changes in known reactions it is always necessary to determine the exact relation which any measured volume of vapor, under consideration, bears to the corresponding molecular volume representing it in the molecular equation governing the reaction.

The coefficients of the quantities in a molecular equation determine the ratios between the volumes of these substances when in the state of vapor. The coefficient unity stands, of course, for the unit of molecular volume (22,400 c.c.), a volume corresponding to a gram-molecular weight of substance. Any fractional part of the gram-molecular weight of a substance will occupy, therefore, under standard conditions, a volume denoted by this same fractional part of the gram-molecular volume, 22,400 c.c. Whatever may be this fractional part of the molecular quantity of a substance under consideration in a reaction, all other substances possible of interaction with this one must be correspondingly reduced from their own molecular quantities.

These coefficients, therefore, are constant for any known molecular equation and stand for the ratio between the volumes of the substances in state of vapor, be they gram-molecular volumes or any definite fractional parts of these. That volume which is represented by the coefficient unity in a molecular equation is indeed the unit upon which all of the other substances, in the state of vapor, enter into the reaction. It may be regarded as the *Volume-Unit* for the reaction given. If the coefficient representing a certain substance in a molecular equation is greater than unity, then, of course, from the actual volume of vapor of the substance here concerned, the true volume-unit for the equation can be derived only by dividing this known volume by the corresponding coefficient.

Calculation of the Volume-Unit from a Single Known Volume. — When once the volume-unit for a reaction is established, the actual volumes of the several substances here entering into combination are easily determined from the product of the several coefficients in the molecular equation by the volume-unit.

Example 55. — What volume of oxygen will be required to burn 300 c.c. of hydrogen and what volume of aqueous vapor will result, the temperature of 100° and the atmospheric pressure remaining constant throughout?

$$2\,H_2 + O_2 = 2\,H_2O.$$

Molecular volumes:

$$2 \quad + 1 \quad = 2 + (1 \text{ vol. contr.}).$$

By placing the molecular volume coefficients out by themselves, the relative volumes of the several substances are indicated. Since we can make our calculations only from the volumes actually given as data, we refer the volume of hydrogen, 300 c.c., directly to the coefficient 2. From this we derive the volume 150 c.c. (300 ÷ 2) as the value for the coefficient of unity, *i.e.*, the volume-unit of the reaction. There remains now only to substitute this value for each coefficient throughout the entire molecular equation.

$$2\,H_2 + O_2 = 2\,H_2O.$$

Molecular volumes: $2 + 1 = 2 + (1\text{ vol. contr.})$.

Volumes upon the unit 150 c.c.:

300 c.c. + 150 c.c. = 300 c.c + (150 c.c. contr.).

The solution of the problem is clearly seen. 150 c.c. of oxygen are required for the combustion of the 300 c.c. of hydrogen, while the volume of aqueous vapor that results will measure 300 c.c.

Calculation of Volume-Unit from Known Mixtures of Gases. — Since the coefficients or integers represent the ratios between the several volumes which enter into chemical combination, it must be understood that these combinations take place only in accordance with these ratios, and that, if any substance is present in amount to exceed the stipulated volume, this excess must remain unaffected in the reaction; if present in amount less than the stipulated volume, the entire reaction must run upon a somewhat smaller scale, or volume-unit, for this particular substance; with the result that the other substance or substances concerned will be in excess of the corresponding volumes stipulated by the ratios, and consequently a fraction of each of these will remain unaffected.

Example 56. — A mixture of 250 c.c. of hydrogen and 150 c.c. of oxygen was submitted to the action of an electric spark. What was the volume of the product after the explosion, the temperature 100° and atmospheric pressure constant?

$$2\,H_2 + O_2 = 2\,H_2O.$$

Molecular volumes: $2 + 1 = 2 + (1\text{ vol. contr.})$.

In making hydrogen the basis for our calculations, we derive from the volume 250 c.c. the value 125 c.c. as the volume-unit. Substituting this value for unity in the equation above we obtain the following:

Volume relations, $\left\{ 250 \text{ c.c.} + 125 \text{ c.c.} = 250 \text{ c.c.} + (125 \text{ c.c. contr.}). \right.$

Volumes given, $\left\{ 250 \text{ c.c.} + 150 \text{ c.c.} \right.$

Excess in oxygen, $\left\{ 25 \text{ c.c.} \right.$

The volume of aqueous vapor formed is 250 c.c. The volume of oxygen, however, is seen to be in excess by 25 c.c. of the volume actually required in the reaction; hence the apparent volume of product will be increased by this same amount:

$$250 \text{ c.c.} + 25 \text{ c.c.} = 275 \text{ c.c.},$$

which is the volume of gaseous mixture after the explosion.

In place of hydrogen as the basis for this calculation of the volume-unit, we may now choose oxygen. The volume given, 150 c.c., will then correspond to a volume-unit in the equation; hence by substituting this value throughout we obtain

$$\begin{array}{rcl} 2\,H_2 + O_2 & = & 2\,H_2O \\ 2 + 1 & = & 2. \end{array}$$

Volume relations: 300 c.c. + 150 c.c. = 300 c.c.

Volumes given: 250 c.c. + 150 c.c.

Here the volume of hydrogen demanded by the equation for combination with 150 c.c. of oxygen actually exceeds the amount of hydrogen at our command. Our volume-unit, therefore, has been placed too high. It is necessary, then, to reduce these high values until the calculated volumes of all the separate components fall equal to or under the volumes of substances actually present. Such, of course, was true in the selection of hydrogen, as above, for the basis of the calculation.

Calculation of True Volume-Unit for a Reaction. — In general, we determine a volume-unit for a reaction from each of the known volumes of substances present; this of course by dividing each volume by the corresponding coefficient which represents it in the molecular equation. Upon comparison of the volume-units thus derived, the smallest will stand for the true unit. In the example above the volume-unit upon the hydrogen basis is 125 c.c., upon the oxygen basis it is 150 c.c; consequently the value 125 c.c. alone fulfills the requirements of the reaction.

Example 57. — 100 c.c. of ammonia and 90 c.c. of oxygen were exploded. What was the final volume of the product? A temperature of 100° and atmospheric pressure constant.

The reaction proceeds in accordance with the equation:

$$4\,NH_3 + 3\,O_2 = 2\,N_2 + 6\,H_2O.$$

$$\begin{array}{l} \text{Molecular} \\ \text{volumes:} \end{array} \left\{ 4 \quad + \quad 3 \quad = \quad 2 \quad + \quad 6 \; - \; (1 \text{ vol. expan.}). \right.$$

From the volume of ammonia:

$$100/4 = 25 \text{ c.c.} = \text{volume-unit.}$$

From the volume of oxygen:

$$90/3 = 30 \text{ c.c.} = \text{volume-unit.}$$

The smaller value, 25 c.c., must be, therefore, the volume-unit for this reaction, while the oxygen will be found slightly in excess of the required amount.

Substituting the value 25 c.c. for unity throughout, we obtain

$$\begin{array}{ll} & 4\,NH_3 + 3\,O_2 = 2\,N_2 + 6\,H_2O \\ & \quad 4 \quad + \quad 3 \quad = \quad 2 \quad + 6 - (1 \text{ vol. expan.}). \\ \begin{array}{l} \text{Volume} \\ \text{relations:} \end{array} & \left\{ 100 \text{ c.c.} + 75 \text{ c.c.} = 50 \text{ c.c.} + 150 \text{ c.c.} \right. \\ \begin{array}{l} \text{Volumes} \\ \text{given:} \end{array} & \left\{ \underline{100 \text{ c.c.} + 90 \text{ c.c.}} \right. \\ \text{Excess:} & \qquad\qquad 15 \text{ c.c. oxygen.} \end{array}$$

Therefore the volume of product will be equal to 50 c.c. + 150 c.c., or 200 c.c., plus the excess of oxygen, 15 c.c., remaining unacted upon, or 215 c.c. in all.

The determination of this volume-unit in combinations between gases is at the basis of all these calculations. In examples where the volume of only one substance is given it is often difficult to ascertain the volumes of other substances that may enter into the specified reaction.

Calculation of Volume-Unit from Measured Volume-Changes. — Where calculations are based alone upon the volumes of gases that enter into combination, the exact proportion of each and every component of the mixture must be known; otherwise the volume-units for the several reactions cannot be determined. If one or more of these factors are unknown, then a study of the various contractions and expansions in the total volume of product over that of the original mixture offers a direct method for the solution. Heretofore we have concerned ourselves only with the components that entered into a reaction. The study of the products, however, offers far greater possibilities for the reason that the numerous condensations and absorptions serve to estimate the volumes of the many substances possible of formation. Through these observations, and a study of the equations involved, we may deduce all of the relations between the various components that entered into a reaction.

These conclusions are made possible by the conditions of a molecular equation, wherein only molecular volumes and multiples of these are concerned. An expansion or contraction in total volume of product over the original volume must be represented, therefore, by a gain or loss in a definite number of molecular volumes. This number will be denoted by the difference between the sum of the molecular volumes on one side of the equation and the sum of the molecular volumes on the other. If this difference corresponds to a single molecular volume, *i.e.*, a volume with coefficient unity, then the expansion or contraction observed is in reality the exact measure of the volume-unit for the reaction; whereas, if this difference is greater or less than unity, the change in volume observed must be reduced, through division by the coefficient for this difference, when a volume is obtained corresponding to a coefficient of unity, *i.e.*, the volume-unit.

Example 58. — 100 c.c. of a sample of air were mixed with 100 c.c. of hydrogen (an excess) and exploded. After the removal of the aqueous vapor by absorption, the volume of dry gaseous product read 140 c.c. Calculate the percentage of oxygen in this sample of air, the room temperature and pressure remaining a constant throughout.

$$2\,H_2 + O_2 = 2\,H_2O.$$

Molecular volumes at 100°: $\quad 2 + 1 = 2 + (1 \text{ vol. contr.}).$

Molecular volumes at room temperature: $\quad 2 + 1 = 0 + (3 \text{ vol. contr.}).$

If the conditions were such that all of the water remained in state of vapor (100°), the contraction observed, and represented by a coefficient of unity, would stand for the contraction of 1 volume-unit in the equation, and from this value the volume of oxygen present — 1 volume-unit — would be found equal in value to the contraction itself.

With the conditions otherwise and the loss of aqueous vapor increasing the molecular volume contraction by 2 molecular volumes (2 volume-units), we note that the observed contraction must be due to the loss of 3 volume-units from the side of the products. The original mixture, 100 c.c. + 100 c.c., or 200 c.c., lost 60 c.c. in this reaction (200 c.c. − 140 c.c.); hence 60 c.c. represents the 3 volume-units, or 1 volume-unit will be equal to 20 c.c. From the equation, the oxygen consumed is exactly 1 volume-unit and hence 20 c.c. This indicates that 20 per cent of the sample of air was oxygen.

Example 59. — A volume of ammonia was mixed with a large excess of oxygen and exploded. The expansion in volume of product over the original mixture was 50 c.c. What was the volume of ammonia? Temperature of 100° and atmospheric pressure a constant.

The equation for this action has been given before:

$$4\,NH_3 + 3\,O_2 = 2\,N_2 + 6\,H_2O.$$

$$\begin{array}{l}\text{Molecular}\\ \text{volumes:}\end{array}\left\{\begin{array}{l} 4 + 3 = 2 + 6. \\ 7 \text{ vol.} = 8 \text{ vol.} - (1 \text{ vol. expan.}). \end{array}\right.$$

In this case the expansion is seen to be exactly equal to a unit coefficient in volume; consequently 50 c.c. is the volume-unit for the reaction. By substituting this value in the molecular equation, the volume of ammonia (4 volume-units), which in its combustion can produce this expansion of 50 c.c., is found equal to 4 × 50 c.c. or 200 c.c.

From a study of the volume of products, and the alterations in this volume through elimination of certain of the substances, we are able to determine the actual composition of unknown mixtures of gases.

Example 60. — 200 c.c. of a mixture of nitrogen and methane were exploded with 400 c.c. of oxygen. The volume of the dry gaseous product measured 500 c.c. What was the percentage of methane in the original mixture? The room temperature and pressure a constant.

$$CH_4 + 2O_2 = CO_2 + 2\,H_2O.$$

$$\text{Molecular volumes:}\quad 1 + 2 = 1 + 2$$

$$\begin{array}{l}\text{Molecular volumes,}\\ \text{aqueous vapor}\\ \text{removed:}\end{array}\left\{\; 1 + 2 = 1 + (2 \text{ vol. contr.}).\right.$$

Here no change in volume results from the explosion when the temperature is 100° or over. When the temperature falls and the aqueous vapor is condensed we have a new relation between the volumes of product and original mixture such that a contraction corresponding to 2 volume-units occurs. In the example the actual contraction due to this removal of the water is 100 c.c., $(200+400-500)$. From this we derive the value of a single volume-unit as equal to 50 c.c. By reference then to the volume equation above, 1 volume-unit, *i.e.*, 50 c.c., represents the amount of methane present in the original mixture, of which it constitutes 25 per cent (by volume). The nitrogen is considered as without action.

In practice the removal of aqueous vapor is usually not carried out. Since at room temperatures the greater part of this vapor condenses to the liquid state, the partial pressure of this vapor at the observed conditions gives at once a means of calculating the volume of dry gaseous product. Some definite conditions of temperature and pressure are of course taken as a basis. In this manner a direct comparison between the volume of product and that of the original mixture can be readily made.

Example 61. — A mixture of 200 c.c. of ethylene and 800 c.c. of oxygen (an excess), at 24° and 756.5 mm. pressure, was exploded. After the explosion the volume of product read 649.1 c.c.; at 27° and this same pressure. Calculate the percentage purity of the ethylene by volume.

The reaction takes place according to the equation:

$$C_2H_4 + 3\,O_2 = 2\,CO_2 + 2\,H_2O.$$

Molecular volumes: $1 + 3 = 2 + 2$

Molecular volumes, aqueous vapor removed: $1 + 3 = 2 + (2\text{ vol.contr.})$

When allowance is made in this final volume of product for the presence of aqueous vapor, which at 27° has a tension of 26.5 mm., we have only to calculate the volume which the gaseous product will occupy at the original conditions, 24° and 756.5 mm. pressure, the basis thus selected for comparison. The expression is

$$V' = 649.1 \left(\frac{297}{300}\right)\left(\frac{730}{756.5}\right) \text{ or}$$

$$V' = 620 \text{ c.c.}$$

The original mixture, 200 c.c. + 800 c.c., or 1000 c.c., suffered therefore a contraction of 380 c.c. (1000 c.c. − 620 c.c.). This contraction, due to the removal of the aqueous vapor from the side of the products, corresponds to 2 volume-units; consequently 1 volume-unit for this reaction is equal to 190 c.c., and the volume of ethylene concerned (1 volume-unit) is also 190 c.c. We may assume, accordingly, the presence of 10 c.c. of some inert gas (e.g. nitrogen) in the original volume (200 c.c.) of ethylene taken. This signifies that the sample of ethylene was only 95 per cent pure.

Considerations into which Different Volume-Units may Enter. — When a contraction arises from the combined effect of two or more reactions it may be impossible to derive any one of the volume-units, for, unless the relative volumes of the several gases going to produce the contraction is known, we cannot properly apportion this volume of contraction between the several equations. In other words, the volume-unit may be different for every equation that is brought into consideration. In such cases as these it is necessary to bring the final products under new conditions, whereby further condensations or absorptions can take place, and the possibility of involving separately only one product from one of the reactions at a time made likely. An individual reaction thus concerned yields itself at once to the determination of its specific volume-unit. By reference of this volume-unit to the several reactions of a problem it is often possible to determine other volume-units. Still further condensations or absorptions through new conditions may be necessary, however, to aid in determining the volume-units of certain equations when a large number of substances are present in the original mixture. When all of these values are found the solution of the problem is comparatively simple.

Example 62. — A mixture of nitrogen, hydrogen and carbon monoxide, 450 c.c. in volume, was exploded with an excess of oxygen, 250 c.c. After the explosion the volume of gaseous product measured 500 c.c. With the removal of the aqueous vapor the volume of product measured 400 c.c. What was the volume of each component in the original mixture? A temperature of 100° and atmospheric pressure considered constant.

The two equations are as follows:

$$2\,H_2 + O_2 = 2\,H_2O.$$

Molecular volumes: $2 + 1 = 2 + (1 \text{ vol. contr.}).$

$$2\,CO + O_2 = 2\,CO_2.$$

Molecular volumes: $2 + 1 = 2 + (1 \text{ vol. contr.}).$

In this problem the dry gaseous product measured 400 c.c., *i.e.*, by loss of the aqueous vapor, a contraction of 100 c.c. was recorded. This contraction is due alone to the reaction of hydrogen with oxygen, and stands for the loss of 2 volume-units of aqueous vapor in the first volume equation. Therefore 1 volume-unit in this equation is equivalent to 50 c.c., and 2 volume-units, representing the actual amount of hydrogen concerned in the reaction, correspond to 100 c.c.

In the combustion of hydrogen the contraction actually possible corresponds to 1 volume-unit of the reaction. This volume-unit has just been determined as 50 c.c. The total contraction in the problem, due to the two reactions and without elimination of aqueous vapor, is recorded as 200 c.c.; hence the difference, 200 c.c. – 50 c.c., or 150 c.c., represents the contraction due to the reaction between carbon monoxide and oxygen. This contraction, as shown in the second volume equation above, is equivalent to 1 volume-unit. Accordingly the volume of the carbon monoxide present — 2 volume-units — must have been 2 × 150 c.c. or 300 c.c. All told, we derive the following composition for the original mixture: 100 c.c. of hydrogen, 300 c.c. of carbon monoxide and 50 c.c. of nitrogen (considered in these problems as an inert gas).

The Algebraic Method for the Calculation of Volume-Units. — More complicated examples may be given, but throughout all the same principles hold. We must first determine the volume-unit for each of the reactions under consideration before we can calculate the several volumes concerned in the problem. When a change in volume of product is found to result, not from one single reaction, but from a combination of several, and when also, through new conditions presented, still further condensations occur, which in turn are found to be due to a combination of reactions, we find it necessary to give the volume-unit for each reaction an algebraic symbol, and solve for the value of each unit from the several equations that may be constructed.

Example 63. — A mixture of nitrogen, carbon monoxide, methane and ammonia, amounting to 1250 c.c., was exploded with an excess of oxygen (1100 c.c.), and the volume of product found to measure 2450 c.c. A temperature of 100° and 760 mm. constant throughout. After withdrawal of aqueous vapor by absorption, the volume of the dry gases at the recorded constant conditions was 950 c.c. After removal of carbon dioxide (by passing gases over lime) the volume read 600 c.c. What was the volume of each component in the original mixture?

The equations for the three reactions are as follows:

$$2\,CO + O_2 = 2\,CO_2$$

Molecular volumes: $2 + 1 = 2 +$ (1 vol. contr.).

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$$

Molecular volumes: $1 + 2 = 1 + 2$.

$$4\,NH_3 + 3\,O_2 = 2\,N_2 + 6\,H_2O$$

Molecular volumes: $4 + 3 = 2 + 6 -$ (1 vol. expan.).

An expansion follows the combustion of ammonia with oxygen. A contraction due to the combustion of carbon monoxide is not sufficient to make up for expansion in the former case, since the final volume, 2450 c.c., is 100 c.c. larger than the volume of the original mixture of gases. As the contraction and expansion are each represented by a volume-unit in their respective reactions, we draw the conclusion that the volume-unit in the ammonia reaction is larger by 100 c.c. than the volume-unit in the carbon monoxide reaction. The withdrawal of aqueous vapor is similarly distributed over two reactions, as is also the withdrawal of carbon dioxide.

The data from this problem do not yield positive information in regard to any single volume-unit of any reaction. Combinations between the reactions are of course easily intelligible. Thus the withdrawal of the water removes 6 volume-units from the ammonia reaction and 2 volume-units from the methane reaction. With all the volume-units unknown we may profitably study the combination of these units with the idea of deriving some one of them and eventually all. For this purpose let x represent the volume-unit of the carbon monoxide reaction, y the volume-unit of the methane reaction, and z the volume-unit of the ammonia reaction. From the preceding remarks and a study of the reactions themselves we may now draw up the following equations.

The expansion is due to the larger value of z compared with x:

$$(a)\quad z - x = 100.$$

The volume of aqueous vapor is represented by 1500 c.c. (2450 c.c. − 950 c.c.), and is therefore expressed by

$$(b)\quad 6z + 2y = 1500.$$

The volume of carbon dioxide corresponds to 2 volume-units of x and 1 volume-unit of y and is represented by 350 c.c. (950 c.c. − 600 c.c.).

$$(c)\quad y + 2x = 350.$$

By combining equations (b) and (c) to eliminate y,

$$\begin{array}{lrcl}
(b) & 6z + 2y & = & 1500. \\
\text{Twice } (c) \text{ or} & \underline{4x + 2y} & \underline{=} & \underline{700}, \text{ and subtracting} \\
 & 6z - 4x & = & 800, \text{ and subtracting} \\
\text{four times } (a) \text{ or} & \underline{4z - 4x} & \underline{=} & \underline{400} \\
 & 2z & = & 400 \\
 & z & = & 200.
\end{array}$$

With the volume-unit of the ammonia equation thus derived and equal to 200 c.c., we have only to derive the value of x from equation (a) as equal to 100 c.c. and then in turn from (b) we derive the value of y as equal to 150 c.c. Substituting these values in their proper equations the volume of carbon monoxide ($2x$) is found to be 200 c.c., that of methane (y) 150 c.c., and that of ammonia ($4z$) 800 c.c., making in all 1150 c.c. Therefore the remaining volume of the original 1250 c.c., or 100 c.c., is calculated as nitrogen.

Considerations into which the Formation of Non-gaseous Substances Enter. — In the study of those molecular equations in which a number of non-gaseous substances come under consideration we have simply another case of removal of molecular quantities.

Example 64. — When phosphorus is burned in a vessel containing 100 c.c. of nitrous oxide, what will be the volume of nitrogen left? The room temperature and pressure constant throughout.

The solid phosphorus pentoxide as well as the phosphorus fall out of consideration in the volume equation:

$$5\,N_2O + P_2 = 5\,N_2 + P_2O_5.$$

$$5\,N_2O = 5\,N_2.$$

Molecular volumes: $5 = 5.$

There is, therefore, no change in volume and 100 c.c. will represent also the volume of the nitrogen.

Again we may consider the reaction of hydrogen chloride upon a carbonate:

Example 65. — An excess of sodium hydrogen carbonate was placed in a vessel containing 100 c.c. of hydrogen chloride. Calculate the volume of dry carbon dioxide liberated in the reaction. Room temperature and pressure a constant.

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

Molecular volumes: $1 = 1 + 1.$

We have in this volume equation 1 volume of hydrogen chloride liberating, from 1 molecule of sodium hydrogen carbonate, 1 volume of carbon dioxide and 1 volume of aqueous vapor. In the dry state, therefore, the volume relations of carbon dioxide and hydrogen chloride are as 1 : 1. In the case of the normal sodium carbonate the volume relations of these dry gases are as 1 : 2.

$$\begin{array}{c} Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2O + CO_2. \\ \qquad\qquad 2 \quad = \qquad\qquad\qquad\quad 1. \end{array}$$

The proportional values of carbon dioxide and hydrogen chloride are different in the two cases. This, however, is dependent upon the nature of the substances concerned and is easily explainable by a study of the two reactions. Whatever be the complexity of the examples here presented, they nevertheless may be made to conform to very simple interpretations when once the molecular equations for the reactions are constructed and a study of the volume relations undertaken.

PROBLEMS.

212. In the combustion of 400 c.c. of hydrogen with oxygen, what volume of oxygen will be required, and what volume of aqueous vapor will result? A temperature of 100° and a pressure of 760 mm. constant throughout. *Ans.* 200 c.c. oxygen.
400 c.c. vapor.

213. A mixture of 300 c.c. of hydrogen and 200 c.c. of oxygen was exploded by electric spark. What was the volume of product? A temperature of 100° and pressure of 760 mm. constant throughout. *Ans.* 350 c.c.

214. A mixture of 300 c.c. of hydrogen and 130 c.c. of oxygen was exploded. What was the volume of product? Temperature of 100° and pressure of 760 mm. constant throughout. *Ans.* 300 c.c.

215. A mixture of 420 c.c. of hydrogen and 180 c.c. of oxygen was exploded. What was the volume of product after the removal of aqueous vapor (by absorption with phosphorus pentoxide)? Temperature of 100° and pressure of 760 mm. a constant. *Ans.* 60 c.c.

216. A mixture of 300 c.c. of methane and 150 c.c. of oxygen was exploded. What was the volume of the product after the removal of aqueous vapor (by absorption)? Temperature of 100° and pressure of 760 mm. constant throughout.

Ans. 300 c.c.

217. A mixture of 250 c.c. of carbon monoxide and 120 c.c. of oxygen was exploded. Calculate the volume of gaseous product. Temperature and pressure a constant.

Ans. 250 c.c.

218. A mixture of 320 c.c. of carbon monoxide and 180 c.c. of oxygen was exploded. Calculate the volume of gaseous product after the removal of the carbon dioxide (absorption by lime). Temperature and pressure a constant. *Ans.* 20 c.c.

219. A mixture of 200 c.c. of methane and 300 c.c. of carbon monoxide was exploded with 600 c.c. of oxygen (excess). Calculate the volume of gaseous product. Calculate, also, the volume of product when deprived of aqueous vapor. Temperature of 100° and pressure of 760 mm. a constant throughout.

Ans. 950 c.c. (moist).
550 c.c. (dry).

NOTE. — Since the oxygen is in excess we know the calculation is to be based upon the CH_4 and CO. The oxygen left unconsumed in these two reactions is readily determined by difference.

220. A mixture of 80 c.c. of methane and 200 c.c. of oxygen was exploded over mercury. Calculate the volume of product. A temperature of 20° and barometric pressure of 757.4 mm. constant throughout. *Ans.* 122.83 c.c.

NOTE. — The volume of dry gaseous product, at 20° and 757.4 mm., is simply to be changed to accord with the observed conditions in the presence of aqueous vapor. These experiments are usually carried out over mercury. The excess of water condenses of course upon the mercury column. If an appreciable quantity were present allowance for its pressure upon the column would need to be made.

221. A mixture of 400 c.c. of hydrogen and 300 c.c. of oxygen was exploded. Calculate the volume of product. A temperature of 25° and pressure of 753.6 mm. constant.

Ans. 103.23 c.c.

222. A mixture of 200 c.c. of carbon monoxide and 300 c.c. of oxygen was exploded over mercury. Calculate the volume of product. A temperature of 27° and pressure of 740 mm. constant throughout. *Ans.* 400 c.c.

223. A mixture of oxygen and hydrogen, measuring 150 c.c. in volume, was exploded by means of an electric spark. The volume of product measured 125 c.c. Temperature of 100° and atmospheric pressure a constant. Calculate the volumes of hydrogen and oxygen concerned in the reaction. The residual gas is of course the excess of either the hydrogen or oxygen present. *Ans.* 50 c.c. hydrogen.
25 c.c. oxygen.

224. A mixture of oxygen and hydrogen, measuring 150 c.c. in volume, was exploded. The volume of product measured 76.47 c.c. Temperature of 17° and pressure of 754.4 mm. a constant. Calculate the volumes of hydrogen and oxygen concerned in the reaction. *Ans.* 50 c.c. hydrogen.
25 c.c. oxygen.

225. 250 c.c. of dry air were mixed with 150 c.c. of hydrogen (an excess) and exploded. The volume of product was 350 c.c. Calculate the percentage of oxygen (by volume) in the sample of air. Temperature of 100° and atmospheric pressure a constant. *Ans.* 20 per cent.

226. 300 c.c. of dry air were mixed with 250 c.c. of hydrogen (an excess) and exploded. The volume of the dry gaseous product was 361 c.c. Calculate the percentage of oxygen (by volume) in the sample of air. Temperature of 20° and pressure of 745 mm. a constant. *Ans.* 21 per cent.

227. A mixture of hydrogen sulphide with an excess of oxygen measured 350 c.c. at 100° and 750 mm. pressure. After explosion (with complete combustion) the volume of dry gaseous product read 260 c.c. at these same conditions. Calculate the volume of hydrogen sulphide in the mixture. *Ans.* 60 c.c.

228. A mixture of hydrogen sulphide with an excess of oxygen measured 200 c.c. at 20° and 747.4 mm. pressure. After explosion (with complete combustion) the volume of product read 143.3 c.c. at these same conditions. Calculate the volume of hydrogen sulphide in the mixture. *Ans.* 40 c.c.

229. A mixture of acetylene, C_2H_2, with an excess of oxygen measured 350 c.c. at 25° and 745 mm. pressure. After explosion the volume of dry gaseous product read 275 c.c. at the same conditions. Calculate the volume of acetylene in the mixture. *Ans.* 50 c.c.

230. A mixture of acetylene, C_2H_2, with an excess of oxygen measured 240 c.c. at 24° and 752.4 mm. pressure. After explosion the volume of product read 221.8 c.c. at 28° and 750.1 mm. pressure. Calculate the volume of acetylene in the mixture. *Ans.* 20 c.c.

231. An excess of oxygen, 400 c.c., was admitted into a volume of ammonia (containing an impurity of air, *i.e.*, nitrogen and oxygen) which measured 240 c.c., and the mixture, at 22° and 745.2 mm. pressure, exploded. The volume of product measured 415.1 c.c. at 24° and the same pressure. Calculate the percentage purity of the sample of ammonia.

Ans. 80 per cent.

232. Into a stoppered tube (90 c.c. in capacity) filled with chlorine, a small quantity of concentrated ammonia water (10 c.c. or an excess) was admitted. After shaking, the mouth of the tube was opened under a dilute acid solution contained in a tall cylinder. The excess of ammonia, together with the hydrogen chloride, formed in the reaction, were thus removed. The residual volume of gas may be considered as nitrogen. Calculate the volume of nitrogen in the tube. The room temperature and pressure considered a constant throughout.

Ans. 30 c.c.

233. A mixture of carbon monoxide and methane containing also nitrogen measured 260 c.c. Into this mixture was admitted an excess of oxygen, 300 c.c., and the whole exploded. After the explosion the volume of product measured 520 c.c., but after the removal of aqueous vapor (by absorption) from the gaseous product the volume measured 320 c.c. Calculate the volume of each component in the original mixture. A temperature of 100° and atmospheric pressure constant.

Ans. 80 c.c. CO.
100 c.c. CH_4.
80 c.c. N.

234. A sample of water gas containing an impurity of air measured 240 c.c. in volume. Into this was admitted an excess of oxygen, 400 c.c., and the mixture exploded. The volume of product measured 540 c.c. After removal of aqueous vapor (by absorption) the volume of product measured 440 c.c. Calculate the percentage of hydrogen and carbon monoxide in the sample. A temperature of 100° and atmospheric pressure constant throughout.

Ans. 41.25 per cent H.
41.25 per cent CO.

235. 500 c.c. of a mixture of ammonia, methane and nitrogen were mixed with 500 c.c. of oxygen and the mixture exploded. The volume of the product measured 1050 c.c. A constant temperature of 100° and pressure of 760 mm. maintained throughout. Upon cooling the gaseous product to remove the aqueous vapor and recalculation of the volume of dry gas to the original conditions (100°), the volume measured 550 c.c. What was the composition of the original mixture?

Ans. 100 c.c. CH_4.
200 c.c. NH_3.
200 c.c. N.

236. A mixture of methane, hydrogen sulphide and air measured 300 c.c. When mixed with an excess of oxygen, 500 c.c., and exploded the volume of product measured 720 c.c. A temperature of 100° and atmospheric pressure constant throughout. Upon cooling the gaseous product to the room temperature and recalculation of the volume of dry gas to the original conditions, the volume measured 320 c.c. Calculate the composition of the original mixture.

Ans. 120 c.c. CH_4.
160 c.c. H_2S.
20 c.c. air.

237. A mixture of methane and acetylene measuring 500 c.c. was mixed with 1500 c.c. of oxygen (an excess) and exploded. The volume of product measured 1850 c.c. A temperature of 100° and atmospheric pressure constant. Upon removal of aqueous vapor (by condensation and recalculation to the original conditions) the volume measured 1150 c.c. Calculate the composition of the original mixture.

Ans. 200 c.c. CH_4.
300 c.c. C_2H_2.

238. A mixture of hydrogen, methane and nitrogen measuring 350 c.c. was exploded with an excess of oxygen, 500 c.c. After the explosion the volume of dry gaseous product measured 475 c.c. Upon removal of carbon dioxide the volume of gas measured 400 c.c. Calculate the composition of the original mixture. Room temperature and pressure a constant.

Ans. 150 c.c. H.
75 c.c. CH_4.
125 c.c. N.

239. A mixture of cyanogen, methane and nitrogen measuring 200 c.c. in volume was exploded with an excess of oxygen, 500 c.c. After the explosion the volume of product measured 619.6 c.c. Upon removal of carbon dioxide (by lime) the volume of dry gas measured 430 c.c. Calculate the composition of the original mixture. A temperature of 25° and pressure of 746.6 mm. constant throughout.

Ans. 50 c.c. CH_4.
60 c.c. C_2N_2.
90 c.c. N.

240. A liter of methane contaminated with the vapor of carbon disulphide was mixed with an excess of oxygen, 3000 c.c., and exploded. The volume of product measured 3840 c.c. Calculate the percentage impurity of the methane. A temperature of 100° and atmospheric pressure constant throughout.

Ans. 16 per cent.

241. An excess of oxygen was admitted to a vessel containing hydrogen and ammonia and the mixture exploded. After the explosion there was observed no change in volume of product from that of the mixture. Calculate the percentage composition of the hydrogen and ammonia mixture. A temperature of 100° and atmospheric pressure constant.

Ans. $33\frac{1}{3}$ per cent H.
$66\frac{2}{3}$ per cent NH_3.

242. A mixture of ethylene and ammonia, contaminated with air measured 600 c.c. When this volume of gas was mixed with an excess of oxygen, 2000 c.c., and exploded, the volume of product measured 2640 c.c. Upon removal of aqueous vapor (by cooling and recalculation) the volume of dry gas

measured 2120 c.c. Calculate the composition of the original mixture. A temperature of 100° and atmospheric pressure constant. *Ans.* 160 c.c. NH_3.
140 c.c. C_2H_4.
300 c.c. air.

243. A mixture of ethylene and ammonia contaminated with air measured 400 c.c. When this volume of gas was mixed with an excess of oxygen, 1200 c.c., and exploded, the volume of product measured 1293.6 c.c. Upon removal of carbon dioxide (by lime) the volume of dry gas measured 1050 c.c. Calculate the composition of the original mixture. A temperature of 26° and pressure of 745.6 mm. constant throughout. *Ans.* 100 c.c. C_2H_4.
120 c.c. NH_3.
180 c.c. air.

244. Into a mixture of cyanogen, ethylene and nitrogen was admitted a large excess of oxygen and the mixture, which measured 1600 c.c. at 22° and 753 mm. pressure, exploded. After the explosion the volume of product measured 1257 c.c. at 24° and 746 mm. pressure. Upon removal of carbon dioxide and moisture the volume of dry gas (still at 24° and 746 mm.) measured 609.7 c.c. Calculate the amount of cyanogen and ethylene in the original mixture. *Ans.* 100 c.c. C_2N_2.
200 c.c. C_2H_4.

245. A mixture of hydrogen and ammonia contaminated with air measured 400 c.c. Into this was admitted an excess of oxygen, 600 c.c., and the final mixture exploded. After the explosion the volume of product measured 1025 c.c. Upon removal of aqueous vapor (by absorption) the volume read 675 c.c. Calculate the composition of the original mixture. A temperature of 100° and atmospheric pressure constant throughout. (Cf. Ex. 63.) *Ans.* 50 c.c. H.
200 c.c. NH_3.
150 c.c. air.

246. A mixture of hydrogen, methane, carbon monoxide and nitrogen measured 500 c.c. Into this was admitted an excess of oxygen, 900 c.c., and the final mixture exploded. After the explosion the volume of product measured 1250 c.c. Upon removal of aqueous vapor (by absorption) the volume measured 1000 c.c. Upon removal of carbon dioxide (by

lime) the volume measured 725 c.c. Calculate the composition of the original mixture. A temperature of 100° and atmospheric pressure constant. (Cf. Ex. 63.) *Ans.* 100 c.c. H.
200 c.c. CO.
75 c.c. CH_4.
125 c.c. N.

247. A mixture of carbon monoxide and methane contaminated with air and measuring 400 c.c. was exploded with an excess of oxygen, 1000 c.c. The volume of product measured 1025.4 c.c. Upon removal of the carbon dioxide (by lime) the volume of dry gas measured 725 c.c. Calculate the composition of the original mixture. A temperature of 21° and pressure of 745.5 mm. constant throughout. *Ans.* 100 c.c. CO.
(Cf. Ex. 63.) 175 c.c. CH_4.
125 c.c. air.

248. A mixture of cyanogen, methane and hydrogen contaminated with air measured 800 c.c. An excess of oxygen, 2000 c.c., was admitted into the vessel containing this mixture and the final mixture exploded. After the explosion the volume of product measured 2750 c.c. After removal of aqueous vapor (by cooling and recalculation) the volume measured 2250 c.c. After removal of carbon dioxide (by lime) the final volume measured 1450 c.c. Calculate the composition of the original mixture. A temperature of 100° and atmospheric pressure constant. *Ans.* 100 c.c. H.
(Cf. Ex. 63.) 200 c.c. CH_4.
300 c.c. C_2N_2.
100 c.c. air.

249. An excess of oxygen, 800 c.c., was added to a mixture of ammonia, ethylene and hydrogen, 310 c.c. in volume, and the final mixture exploded. After the explosion the volume of product measured 648.35 c.c. Upon removal of carbon dioxide (by lime) the volume of dry gas measured 435 c.c. Calculate the composition of the original mixture. A temperature of 18° and pressure of 746 mm. constant throughout. (Cf. Ex. 63.) *Ans.* 50 c.c. H.
100 c.c. C_2H_4.
160 c.c. NH_3.

NOTE. — The contraction due to the reactions is here masked in the contraction from the loss of aqueous vapor. Construct the third equation from the volume of oxygen required in the several combustions, bearing in mind that the volume, 365 c.c. (800 c.c. − 435 c.c.), which nominally represents this quantity in the problem, is in fact less than the actual volume by that volume of nitrogen left free.

250. A mixture of methane and ethylene measuring 300 c.c. was exploded with an excess of oxygen, 1500 c.c. After the explosion the volume of dry gaseous product (calculated to observed conditions of temperature and pressure) measured 1200 c.c. In order to determine the volume of oxygen actually consumed in this combustion and thus present data upon which a second equation may be constructed, an excess of hydrogen, 900 c.c., was admitted to the vessel containing the dry gaseous product. After an explosion the volume of this second product measured 1400 c.c. (calculated as above, with absence of aqueous vapor). Calculate the amount of methane and ethylene in the original mixture. The room temperature and pressure remained constant throughout. *Ans.* 200 c.c. CH_4.
(Cf. Ex. 63.) 100 c.c. C_2H_4.

251. A volume of nitric oxide, NO, measuring 400 c.c. was required for the combustion of a definite weight of phosphorus. What volume of nitrogen remained free? The room temperature and pressure a constant. *Ans.* 200 c.c.

252. A quantity of phosphorus was burned in a vessel over water holding 222.7 c.c. of nitrous oxide, N_2O, measured at 20° and 750 mm. pressure. What volume of nitrogen remained, the temperature and pressure constant?

Ans. 222.7 c.c.

253. What volume of water gas is theoretically possible from the action of 1 liter of steam upon heated coke? Temperature and pressure a constant. *Ans.* 2000 c.c.

254. In the decomposition of methane by chlorine what volume of hydrogen chloride corresponds to 1 volume of methane? Temperature and pressure constant. *Ans.* 4 volumes.

255. A mixture of 400 c.c. of methane and 1000 c.c. of chlorine was exploded. Calculate the volume of gaseous product, temperature and pressure a constant. *Ans.* 1800 c.c.

256. What volume of gaseous product may be obtained in the decomposition of 100 c.c. of ammonia by heated cupric oxide? Temperature and pressure a constant.

Ans. 200 c.c.
(Steam + N).

CHAPTER XII.

COMPLEX EQUATIONS.

THE study of chemical reactions as outlined in Chapter IX was not inclusive of those examples where a change in the valence of an element occurs. Although these changes may complicate the matter of drawing up the equations, the same principles as already discussed will be found to apply. The definite quantity of each element concerned, whether or not it exerts the same combining capacity for other elements on the two sides of an equation, is nevertheless a constant for the particular equation in question. The exact application of these principles will rest, of course, upon the construction of the equations in their molecular form.

Oxidation and Reduction. — The increase in valence or combining capacity* which accompanies an element when, for instance, it passes from a lower to a higher oxide, has been taken as the measure of the degree of oxidation. The position of oxygen in this connection might be filled by almost any non-metallic element and still we may have the means of measuring the increase in combining capacity of a metallic element or radical acting as such toward a non-metallic element, *i.e.*, *oxidation*. The unit of measure, rather than oxygen with its 2 combining capacities, is referred to an element with but 1

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* The author is indebted to his colleague, Professor S. Laurence Bigelow, for this interpretation of valence as the capacity factor of chemical energy, *i.e.*, the combining capacity of a unit quantity of an element or radical.

capacity, e.g. hydrogen. Thus 1 molecule of chromic oxide, $Cr_2^{III}O_3^{II}$, undergoes oxidation to 2 molecules of chromium trioxide, 2 $Cr^{VI}O_3^{II}$, and the oxygen intake for this definite quantity of chromium is 3 oxygen atoms, *i.e.*, the equivalent of 6 hydrogen atoms in combining capacity, or 6 combining capacities. This amount for 2 atoms of chromium is equivalent to 3 combining capacities for 1 atom of chromium and thus this increase will be denoted in the second compound $Cr^{VI}O_3^{II}$.

The reverse process, or a decrease in this combining capacity toward a non-metallic element, is known as *reduction*. For example, ferric iron as $Fe^{III}Cl_3^{I}$ is reduced to ferrous iron, $Fe^{II}Cl_2^{I}$.

Analogous to this the increase in combining capacity of a non-metallic element, or a radical acting as such, for oxygen or some other non-metal will be a measure of the oxidation, e.g. $Cl_2^{I}O^{II} \rightarrow Cl_2^{VII}O_7^{II}$. When, however, this capacity of a non-metal is considered in relation to its combination with metallic groups the increase in its combining capacity is in fact a measure of its *reduction*. Thus potassium ferricyanide, $K_3^{I}[Fe^{III}(CN)_6^{I}]^{III}$, is reduced to potassium ferrocyanide, $K_4^{I}[Fe^{II}(CN)_6^{I}]^{IV}$, when the ferricyanide radical increases its combining capacity toward the metallic element potassium. This result is of course due to the reduction of the ferric iron in the former radical to ferrous iron in the latter. In general the increase in the combining capacity of a non-metallic radical for a metallic one signifies a demand for a lower number of these capacities required of an intra-radical metal for complete combination, or what was previously interpreted as a reduction.

Reaction-Quantities Involved in Oxidation and Reduction. — The change of an element from the non-metallic to the metallic groupings, or vice versa, may be accompanied by a loss or gain in its combining capacity, and consequently we speak of it as undergoing a reduction or oxidation. Thus potassium dichromate, $K_2Cr_2O_7$, contains the chromium associated directly with oxygen in the form of the acid H_2CrO_4 (or oxide $Cr^{VI}O_3^{II}$), but by the action of a strong acid this chromium, with a combining capacity of 6, is completely transformed into a chromic compound (where chromium is the basic element) and then has a combining capacity of only 3, $Cr_2^{III}O_3^{II}$. The action therefore is described as one of reduction.

In illustration of these points a few of the more common examples will be given. First we may mention the action of hydrogen sulphide upon a solution of ferric chloride:

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S.$$

Expressed by ions:

$$\begin{aligned} &2\,Fe^{\cdot\cdot\cdot} + 6\,Cl' + 2\,H^{\cdot} + S'' \\ &\quad = 2\,Fe^{\cdot\cdot} + 4\,Cl' + 2\,H^{\cdot} + 2\,Cl' + S, \end{aligned}$$

where the combining capacities are represented in solution as ionic charges.

From the reaction-quantities noted we may draw up the several ratios of proportionality here existent. For example the amount of ferrous chloride resulting from a definite weight of ferric chloride is expressed by the ratio $FeCl_2/FeCl_3$, and then again the weight (as well as the volume eventually) of hydrogen sulphide necessary for this reduction of the ferric chloride is in accord with the ratio $H_2S/2\,FeCl_3$. The hydrogen sulphide molecule is equivalent therefore in its reducing action to 2 units of hydrogen, whereas 2 molecules of ferric chloride are equivalent in oxidizing action to 1 oxygen atom.

Oxidizing Action of Potassium Dichromate. — As has been stated, the oxidizing action of potassium dichromate, $K_2Cr_2O_7$, in the presence of a strong acid and substance capable of oxidation, is due to the transformation of the dichromate (Cr^{VI}) into a chromic compound (Cr^{III}). The oxidizing power of this substance is measured by the liberation of 3 atoms of oxygen per molecule of dichromate, as may be shown by the following hypothetical equation for the action with sulphuric acid:

$$K_2Cr_2O_7 + 4\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,O.$$

When an active reducing agent, e.g. ammonium sulphide, is present the reduction of the dichromate may be accomplished without the presence of an acid:

$$\begin{aligned} &K_2Cr_2O_7 + 3\,(NH_4)_2S + 7\,H_2O \\ &\qquad = 2\,Cr(OH)_3 + 2\,KOH + 6\,NH_4OH + 3\,S. \end{aligned}$$

In other cases some oxidizable substance must be added to the acid mixture in order that the oxygen capable of liberation may be actually consumed and the reaction proceed.

A number of substances, such as hydrogen sulphide, sulphur dioxide, carbon monoxide and alcohol, are readily oxidized in this manner to sulphur, sulphur trioxide, carbon dioxide and aldehyde, respectively. Thus with hydrogen sulphide:

$$\begin{aligned} &K_2Cr_2O_7 + 4\,H_2SO_4 + 3\,H_2S \\ &\qquad = K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,H_2O + 3\,S. \end{aligned}$$

The presence of 3 molecules of hydrogen sulphide is necessary for interaction with the 3 atoms of oxygen liberated per molecule of dichromate; the products by this oxidation are indicated in the equation. 1 molecular weight of potassium dichromate is here directly proportional to 3 molecular weights of hydrogen sulphide, hence in this reaction all values for these substances must accord with the ratio

$$\frac{3\ H_2S}{K_2Cr_2O_7}, \text{ or } \frac{3\ (34.09)}{294.2}.$$

From the relation between the molecular weight of a substance and its volume as a vapor we are able to calculate, for example, the volume of hydrogen sulphide that can be oxidized by a corresponding proportional weight of the dichromate.

Example 66. — What volume of hydrogen sulphide, at standard conditions, can be oxidized by 7.36 grams of potassium dichromate in an acid solution?

The volume of hydrogen sulphide oxidized by 1 gram-molecular weight of potassium dichromate (294.2 grams) is that volume corresponding to 3 gram-molecular weights of the gas, or 67,200 c.c. (*i.e.*, 3 × 22,400 c.c.) at standard conditions. The direct proportionality between the gram-molecular weight and the actual weight of dichromate here given, determines also the proportionality between the respective volumes of hydrogen sulphide corresponding to these values:

$$294.2 : 7.36 = 67{,}200 : x,$$

in which x represents the volume (1681 c.c.) of gas oxidized.

The weight of sulphur precipitated, as well as any other substance present, may be calculated from the standpoint of these proportional values expressed in the equation. For example, the relation between the sulphur and potassium dichromate is expressed by the ratio:

$$\frac{3\ S}{K_2Cr_2O_7}, \quad \text{or} \quad \frac{96.21}{294.2}.$$

When hydrochloric acid is used the excess of acid is itself oxidized by the liberated oxygen with the production of free chlorine and water:

$$K_2Cr_2O_7 + 14\,HCl = 2\,KCl + 2\,CrCl_3 + 7\,H_2O + 3\,Cl_2.$$

Standard Oxidizing Solutions with Potassium Dichromate. — From reactions of oxidation with a potassium dichromate solution we are able to draw up the value of such a solution in terms of the hydrogen equivalent. 1 atom of oxygen will oxidize and combine with 2 atoms of hydrogen, hence the equivalence of 3 atoms of oxygen in terms of hydrogen is necessarily 6. Since 1.01 grams of hydrogen or this unit equivalent are required per liter of a normal solution, we shall require here in a normal solution of potassium dichromate—that solution which per liter can furnish just sufficient oxygen to unite with 1.01 grams of hydrogen — exactly one-sixth of the gram-molecular weight of this salt, *i.e.*, 294.2/6 or 49.03 grams. In the work of titration with standard solutions of this salt the change in color from red to green indicates complete reduction, but for accurate determination of this point it is customary to involve small portions of the solution in further reactions.

Example 67. — What is the normality of that potassium dichromate solution, 40 c.c. of which oxidized 0.590 gram of ferrous sulphate to the ferric state?

The more commonly used ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6\,H_2O$, is here replaced by ferrous sulphate, $FeSO_4$, for the sake of simplicity. The reaction for the oxidation of this latter to ferric sulphate involves 1 oxygen atom, with 1 molecule of sulphuric acid, per 2 molecules of the ferrous salt:

$$2\,FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Consequently to include this action in the equation which represents the oxidation by means of 1 molecule of potassium dichromate, with its 3 possible oxygen atoms, we shall need to multiply the equation above by 3 and thus obtain 3 O as a reaction-quantity common to both equations:

$$K_2Cr_2O_7 + 4\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3\,O$$
$$6\,FeSO_4 + 3\,H_2SO_4 + 3\,O = 3\,Fe_2(SO_4)_3 + 3\,H_2O.$$

It comes to the same end if we simply combine these equations and let this common quantity (3 O) drop out, when we shall have the final expression:

$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7\,H_2O.$$

In either case the reaction-quantities 6 $FeSO_4$ and $K_2Cr_2O_7$ are directly proportional to each other, and the ratio 6 $FeSO_4/K_2Cr_2O_7$, or 911.52/294.2, determines the ratio between all weights which severally may represent these quantities.

In the example 0.590 gram of $FeSO_4$ was oxidized. Therefore the following equivalence in the ratios:

$$\frac{911.52}{294.2} = \frac{0.590}{x}.$$

The value for x is found to be 0.1904 gram. This weight, however, was present in 40 c.c. of solvent, consequently in 1 liter we should have 25 × 0.1904 or 4.76 grams of potassium dichromate. A normal solution of this salt contains 49.03 grams per liter (p. 153), hence we have a solution of 4.76/49.03 normality, *i.e.*, 0.0971 normal, a trifle less than N/10.

Oxidizing Action of Potassium Permanganate. — As a second illustration the oxidizing action of potassium permanganate is of much importance. The action in an acid solution is analogous to that of potassium dichromate, only the reduction of Mn^{VII} to Mn^{II} is accompanied here with the liberation of 5 atoms of oxygen for every 2 molecules of permanganate:

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O.$$

The presence of some substance capable of oxidation is necessary in order to bring about this reaction in dilute solutions. We may take again the example of hydrogen sulphide as affected by an oxidizing agent:

$$\begin{aligned}&2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2S\\ &\quad = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,H_2O + 5\,S.\end{aligned}$$

From this equation the relative amounts of hydrogen sulphide and potassium permanganate involved will always accord with the ratio between their respective reaction-quantities:

$$\frac{5\,H_2S}{2\,KMnO_4}, \text{ or } \frac{5\,(34.09)}{2\,(158.03)}.$$

When expressed by molecular equations the substances here concerned may be studied also in regard to their volume relations.

Example 68. — What weight of potassium permanganate will be reduced by 2800 c.c. of hydrogen sulphide, at standard conditions of temperature and pressure?

The reaction already discussed supplies the necessary data: 2 gram-molecular weights (316.06 grams) of the permanganate are reduced by 5 × 22,400 c.c. of hydrogen sulphide. By simple proportion the weight of permanganate that can be reduced by 2800 c.c. is derived as follows:

$$(5 \times 22.400) : 2800 = 316.06 : x,$$

where x, or 7.9 grams, is this weight of permanganate.

The reverse operation, or that of determining the weight (or volume) of hydrogen sulphide oxidized by a known weight of potassium permanganate, follows the same principle.

Standard Oxidizing Solutions with Potassium Permanganate. — The liberation of 5 atoms of oxygen per 2 molecules of permanganate also determines the amount of this salt that must be present in one liter of its normal solution for use in the presence of acid. By calculation, in a manner similar to that described under the standard dichromate solution, it is found necessary to have one-tenth of the 2 gram-molecular weights of potassium permanganate (316.06 grams), or 31.606 grams, in each liter of solution; whereby this volume of solution will be capable of furnishing just sufficient oxygen to oxidize 1.01 grams of hydrogen. The change from the deep purple color of the permanganate to the almost colorless manganous salt serves admirably to mark the point when the reduction is complete and hence to fix the end-point in titration with a permanganate solution.

Example 69. — 100 c.c. of a hydrogen peroxide solution were required to decolorize 500 c.c. of N/10 potassium permanganate solution (acidulated). What was the percentage concentration of the hydrogen peroxide solution?

$$\begin{aligned}&2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 \\ &\qquad = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,H_2O + 5\,O_2.\end{aligned}$$

As the equation indicates, the 5 atoms of oxygen liberated from the permanganate withdraw 5 atoms of oxygen from 5 molecules of hydrogen peroxide and are together removed from the reaction in the molecular form (5 molecules). 500 c.c. of N/10 potassium permanganate solution are equivalent to 50 c.c. of the normal solution. One liter of a normal potassium permanganate solution, containing 31,606 grams (1/10 of 316.06 grams as represented by the reaction-quantity), can only react with 1/10 of the quantity 5 H_2O_2 required by the reaction, or with 1/2 of one molecule of hydrogen peroxide. Here 50 c.c. (1/20 liter) can act upon just 1/20 of the amount of hydrogen peroxide that a liter of the normal solution can oxidize (namely, 1/2 of a gram-molecular weight, or 17 grams), *i.e.*, 1/20 of 17 grams or 0.85 gram. Consequently in 100 c.c. of the hydrogen peroxide solution there is only this amount, 0.85 gram, of the compound, and if the weight of the solution is assumed to be 100 grams, then the percentage of hydrogen peroxide present is 85/100 of 1 per cent.

From the conditions of this reaction the amount of any one substance present can be calculated also from the volume of oxygen evolved.

Just as potassium dichromate so also an acidulated solution of potassium permanganate readily oxidizes solutions of ferrous salts to the ferric state. The equation indicates, of course, this liberation of 5 oxygen atoms per 2 molecules of permanganate:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4$$
$$= K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O.$$

Again the action of an acidulated potassium permanganate solution upon a hot solution of oxalic acid (weighed out as $C_2H_2O_4 \,.\, 2\,H_2O$), with the complete oxidation of the latter into carbon dioxide and water, affords an admirable means for the titration and standardization of permanganate solutions:

$$2\,KMnO_4 + 5\,C_2H_2O_4 \,.\, 2\,H_2O + 3\,H_2SO_4$$
$$= K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O + (10\,H_2O).$$

Hydrochloric acid, except in the cold and under proper precautions, is rarely ever used for the acidulation of permanganate solutions owing to its ready oxidation, similar to that by potassium dichromate, into chlorine and water:

$$2\,KMnO_4 + 16\,HCl = 2\,KCl + 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O.$$

In neutral or alkaline solutions potassium permanganate is reduced by the presence of oxidizable substances to manganese dioxide (precipitated), and somewhat less oxygen per molecule of permanganate is thereby liberated. The action may be represented in part as follows:

$$2\,KMnO_4 + H_2O = 2\,KOH + 2\,MnO_2 + 3\,O.$$

The 3 oxygen atoms liberated from 2 molecules of potassium permanganate determine the amount of this salt in its normal solution to be 1/6 of 316.06 grams (represented by the reaction-quantity $2\,KMnO_4$), or 52.67 grams per liter.

Iodimetry. — The action of iodine in the presence of water upon a number of compounds is interesting to show one of the indirect methods of estimating substances in solution.

Iodine dissolves readily in water containing potassium iodide. This solution acts as a mild oxidizing agent as may be seen from the following equation:

$$SO_2 + 2\,H_2O + I_2 = H_2SO_4 + 2\,HI.$$

In the presence of an oxidizable substance the one molecule of iodine, through the decomposition of water present, furnishes sufficient oxygen to oxidize one molecule of sulphur dioxide to the trioxide, or an amount capable also of oxidizing two atoms of hydrogen. The normal value, therefore, of such an iodine solution must be fixed at one-half the gram-molecular weight (253.84 grams), or 126.92 grams per liter. The employment, however, of a more dilute solution as N/10, etc., is more common in practice. The end-point in titrations with iodine solutions is detected by the addition of a slight amount of a starch solution, with which substance the iodine, when occurring in slight excess, forms a deep blue mixture.

An iodine solution may also exert an oxidizing action by withdrawing a number of positively charged ions from a salt in solution:

$$2\,Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\,NaI, \text{ or}$$
$$4\,Na^{\cdot} + 2\,S_2O_3'' + I_2 = 2\,Na^{\cdot} + S_4O_6'' + 2\,Na^{\cdot} + 2\,I'.$$

A solution of sodium thiosulphate can be easily made up from the well crystallized salt, $Na_2S_2O_3 \cdot 5\,H_2O$, and this solution titrated against an iodine solution, using starch as an indicator. One molecule of iodine reacts with two molecules of the thiosulphate; consequently a normal solution of the latter will contain (with reference to a normal solution of iodine) just one-half of this reaction-quantity or one gram-molecular weight per liter.

Substances that are capable of liberating iodine from potassium iodide, e.g. chlorine, bromine, etc., may be brought in this way into estimations by volumetric analysis:

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$

The amount of iodine liberated is in exact accord with the proportional amount of chlorine under investigation, and the iodine in turn is open to determination from the amount of thiosulphate required for titration. This interesting application of volumetric analysis is known as *Iodimetry*.

Example 70. — An unknown weight of sodium dichromate was warmed with an excess of hydrochloric acid, and the chlorine, set free, passed into a solution of potassium iodide. 400 c.c. of N/10 sodium thiosulphate solution were required for the titration of the iodine thereby liberated. Determine the amount of chlorine evolved, and also the weight of dichromate reduced.

400 c.c. of N/10 sodium thiosulphate solution are equivalent to 40 c.c. of a normal solution. 1 liter of a normal solution of this salt exactly decolorizes 1 liter of a normal solution of iodine, or this amount of iodine (126.92 grams) in whatever volume of solution it is contained. Consequently 40 c.c. of the normal thiosulphate solution will act upon that amount of iodine as indicated in the proportion:

$$1000 : 40 = 126.92 : x, \text{ or } x = 5.177 \text{ grams.}$$

The amount of chlorine proportional to this weight of iodine is in accord with the ratio Cl/I, or 35.46/126.92, as indicated by the reaction above. By proportion we have: $126.92 : 35.46 = 5.177 : x$, where x, or 1.45 grams, is the weight of chlorine set free and thus made capable of liberating the amount of iodine above calculated. The determination of the amount of sodium dichromate necessary to liberate this weight of chlorine rests upon an equation exactly analogous to the action of hydrochloric acid upon potassium dichromate (see p. 153), and is indicated by the ratio:

$$\frac{3\,Cl_2}{Na_2Cr_2O_7}, \text{ or } \frac{212.76}{262}.$$

Accordingly, $212.76 : 262 = 1.45 : x$. From this we calculate the weight of dichromate as 1.786 grams.

No matter how complex the equations may become, the true relationship between all of the substances concerned is found to be in direct proportionality to their respective reaction-quantities.

PROBLEMS.

257. What weight of ferric chloride, $FeCl_3$, can be reduced to ferrous chloride, $FeCl_2$, by 8.52 grams of hydrogen sulphide? *Ans.* 81.10 grams.

258. What volume of hydrogen sulphide (at standard conditions) will be required for the reduction of 100 grams of ferric chloride, $FeCl_3$, to the ferrous salt? *Ans.* 6903.8 c.c.

259. Calculate the weight of sulphur precipitated in the reduction of 100 grams of ferric chloride, $FeCl_3$, to the ferrous salt by the action of hydrogen sulphide. *Ans.* 9.884 grams.

260. 1000 c.c. of hydrogen sulphide (at standard conditions) will reduce what weight of potassium dichromate in acid solution? *Ans.* 4.378 grams.

261. What volume of hydrogen sulphide (at standard conditions) will be required for the reduction of 100 grams of potassium dichromate in acid solution? *Ans.* 22,842 c.c.

262. What weight of hydrogen sulphide can be oxidized by 400 grams of potassium dichromate, in acid solution? What weight of sulphur will be precipitated?

Ans. 139.05 grams H_2S.
130.81 grams S.

263. What volume of sulphur dioxide (at standard conditions) can be oxidized by 30 grams of potassium dichromate in acid solution? *Ans.* 6852 c.c.

264. What volume of hydrogen sulphide, at 24° and 750 mm. pressure, can be oxidized by 10 grams of potassium dichromate in acid solution? *Ans.* 2518 c.c.

265. What weight of potassium dichromate, in acid solution, will be reduced by 1653.5 c.c. of sulphur dioxide at 22° and 745 mm. pressure? *Ans.* 6.567 grams.

266. Calculate the volume of chlorine liberated in the action of 40 grams of potassium dichromate upon a hydrochloric acid solution. *Ans.* 9137 c.c.

267. What weight of sodium dichromate must enter into reaction with a hydrochloric acid solution in order to liberate 100 grams of chlorine? *Ans.* 123.14 grams.

268. Determine the normality of a potassium dichromate solution, 25 c.c. of which oxidized 1.24 grams of ferrous sulphate to the ferric salt. *Ans.* 0.3265 N.

269. Determine the normality of a sodium dichromate solution, 50 c.c. of which oxidized 3.85 grams of ferrous ammonium sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6\ H_2O$ to the ferric salt.
Ans. 0.1963 N.

270. What volume of hydrogen sulphide, at standard conditions, will be required to reduce 200 c.c. of N/10 potassium dichromate solution (acidulated)? *Ans.* 224 c.c.

271. What weight of potassium permanganate, in acid solution, will be reduced by 5000 c.c. of hydrogen sulphide at standard conditions? *Ans.* 14.11 grams.

272. Calculate the volume of hydrogen sulphide, at standard conditions, that can be oxidized by 4 grams of potassium permanganate in acid solution. *Ans.* 1417.4 c.c.

273. What weight of sulphur dioxide can be oxidized by 200 grams of potassium permanganate in acid solution?
Ans. 202.7 grams.

274. 50 c.c. of a solution of hydrogen peroxide were required to decolorize 400 c.c. of N/5 potassium permanganate solution (acidulated). Calculate the percentage concentration of the hydrogen peroxide solution. *Ans.* 2.72 per cent.

275. Calculate the weight of crystallized oxalic acid, $C_2H_2O_4 . 2\ H_2O$, required for the reduction of 100 grams of potassium permanganate in acid solution. What volume of carbon dioxide, at standard conditions, would be liberated?
Ans. 199.4 grams.
70,873 c.c. CO_2.

276. 50 c.c. of an acidulated potassium permanganate solution were reduced by 2.4 grams of anhydrous oxalic acid, $C_2H_2O_4$. Calculate the normality of the permanganate solution.
Ans. 1.066 N.

277. What weight of sulphur dioxide will be oxidized by 50 grams of potassium permanganate in alkaline solution?
Ans. 3.04 grams.

278. The bromine set free by the action of manganese dioxide upon a hydrobromic acid solution was passed into a solution of potassium iodide. 200 c.c. of N/10 sodium thiosulphate solution were required for the titration of the free iodine. Calculate the weight of bromine evolved.

Ans. 1.6 grams.

279. Determine the purity of a sample of manganese dioxide, 2.2 grams of which, with excess of hydrochloric acid, set free sufficient chlorine to liberate a quantity of iodine that required 250 c.c. of N/5 sodium thiosulphate solution for titration.

Ans. 98.79 per cent pure.

280. 0.2452 gram of potassium dichromate, acting upon an excess of hydrochloric acid, set free an amount of chlorine which, when passed into a solution of potassium iodide, liberated iodine sufficient for the titration of 50 c.c. of an unknown sodium thiosulphate solution. Calculate the normality of this latter solution. *Ans.* N/10.

APPENDIX.

APPENDIX I.

Correction of Barometic Readings.

A barometric reading at room temperature is reduced to the corresponding height of a column of mercury at 0° by subtracting from the actual reading in millimeters that number in the second column below (Correction) set opposite the observed temperature. The barometric readings throughout these problems are given in corrected form.

Temperature.	Correction.	Temperature.	Correction.	Temperature.	Correction.
12	1.6	17	2.2	23	3.0
13	1.7	18.5	2.4	24.5	3.2
14	1.8	20	2.6	25	3.3
15	2.0	21.5	2.8	26	3.4

APPENDIX II.

Tension of Aqueous Vapor in Millimeters.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
0°	4.6	16°	13.5	26°	25.1
5	6.5	17	14.4	27	26.5
8	8.0	18	15.4	28	28.1
9	8.6	19	16.3	29	29.8
10	9.2	20	17.4	30	31.5
11	9.8	21	18.5	31	33.4
12	10.5	22	19.7	32	35.4
13	11.2	23	20.9	33	37.4
14	11.9	24	22.2	34	39.6
15	12.7	25	23.6	100	760.0

APPENDIX III. — Four-Figure Logarithms.

First two figures.	Third figure.										Fourth-figure differences.								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3224	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Four-Figure Logarithms.

First two figures.	Third figure.										Fourth-figure differences.								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

APPENDIX IV. — Antilogarithms.

First two figures of mantissa.	Third figure.										Fourth-figure differences.								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Antilogarithms.

First two figures of mantissa.	Third figure.										Fourth-figure differences.								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
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