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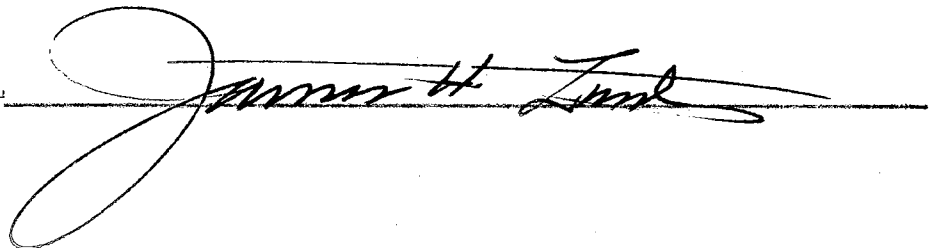
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Scope of Study: Analysis of seven high school chemistry texts which represent a typical cross section provides the authority for the inclusion of the theory and problems in this report concerning chemical calculations for secondary schools. In addition to the material in these texts, certain selected college texts were used as source material. The report involves a qualitative and quantitative treatment of the four major divisions of problems in which the many types of problems discovered in the seven high school texts can be organized. These four major divisions are: (1) atomic weights, molecular weights, and chemical formulas, (2) behavior of gases, (3) chemical equations, and (4) solutions. The theory relative to each type of problem precedes the quantitative treatment. The material compiled and formulated in this report provides a source of reference of the theory and typical problems encountered in teaching a course of chemistry in the secondary schools.

Findings and Conclusions: General high school chemistry texts differ in the treatment of theory involved in problems and the illustration of these principles through typical problems. The texts are written in the language of the student and are limited in the depth and breadth of source material essential for the understanding and thorough preparation of a teacher in presenting these principles and problems. In combining the theory, typical problems which illustrate the theory, and methods of reaching a solution, a teacher's perception will be facilitated as he visualizes the picture as a whole, instead of as parts.

ADVISER'S APPROVAL



FUNDAMENTALS OF CHEMICAL CALCULATIONS
FOR SECONDARY SCHOOLS

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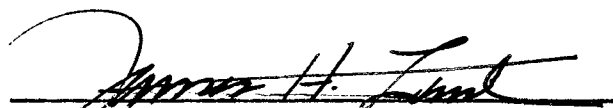
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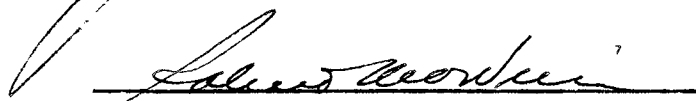
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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. FUNDAMENTALS OF ATOMIC WEIGHTS, MOLECULAR WEIGHTS, AND CHEMICAL FORMULAS	5
Atomic Theory	5
Analysis of the High School Texts	5
Atomic Weights	6
Molecular Weights	9
Chemical Formula	16
III. FUNDAMENTALS CONCERNING BEHAVIOR OF GASES	20
Definition of a Gas	20
Characteristics	20
Analysis of the High School Texts	21
Standard Conditions of Temperature and Pressure	22
Boyle's Law	25
Charles' Law	27
Combination Gas Law	29
Dalton's Law of Partial Pressures	31
Graham's Law of Diffusion	32
Deviations from the Gas Laws	34
Comments on Methods of Solving Gas Problems	35
IV. FUNDAMENTALS OF CHEMICAL EQUATIONS	36
Significance and Importance	36
Definition and Components	36
Analysis of the High School Texts	37
Weight-Weight Problems	37
Weight-Volume Problems	40
Volume-Volume Problems	42
V. FUNDAMENTALS OF SOLUTIONS	44
Significance and Importance	44
Definitions and Components	45
Analysis of the High School Texts	45
Concentration	46
A SELECTED BIBLIOGRAPHY	56

CHAPTER I

INTRODUCTION

Chemistry is a quantitative as well as a qualitative science. In the atmosphere of qualitative observations, predictions, and conclusions, a science is born. On the framework of these general principles, a science can stretch toward its maximum growth and usefulness only as it consumes the energy of precise measurement and mathematical relations. Perhaps the most striking illustration of this principle is the story of Lavoisier's experiments on burning. Many of the chemists of Lavoisier's time had observed that certain metals, such as mercury, gained weight and produced an ash when heated in air. When they reversed this procedure, the metal ash upon being strongly heated lost weight and returned to the pure metal. Lavoisier, however, was the first to measure this change in weight and to relate this difference to the change in weight of the air in which the metal was heated. Through this experiment in the atmosphere of qualitative observation, Lavoisier brought life to the quantitative character of chemistry and initiated the age of modern chemistry. Modern science simply did not exist until man learned to measure accurately such quantities as volume, weight, distance, temperature, pressure, and time. As suitable devices were designed and invented for measuring these quantities, scientists were able to obtain quantitative data in addition

to being able to use mathematical ideas in interpreting their observations. In his equation for chemical progress, Dr. Fred C. Hess sets forth this concept: "Careful observation + persistent search for truth = progress."¹

Chemistry, in its various branches, is both descriptive and exact, and here, for many chemists, lies its fascination. As time marches on, chemistry becomes more and more an exact science, with consequently more and more emphasis on the mathematical description of chemical phenomena. No student of elementary chemistry can hope to gain an understanding or appreciation of the subject unless he gains first some mental proficiency in a few simple arithmetical methods.²

Since chemistry is an exact science, chemical substances have exact properties and chemical changes take place in accordance with exact laws. For example, at exactly 0° Centigrade, pure water freezes, and all water contains 11.11% hydrogen and 88.89% oxygen. When burned in air, 100 grams of pure carbon combines with 266.66 grams of oxygen to produce 366.66 grams of carbon dioxide gas. Heating 20 grams of potassium chlorate to a high temperature always gives 7.83 grams of oxygen. Therefore, the teacher of chemistry must present and discuss these exact properties, exact laws, and exact behaviors. Solving problems illustrating these concepts and fundamental principles of chemistry is the proper and accepted method of teaching and understanding the exact features of chemistry.

¹Fred C. Hess, Chemistry Made Simple (Garden City, 1955), p. 10.

²P. W. Selwood, General Chemistry (New York, 1954), p. 54.

The difficulty that most students and teachers have in solving problems stems from the fact that they do not understand adequately and completely the particular principle or law the problem is trying to teach. A golf pro cannot teach the art of playing golf without the use of clubs and a ball; one cannot learn how to play golf without practicing with a ball and clubs. In like manner, a chemistry teacher cannot teach the exact features of chemistry without the use of problems; one cannot learn the exact features of chemistry without solving problems.³

General chemistry texts differ in the treatment of theory involved in problems and the illustration of these principles through typical problems. A particular author will emphasize certain types of problems and methods of problem solving whereas another author will stress the theory relative to the problems to a greater extent. The high school texts are written in the language of the student and are limited in the depth and breadth of source material essential for the understanding and preparation of a teacher in presenting these principles and problems. In combining the theory, typical problems which illustrate this theory, and methods of reaching a solution, a teacher's perception will be facilitated as he visualizes the picture as a whole, instead of parts. Therefore, the author's purpose in compiling and formulating the material in this report is to provide a source of reference of the theory and typical problems encountered in teaching a course of chemistry in the secondary schools.

³C. H. Sorum, How to Solve General Chemistry Problems (Englewood Cliffs, 1952), p. 1.

Analysis of seven high school chemistry texts which represent a typical cross section provides the authority for the inclusion of the theory and problems in this paper. These chemistry books and authors are as follows: Brownlee, Fuller, Whitsit, Hancock, and Sohon's Elements of Chemistry; Dull, Brooks, and Metcalfe's Modern Chemistry; Jaffe's New World of Chemistry; Hopkins, Smith, Davis, McGill, and Bradbury's Chemistry and You; Lanford's Using Chemistry; Rawlins and Struble's Chemistry in Action; and Weaver and Foster's Chemistry for our Times. Supplementing the material used from these seven high school chemistry books will be certain college books.

The chapters within this report involve a treatment of the four major divisions of problems in which the many types of problems discovered in the listed high school texts can be organized. These four major divisions involve chemical formulas and molecular weights, behavior of gases, chemical equations, and solutions. Introductory statements relative to the significance of the calculations, general considerations, and an analysis of the seven high school chemistry texts pertaining to the occurrence and treatment of the fundamental principles and illustrative problems along with a telescopic view of the material will be presented in the beginning of each chapter. Following these introductory remarks will be the body, subdivided into the various kinds of problems under the particular major division. In addition, concluding the chapter, the theory concerning each subdivision will precede the typical problem and method of solution and will originate from the seven high school chemistry texts and selected college references.

CHAPTER II

FUNDAMENTALS OF ATOMIC WEIGHTS, MOLECULAR WEIGHTS, AND CHEMICAL FORMULAS

1. Atomic Theory. The modern atomic theory, revised from John Dalton's observations and experimentation, consists of several statements concerning the nature of matter. All matter is made up of very small particles called atoms. The atoms of a given element, which are chemically different in different elements, have a definite average weight and are not subdivided in ordinary chemical reactions.⁴ The atomic theory enables us to explain the Law of Constant Composition in which each compound has a definite composition by weight and the Law of Multiple Proportions in which the combination of two elements to form more than one compound has the ratio of small whole numbers with the weight of one element remaining fixed.⁵

2. Analysis of the High School Texts. As a whole, the qualitative and quantitative aspects of the principles involved in atomic theory, atomic weight, molecular weights, chemical formulas, and experimental determinations of atomic and molecular weights have been widely and thoroughly treated and emphasized in the seven high school texts. This emphasis is justified on the basis that these topics provide the foundation upon which other principles and

⁴Charles E. Dull et al., Modern Chemistry (New York, 1954), p. 103.

⁵E. C. Weaver and Laurence S. Foster, Chemistry for Our Times (New York, 1954), p. 126.

considerations are built. Jaffe states, "The table of atomic weights is the foundation of chemical mathematics."⁶ All of the authors discuss atoms and molecules and lead up to the meaning of a chemical formula and methods of calculations of atomic and molecular weights and percentage composition of the elements in the compound by using the chemical formula. The simplest formula has been treated quantitatively by Dull, Jaffe, Rawlins, Lanford, and Weaver. In addition, chemical and physical experimental methods along with qualitative and quantitative explanations concerning molecular and atomic weights of gases along with non-electrolytes and electrolytes in solution have been included in the texts by all of the authors in a thorough, yet varied manner. It seems that Dull and Jaffe discuss the theory and quantitative aspects to a greater extent than any of the other authors. Using the above analysis of the texts, the following topics will be presented qualitatively and quantitatively: atomic weights, molecular weights of gases, non-electrolytes, and electrolytes experimentally, molecular weight from the formula, percentage composition from the formula, and derivation of the formula.

3. Atomic Weights. The atomic weight of an element is a number that shows the comparison of the weight of one of its atoms to the weight of one atom of oxygen, which is considered to be sixteen. Hence, the atomic weights are merely relative weights.⁷ In other words, the smallest part of the molecular weight of a compound contributed by a single element is its atomic weight. Atomic

⁶Bernard Jaffe, New World of Chemistry (New York, 1955), p. 127.

⁷Ibid., p. 128.

weights have been determined both by chemical methods and physical methods, such as the mass spectrometer.

A gram-atom or a gram-atomic weight of an element is the atomic weight of that element expressed in grams and contains 6.023×10^{23} atoms, Avogadro's number.⁸ "The importance of the unit gram-atomic weight is that in a chemical reaction we are concerned with a re-pairing of atoms. Therefore, quantities of different elements which contain the same number of atoms are of more significance than merely equal weights of different elements which would not contain the same number of atoms."⁹

The relationship between the weights of different atoms which react with one another is of extreme importance to the chemist, for it enables him to predict the quantities of materials which will be involved in chemical reactions.¹⁰ Another author states, "In order to understand more about the quantitative aspects of chemical reactions, one should know something about the weights of atoms of the various elements."¹¹

3. a. Experimental Determination of the Element Occurring in Gaseous Compounds. This method involves four distinct steps. First, the molecular weights of a number of gaseous compounds containing an element are determined by finding the density of the vapor and calculating the weight of 22.4 liters of vapor at standard conditions. Second, by means of straightforward experimental procedures,

⁸Daniel Schaum et al., Schaum's Outline of Theory and Problems for Students of College Chemistry (New York, 1949), p. 26.

⁹Oscar E. Lanford, Using Chemistry (New York, 1955), p. 28.

¹⁰Dull, p. 103.

¹¹Lanford, p. 20.

the percentage of this element in each substance is determined. Third, the weight of the element in one mole of each substance is found by taking the percentage of the element and multiplying it by the molecular weight of the substance. Then, the smallest number found is the probable atomic weight. The larger the number of compounds used, the greater is the chance that the smallest number is the correct atomic weight.¹²

Problem: Determine the atomic weight of chlorine.

Solution:

Substance	Molecular Weight	Percentage Chlorine	Weight of Cl Per Mole
HCl	36.5	97.3	35.5
ClO ₂	51.5	69.0	35.5
PCl ₃	137.5	77.5	106.5
PCl ₅	208.5	85.0	177.5
CCl ₄	154.0	92.2	142.0
CH ₃ Cl	50.5	70.3	35.5

The figures in the final column, giving the weight of chlorine in a mole of substance, are either 35.5 or some simple multiple of 35.5. No molecule in which chlorine is present could contain less than one atom of chlorine; therefore, it is concluded that 35.5, being the smallest weight of chlorine ever found in a large group of chlorine-containing compounds, must represent the atomic weight of chlorine.¹³

¹²Jaffe, p. 643.

¹³Selwood, p. 91.

3. b. Experimental Determination of the Element Not Occurring in Gaseous Compounds. The approximate atomic weight is determined by applying the Law of Dulong and Petit. This law states that the product of the atomic weight of an element and the specific heat of that element is equal to 6.4. If the specific heat of an element is known, then the approximate atomic weight can be calculated by using the principle set up by Dulong and Petit. In a mathematical relationship, the law is as follows:¹⁴

$$\text{Atomic Weight} \times \text{Specific Heat} = 6.4$$

$$\text{Atomic Weight} = \frac{6.4}{\text{Specific Heat}}$$

Problem: The specific heat of an element is .031. Calculate the approximate atomic weight.¹⁵

Solution: Substitute in the above relationship.

$$\text{Atomic Weight} = \frac{6.4}{.031} = 206.4$$

4. Determination of Molecular Weights of Compounds Experimentally Gases, non-electrolytes, and electrolytes are the compounds whose molecular weights will be determined from the experimental standpoint.

4. a. Molecular Weights of Gases. One method of determining the atomic weight of a gaseous substance is utilizing vapor density data. The molecular weight of a gas is equal to twice its vapor

¹⁴Sorum, p. 125.

¹⁵Selwood, p. 91.

density. This is apparent from the following:

$$\text{Vapor Density} = \frac{\text{Weight of 22.4 Liters of Gas}}{\text{Weight of 22.4 Liters of Hydrogen}}$$

Since 22.4 liters of hydrogen is two grams, then the vapor density multiplied by two gives the molecular weight.

$$\text{Vapor Density} \times 2 = \text{Molecular Weight}^{16}$$

Problem: The vapor density of oxygen is 16. What is the molecular weight?

Solution: Use the above relationship.

$$\text{Molecular Weight} = 16 \times 2 = 32$$

Another method for calculating the molecular weights of substances which may exist as a vapor is based upon Avogadro's Hypothesis. Using this law, then, the weight of 22.4 liters of any vapor under standard conditions equals the gram-molecular weight of the compound. Thus, by weighing 22.4 liters, or some convenient fraction of this volume, the molecular weight of the compound can be determined. Both the Dumas and Victor Meyer methods are based on this law.¹⁷

Problem: What is the molecular weight of oxygen?

Solution: One liter of oxygen weighs 1.429 grams.

Therefore, 1.429 grams/liter \times 22.4 grams/liter = 32

¹⁶John R. Lewis, An Outline of First Year College Chemistry (New York, 1943), p. 61.

¹⁷Ibid.

4. b. Molecular Weights of Non-Electrolytes. It is apparent that the molecular weight of a substance which cannot be changed into a gaseous form cannot be determined by the methods just described. Hence, the methods used for determining the molecular weights are solution methods; namely, freezing-point depression and boiling-point elevation. Each of these methods has its advantages and disadvantages; in order to select the method most suitable for any given substance, it is necessary to be clearly aware of these advantages and disadvantages. The consensus of opinion is that the freezing-point depression method is the favorite of the solution methods.

The qualitative basis for these methods stems from Raoult's Law. "As it was originally discovered, the law says that in dilute solutions of non-volatile non-electrolytes the depression is proportional to the mole fraction of the solute, or the solution vapor pressure is proportional to the mole fraction of the solvent."¹⁸ This is explained by the theory that the solvent molecules cannot escape so readily into the vapor phase when part of the liquid surface is occupied by solute molecules. Because of this lowering of the vapor pressure, the boiling point is raised and the freezing point is lowered.

Freezing-point Depression Method. When most dilute solutions are cooled, pure solvent begins to crystallize before any solute crystallizes. The freezing point of the solution is the temperature at which solvent crystallization begins. The freezing point of a pure solvent is always higher than the freezing point of a solution.

¹⁸Schaum, p. 71.

In dilute solutions, the lowering of the freezing point of a solution is proportional to the number of solute molecules or moles in a given weight of solvent. This relation indicates a method of determining the molecular weights of substances in solution. The lowering of the freezing point of a solvent caused by one mole, 6.023×10^{23} molecules, of any non-electrolyte dissolved in 1000 grams of solvent is called the molal freezing point constant of the solvent. For water, the molal freezing point constant is 1.86° Centigrade. Thus, if one mole of cane sugar, 342 grams, is dissolved in 1000 grams of water, the solution will freeze at -1.86° Centigrade.¹⁹

Problem: A solution containing 4.50 g of a non-electrolyte dissolved in 125 g of water freezes at $-.372^\circ\text{C}$. Calculate the approximate molecular weight of the solute.²⁰

Solution: One mole of solute lowers the freezing point of 1000 g of water by 1.86°C . First calculate the weight of solute that would be dissolved in 1000 g of water to give a solution of the same concentration, as 4.50 g solute in 125 g water.

In 1 gram of water there are $\frac{4.50}{125}$ grams of solute. Then

in 1000 g of water, there are $1000 \times \frac{4.50}{125}$ or 36 grams.

Since 1.86°C lowering is produced by 1 mole solute in 1000 g water, $.372^\circ\text{C}$ lowering is produced by $\frac{.372^\circ\text{C}}{1.86^\circ\text{C}} = .2$ mole in

1000 grams of water. Then .2 mole solute is contained in 36 grams of solute, and 1 mole is contained in $\frac{36 \text{ g}}{.2} = 180 \text{ g}$.

Thus, the molecular weight is 180.

¹⁹Ibid., p. 72.

²⁰Ibid., p. 73.

An alternate method of solving this freezing-point depression problem is as follows: 36 g solute per kilogram of solvent produces a lowering of $.372^{\circ}\text{C}$. and one mole solute produces a lowering of 1.86°C . Knowing this, a proportion can be set up.

$$\frac{36 \text{ g}}{.362^{\circ}\text{C.}} = \frac{1 \text{ mole}}{1.86^{\circ}\text{C.}}$$

$$\text{Solving, } 1 \text{ mole} = 36 \text{ g} \times \frac{1.86^{\circ}\text{C.}}{.372^{\circ}\text{C.}}$$

$$1 \text{ mole} = 180 \text{ g} ; \text{ Molecular Weight} = 180$$

Boiling-point Depression Method. The temperature at which a solution boils is higher than that of the pure solvent if the solute is comparatively non-volatile. In dilute solutions, the number of solute molecules or moles is directly proportional to the rise of the boiling point. This relationship gives a means of determining the molecular weight of the solute in solution. The elevation of the boiling point of a solvent caused by one mole of any non-volatile non-electrolyte dissolved in 1000 grams of solvent is known as the molal boiling point constant of the solvent. For water, this constant is $.52^{\circ}\text{Centigrade}$. Thus, if one mole of cane sugar is dissolved in 1000 g of water, the solution will boil at $100.52^{\circ}\text{Centigrade}$ at standard pressure. ²¹

Problem: A solution containing 4.81 g of a non-volatile non-electrolyte dissolved in 250 g of water boils at 100.17°C . Calculate the approximate molecular weight of the solute. ²²

²¹Ibid., p. 72.

²²Ibid., p. 74.

Solution: One mole of solute raises the boiling point of 1000 g of water by $.52^{\circ}\text{C}$. In 1 gram of water, there are $\frac{4.81}{250}$ grams of solute. In 1000 g of water, there are 19.2 grams of solute since $1000 \times \frac{4.81}{250}$ grams gives this amount. Since $.52^{\circ}\text{C}$. elevation is produced by 1 mole solute in 1000 g of water, $.17^{\circ}\text{C}$. elevation is produced by $\frac{.17^{\circ}\text{C}}{.52^{\circ}\text{C}}$ mole or .33 mole in the same amount of water. Then .33 mole solute is contained in 19.2 g solute, and 1 mole solute is contained in $\frac{19.2}{.33}$ or 58 g. Therefore, the molecular weight is 58.

An alternate solution is as follows: 19.2 g solute produce an elevation of $.17^{\circ}\text{C}$. and 1 mole solute produces an elevation of $.52^{\circ}\text{C}$. Then the following proportion exists:

$$\frac{19.2 \text{ g}}{.17^{\circ}\text{C}} = \frac{1 \text{ Mole}}{.52^{\circ}\text{C}}$$

$$\text{Solving, } 1 \text{ Mole} = 19.2 \text{ g} \times \frac{.52^{\circ}\text{C}}{.17^{\circ}\text{C}}$$

$$1 \text{ Mole} = 58 \text{ g}; \text{ Molecular Weight} = 58$$

4. c. Molecular Weights of Electrolytes. The methods used for the determination of the molecular weights of non-electrolytes do not apply to certain substances whose water solutions conduct an electric current because they alter the freezing and boiling points in an abnormal manner.

The Theory of Ionization, first proposed by Arrhenius, and then modified by subsequent investigation, helps to explain the behavior of dilute solutions of electrolytes. The main postulates of Arrhenius'

theory are as follows: an electrolyte dissociates into positively-charged and negatively-charged particles; the degree of ionization depends on the nature of the electrolyte, the concentration, and the temperature; ionization is complete in an infinitely dilute solution; the ions are free to move independently and this movement constitutes the current produced by the solution; the ions are responsible not only for the electrical properties, but also for the chemical properties.²³ However, there are some chief difficulties with the Arrhenius theory. The important effect of the solvent molecules in promoting solution and ionization is not explained. The effect of the oppositely charged ions on each other is not considered. In addition, for many electrolytes, different methods of obtaining the degree of ionization do not agree.²⁴

Numerous attempts have been made to amplify or alter the Arrhenius Theory of Ionization. The best known of the newer theories is that of Debye and Huckel, or the Inter-Ionic Attraction Theory. Briefly, this theory postulates that strong electrolytes, including nearly all salts, are one hundred per cent ionized. The properties of such solutions are dependent in part on solvent molecules attaching themselves to the ions, and on the effects of oppositely charged ions clustering about each other. The one hundred per cent ionization for strong electrolytes is supported by X-ray evidence on the existence of ions in the solid state along with theoretical views concerning the nature of the valence forces in electrovalent types of compounds.²⁵ In other terms, the Inter-Ionic Attraction

²³L. H. Cragg and R. P. Graham, An Introduction to the Principles of Chemistry (New York, 1955), p. 414.

²⁴Selwood, p. 213.

²⁵Ibid.

Theory, or the Debye-Huckel Theory, refined the ideas of Arrhenius and took into account the fact that forces exist between the oppositely charged ions in solution.²⁶

Jaffe explains in more simple terms how the theory proposed by Arrhenius accounts for the abnormal behavior of the boiling and freezing points of electrolytic solutions. The electrolyte dissociates and produces two or three times as many particles as there are molecules of undissociated non-electrolytes. The higher percentage of dissociation produces a greater increase in the boiling point and a greater decrease in the freezing point since the actual number of particles in solution determines both the boiling and freezing points of a solution.²⁷

The modern theories concerning solutions of electrolytes supplement, not supplant, the postulates proposed by Arrhenius. Without the groundwork laid by him, no understanding of solutions is possible. To be more exact, the chemist's understanding of the properties of solutions of electrolytes is as yet far from complete. Yet, a turning point in the history of science is marked by this theory, for physical chemistry came into existence.²⁸

The calculations concerning electrolytic solutions are reserved for more advanced courses since the quantitative aspects are highly mathematical in nature.²⁹

5. Chemical Formula. Formulas for compounds do not just suddenly appear from nowhere. When each new compound is discovered,

²⁶Cragg and Graham, p. 435.

²⁷Jaffe, p. 237.

²⁸Selwood, p. 214.

²⁹Cragg and Graham, p. 435.

chemists must determine its formula by laboratory measurements. The chemical formula is an abbreviated form of a compound which represents the name, one molecule, and one molecular weight of the compound.³⁰

5. a. Molecular Weight from the Formula. The molecular weight is the ratio of the weight of one molecule of a compound to the atomic weight of oxygen. Similar to the atomic weight, it is only a relative weight. In determining the molecular weight from the chemical formula, one adds the atomic weights of the atoms in the particular molecule.³¹

Problem: Calculate the molecular weight of calcium sulfate.

Solution: Use the atomic weights found on a standard chart. If the element is followed by a subscript, multiply the atomic weight by this subscript.

$$\begin{array}{rcccccc} \text{Ca} & & \text{S} & & \text{O}_4 & & \\ 40 & + & 32 & + & 16(4) & = & 136 \end{array}$$

5. b. Percentage Composition of a Compound from the Formula.

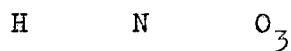
The percentage composition of a compound is found by computing the percentage by weight of each different element in a compound. Thus, the procedure consists of dividing the atomic weight of each element by the molecular weight of the compound and multiplying the fraction by one hundred.

Problem: Find the percentage composition of nitric acid.

³⁰Jaffe, p. 128.

³¹Ibid.

Solution:



$$1 + 14 + 16 (3) = 63 ; \text{molecular weight}$$

% of H

$$\frac{\text{Atomic Weight of H}}{\text{Molecular Weight of HNO}_3} \times 100 = \frac{1 \times 100}{63} = 1.6\%$$

% of N

$$\frac{\text{Atomic Weight of N}}{\text{Molecular Weight of HNO}_3} \times 100 = \frac{14 \times 100}{63} = 22.2\%$$

% of O

$$\frac{\text{Atomic Weight of O}}{\text{Molecular Weight of HNO}_3} \times 100 = \frac{48 \times 100}{63} = 76.2\%$$

$$\text{Total} = 100\%$$

5. c. Simplest Formula of a Compound from its Percentage

Composition. According to the Law of Definite Proportions, elements always combine in the same ratios to form compounds. This knowledge enables one to write the simplest formula of a compound when one knows the relative amounts, or percentages, of each of its elements. The percentage composition is determined by laboratory analysis of the compound.³²

Problem: Find the simplest formula of a compound that contains 63.6 % nitrogen and 36.4 % oxygen.³³

³²Jaffe, p. 636.

³³Ibid., p. 637.

Solution: Divide the percentage of each element by its atomic weight. Divide the quotients from the first step by their highest common factor. The highest common factor of two or more numbers is the largest number by which each of the numbers is divisible. The quotients from step one may not always be exactly divisible by the highest common factor; in this case, round the numbers off to the nearest whole number. The numbers now obtained in step two represent the smallest number of atoms of each element that can be present in one molecule of the compound. Therefore, used as subscripts for the symbols of their respective elements, they give the simplest formula of the compound. Problems of this type can be checked by finding the percentage composition of the formula that is determined. This percentage should agree with the data given in the problem.

$$\frac{\text{Percentage of N}}{\text{Atomic Weight of N}} = \frac{63.6}{14} = 4.54$$

$$\frac{\text{Percentage of O}}{\text{Atomic Weight of O}} = \frac{36.4}{16} = 2.28$$

$$\text{N} = \frac{4.54}{2.28} = 1.99 = 2$$

$$\text{O} = \frac{2.28}{2.28} = 1$$

$$\text{Simplest Formula} = \text{N}_2\text{O}$$

CHAPTER III

FUNDAMENTALS CONCERNING BEHAVIOR OF GASES

1. Definition of a Gas. Substances do not fall neatly into separate categories as suggested by the terms gas, liquid, and solid. Rather, matter can exist in either the gaseous, or the liquid, or the solid state. A given substance may exist in any one of these three states, depending on the conditions.³⁴ A gas then, is a state of matter that has neither shape nor volume and has independent molecules.³⁵ Thus, the states of matter are related to our concept of the structure of matter which enables one to distinguish or explain the properties of these three different states of matter. A study of the states of matter will familiarize one with the chemical behavior of matter; however, in the following presentation, the attention will be centered on the behavior of matter in the gaseous state.

2. Characteristics. Gases are characterized and distinguished from solids and liquids by the following properties: compressibility and expansibility, permeability, diffusibility, pressure in all directions, and liquefiability.³⁶ As scientists attempted to explain these properties based upon experimental evidence, the

³⁴Cragg and Graham, p. 177.

³⁵Weaver and Foster, p. 644.

³⁶Lanford, pp. 78-79.

Kinetic Molecular Theory was developed. This picture of the nature of gases received its name from the fact that molecules which make up the gases also possess kinetic energy. Molecules are widely separated and can be forced closer together; this explanation accounted for the compressibility of gases. Gases expand on heating, for the speed of molecules or the kinetic energy increases as the temperature increases. Molecules constantly move rapidly and haphazardly which would explain the diffusibility of gases. As molecules strike each other and the walls of the container without losing energy, the gases exert pressure which is proportional to the concentration. Since molecules attract each other at close range, liquefiability may be accomplished.

3. Analysis of the High School Texts. Upon analysis of the seven high school texts, there was found to be some variation in the treatment of the behavior of gases by the authors. Brownlee, Jaffe, Hopkins, and Weaver discuss the scientific laws of gases by Boyle, Charles, Gay-Lussac, and Avogadro in the text and reserve a quantitative treatment for the appendix. One author states, "A discussion of the way in which gases act at low temperatures and under high pressures is beyond the scope of an introductory course in chemistry."³⁷ To a greater extent, Dull, Lanford, and Rawlins discuss the scientific laws of gases already mentioned both qualitatively and quantitatively; in addition, Lanford includes Graham's Law of Diffusion and presents it quantitatively. Both Dull and Lanford include the principle of partial pressure in which this principle is used in correction of a volume of gas

³⁷Jaffe, p. 277.

collected over water. All the authors present the topic of standard temperature and pressure; however, Brownlee, Dull, and Jaffe give the best explanations. The methods of solution which are included condense to the form of substituting in an equation for the certain law or a logical, reasoning method. As a rule, Jaffe uses the gas equation whereas Dull uses the reasoning method. In his book, Dull starts the information concerning the behavior of gases and states that the solution of these problems may be reserved for the better students. In conclusion, Lanford, gives a more thorough description of the gas laws both quantitatively and qualitatively.

In using the results of this analysis, the following topics will be presented: standard temperature and pressure, Boyle's Law, Charles' Law, Combination Gas Law, Dalton's Law of Partial Pressure, Graham's Law of Diffusion, behavior of an ideal gas, and deviations from the gas laws along with a contrast of the methods used in solving these problems concerning the behavior of gases.

4. Standard Conditions of Temperature and Pressure. In dealing with gases, the same number of molecules can occupy widely different volumes. The expression "a cubic foot of air" means nothing unless we also know the temperature and pressure at which it is measured. According to the Kinetic Molecular Theory, the molecules are not packed closely together, as in the case of liquids and solids, but are usually comparatively far apart. An example will make this clear. Scientists have computed that if the molecules of the air that surround us could be magnified until they were as big as baseballs, the average distance between them would be about two feet. This gives one a relative idea of the

average distances between the tiny molecules. It also explains why one can crowd many more molecules of a gas within a given space. Raising the temperature of a gas increases the velocity of its molecules and causes them to move farther apart. Accordingly, one must consider both the temperature and pressure when measuring the volume of gases. Therefore, variations in gas volumes make it necessary to select some standard temperature and pressure.³⁸ The abbreviation for standard temperature and pressure is S. T. P.

4. a. Temperature. Three different temperature scales, Fahrenheit, Centigrade, and Absolute or Kelvin, are in common use. The Fahrenheit scale has 180 degrees between the two standard reference points, 32°F. as the freezing point of water and 212°F. as the boiling point of water, The Centigrade scale has 100 degrees between the two standard reference points, 0°C. and 100°C. These values are true at 760 mm pressure. The ratio of the number of degrees Centigrade to the number of degrees Fahrenheit is 100 to 180 or 5 to 9. Since the Fahrenheit scale does not start at zero, subtract 32° in order to get an accurate relationship.³⁹

$$\frac{C}{F - 32} = \frac{5}{9}$$

The author believes that the above relationship is the best method of converting Fahrenheit readings to Centigrade or changing Centigrade readings to Fahrenheit. One frequently forgets the specific formula for the preferred conversion.

³⁸Dull, p. 56.

³⁹Weaver and Foster, p. 623.

The zero point on the Absolute or Kelvin scale, K, is taken at -273°C . Thus, the Kelvin and Centigrade scales differ only in the choice of the zero point, and the Kelvin temperature is found by adding 273 to the Centigrade temperature. Absolute or Kelvin temperatures are always used in solving gas volume change problems.⁴⁰

4. b. Pressure. The pressure of a gas is the force it exerts on a unit surface area. It is frequently expressed in grams per square centimeter, in pounds per square inch, in atmospheres, and in millimeters of mercury. Since air has weight, it exerts a pressure. Thus, the atmospheric pressure is due to the weight of the overlying air. The pressure due to a column of a fluid is equal to the height multiplied by the density of the fluid. Standard pressure is the pressure exerted by the weight of a column of mercury exactly 760 mm high at 0°C ; this value is approximately the average pressure of the atmosphere at sea level and is equivalent to one atmosphere.⁴¹

Pressure = Height of Column of Hg x Density of Hg

$$1 \text{ Atmosphere} = 76 \text{ cm of Hg} \times 13.60 \text{ g/cm}^3 = 1034 \text{ g/cm}^2$$

$$1 \text{ Atmosphere} = 29.9 \text{ in of Hg} \times .491 \text{ lb/in}^3 = 14.7 \text{ lb/in}^2$$

Hence, standard conditions of temperature and pressure (S.T.P.) denote a temperature of 0°C or 273°K and a pressure of 760 mm of mercury, or one atmosphere. As both the volume and density of any gas are affected by changes of temperature and pressure, it is customary to reduce all gas volumes to standard conditions for purposes of comparison.

⁴⁰Schaum, p. 11.

⁴¹Ibid., p. 13.

5. Boyle's Law. This relationship deals with the change of the volume of gases due to the change in pressure. "If the temperature of a certain mass of gas is kept constant and the pressure on the gas is changed, the volume is inversely proportional to the pressure."⁴² This means that the volume decreases in the same proportion as the pressure increases. For example, if the pressure is doubled, the volume is reduced by one-half. All the molecules have been squeezed into half the volume they formerly occupied. Consequently, each molecule will hit the wall of the container twice as many times per second. This condition will produce a pressure twice as great as the original condition although the velocity of the molecule has not been changed. The Kinetic Molecular Theory then is the explanation for this relationship.⁴³

The derivation of the equations for Boyle's Law is as follows:⁴⁴

The product of the pressure P and the volume V of a given weight of gas is constant, if the temperature is constant.

$$P V = C$$

It follows that $P_1 V_1 = P_2 V_2$, where P_1 and P_2 represent the old and new pressures, and V_1 and V_2 represent the old and new volumes respectively. By dividing both sides of the latter equation by P_2 , the new volume may be obtained. By dividing both sides of the same equation by

⁴²Lanford, p. 82.

⁴³Ibid., p. 93.

⁴⁴George M. Rawlins and Alden H. Struble, Chemistry in Action (Boston, 1952), p. 549.

V_2 , the new pressure may be obtained.

$$V_2 = \frac{V_1 P_1}{P_2} \qquad P_2 = \frac{P_1 V_1}{V_2}$$

In solving problems involving the change in volume of a gas with changes in pressure, one must first do a little simple reasoning. Will the change in pressure make the volume of the gas larger or smaller? If the new volume is to be larger, then the old volume must be multiplied by the pressure effect which is greater than one. In other words, the pressure effect will be a fraction whose numerator is larger than the denominator. If the new volume is to be smaller, then the old volume must be multiplied by the pressure effect which is smaller than one. Similarly, the pressure effect will be a fraction whose numerator is smaller than the denominator.⁴⁵

Another method of solution of this type of problem is substitution in an exact formula representing Boyle's Law. However, most people prefer the reasoning method since it does not involve remembering an exact formula. Yet, solving by substitution in the Boyle's Law formula is an excellent method as long as one understands the formula in the first place and is careful to keep the values straight.

Problem: The volume of a gas is 100 cc. at a pressure of 760 mm. What volume will it occupy at 720 mm pressure, temperature being constant?⁴⁶

Solution: By reasoning, New Volume = Old Volume x Pressure Effect. Since the pressure is decreased, the new volume must be greater than the old volume. This means that the pressure effect must have a value greater than one. Therefore, the 760 goes in the numerator and the 720 goes in the denominator.

⁴⁵Sorum, p. 32.

⁴⁶Ibid.

$$\text{New Volume} = 100 \text{ cc} \times \frac{760 \text{ mm}}{720 \text{ mm}}$$

$$\text{New Volume} = 105 \text{ cc}$$

Solution: By formula substitution, $\frac{V_1}{V_2} = \frac{P_2}{P_1}$

$$V_1 = 100 \text{ cc}; \quad P_1 = 760 \text{ mm}; \quad P_2 = 720 \text{ mm}$$

$$V_2 = \frac{100 \text{ cc} \times 760 \text{ mm}}{720 \text{ mm}} = 105 \text{ cc}$$

6. Charles' Law. This relationship deals with the change in volume of gases due to the change in temperature. "The Kinetic Molecular Theory states that the kinetic energy of the gas molecules depends only on the temperature and that it is proportional to the Absolute temperature."⁴⁷ For example, a certain number of molecules of a gas is confined in a container at a temperature of 273° Absolute and a pressure of one atmosphere. Assume the temperature is raised to 546° Absolute. This means that the kinetic energy of the molecules will be doubled. But if the molecules move faster, they will hit the wall more often and also harder. In other words, the pressure of the gas will increase as the absolute temperature increases if the volume is kept constant. If the gas previously mentioned is confined by a movable piston with a twenty-five pound weight, then as the temperature is raised, the increased activity of the molecules will push the weight up until the increased activity of the molecules has been counterbalanced by their being less concentrated.⁴⁸

⁴⁷Lanford, p. 93.

⁴⁸Ibid., p. 94.

The French scientist, Charles, in studying the relationship between the volume of a gas and its temperature discovered that the volume of a gas increased by $1/273$ for each degree Centigrade its temperature is increased. From this he reasoned that a temperature of -273°C . was the lowest possible attainable temperature and designated this temperature Absolute zero. The Absolute temperature scale and Centigrade scale are related as discussed in the preceding section on temperature. Thus, Charles' studies led to the discovery that at a given pressure, the volume occupied by a gas is directly proportional to the Absolute temperature of the gas. Expressed as an equation, Charles' Law is as follows:

$$V = k T$$

where V is the volume of the gas sample, T is the Absolute temperature, and k is the constant. Solving this expression for k , one finds that the ratio of the volume of a gas to its Absolute temperature is a constant:

$$\frac{V}{T} = k$$

Thus, for a given gas sample, if the temperature is changed, this ratio must remain constant. Therefore, the volume must change in order to maintain the constant ratio. The ratio at a new temperature must be the same as the ratio at the original temperature. Then, one can write the following relationship:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where V_1 and T_1 are the original volume and original Absolute temperature, and V_2 and T_2 are the new volume and new Absolute temperature of the sample of gas respectively.⁴⁹

In applying the principle of Charles' Law, one must understand that when a gas is heated it expands and, conversely, that when a gas is cooled it contracts.

Problem: Find the volume of gas occupied by 60 liters of carbon dioxide when the temperature changes from 27°C. to 57° C. and the pressure remains constant.⁵⁰

Solution: Convert the Centigrade temperatures to the Absolute scale by adding 273°. Since the gas is changed to a higher temperature, the volume increases. Therefore, the original volume is multiplied by a temperature effect greater than one in order to make the volume increase.

$$60 \text{ liters} \times \frac{330^\circ \text{ K.}}{300^\circ \text{ K.}} = 66 \text{ liters}$$

Substitution in the Charles' Law formula is another method of solving the change in volume of a gas due to changes in pressure. However, the logical, reasoning process is shorter perhaps and is less open to errors of substitution.

7. Combination Gas Law. By combining the formulas for Boyle's Law and Charles' Law, one gets the general formula for expressing the change of volume when both the pressure and temperature change.

$$\frac{V_1}{V_2} = \frac{T_1 \times P_1}{T_2 \times P_2}$$

⁵⁰Weaver and Foster, p. 625.

One can also reason logically that:

New Volume = Old Volume x Temperature Effect x Pressure Effect

Hence, using the combined formula or the combined logic, one can calculate volume changes resulting from changes in both pressure and temperature.⁵¹

Problem: The volume of a gas is 200 liters at 12°C. and 750 mm. What volume will it occupy at 40°C. and 720 mm? ⁵²

Solution: 12°C. = 285°K.; 40°C. = 313°K.
Since the temperature increases, the volume must thereby be increased. Therefore, the temperature effect is greater than one, and the larger Absolute temperature is placed in the numerator. The pressure decreases; therefore, the volume must increase. Then the larger pressure is placed in the numerator of the pressure effect factor in order to have a fraction greater than one. Using the logical method, then:

$$\text{New Volume} = 200 \text{ liters} \times \frac{313^{\circ}\text{K.}}{285^{\circ}\text{K.}} \times \frac{750 \text{ mm}}{720 \text{ mm}}$$

$$\text{New Volume} = 229 \text{ liters}$$

Solution: One can also solve the problem by substituting in the general formula.

$$\frac{V_1}{V_2} = \frac{T_1 \times P_1}{T_2 \times P_2}$$

$$\frac{200 \text{ liters}}{V_2} = \frac{285^{\circ} \text{ K.} \times 720 \text{ mm}}{313^{\circ} \text{ K.} \times 750 \text{ mm}}$$

$$V_2 = 229 \text{ liters}$$

⁵²Sorum, p. 36.

8. Dalton's Law of Partial Pressures. "If two or more gases are mixed, their total pressure is the sum of the pressures that each gas would exert if it were alone."⁵³ The partial pressure is the pressure exerted by each gas in the mixture of gases.

Gas pressure is proportional to the number of gas molecules per unit volume. Thus, Dalton's Law merely states the obvious fact that the total number of molecules in a given volume is equal to the sum of the numbers of the molecules of each kind.⁵⁴

Dalton's Law of Partial Pressures is of special value in correcting the volume of a gas which has been collected by displacement of water. Whenever a gas is collected in contact with water, the gas contains some water vapor. The partial pressure of this water vapor depends on the temperature. In applying the Boyle's Law to the correction of gas volumes, one has to consider that the pressure apparently exerted by a gas collected over water is the pressure of the gas and the vapor pressure of water. The pressure exerted by the dry gas may be obtained by subtracting the vapor pressure of water at the particular temperature from the total pressure. No correction is needed for the gas volume when a gas is collected over mercury, for the vapor pressure of mercury is negligible at ordinary temperatures.⁵⁵

Problem: Under 700 mm of pressure, 275 cc of oxygen is collected over water at 23° C. What is the volume of the dry gas at standard pressure?

⁵³Selwood, p. 67.

⁵⁴Schaum, p. 14.

⁵⁵Selwood, p. 68.

Solution: The vapor pressure of water at 23° C. is about 21 mm. The partial pressure of the oxygen is therefore 700 mm - 21 mm.

$$V = 275 \text{ cc} \times \frac{700 \text{ mm} - 21 \text{ mm}}{760 \text{ mm}} = 246 \text{ cc}$$

9. Graham's Law of Diffusion. One gas diffuses into a space already occupied by another gas quite readily until both are uniformly distributed throughout the space. A simple way to demonstrate Graham's Law of Diffusion is to withdraw the stoppers from a bottle of concentrated ammonium hydroxide and a bottle of concentrated hydrochloric acid. In holding the stoppers about a foot apart, a smoke appears around the stopper of the hydrochloric acid stopper but not around the other stopper. The small amounts of solutions on the stoppers give off the colorless gases ammonia and hydrogen chloride. Since the ammonia diffuses more rapidly than the hydrogen chloride, it reaches the stopper from the hydrochloric acid bottle before the hydrogen chloride gas can reach the ammonium hydroxide stopper. The explanation is that the density of the ammonia is less than half the density of the hydrogen chloride; thus, the ammonia diffuses faster. As it reaches the hydrogen chloride, the two unite to form ammonium chloride, a white solid.⁵⁶

One mole of any gas occupies a volume of 22.4 liters at standard temperature and pressure, exerts a pressure of 760 mm at 0° C. when placed in a 22.4 liter container, and contains 6.023×10^{23} molecules. Thus, one molecule of one gas at a given temperature exerts the same pressure as one molecule of any other gas at the

⁵⁶Lanford, p. 86.

same temperature. This molecule can exert pressure because it has kinetic energy. In addition, at a given temperature one molecule of one gas has the same kinetic energy as one molecule of any other gas. For example, the molecular weight of the gases sulfur dioxide and methane is 64 and 16 respectively. The sulfur dioxide molecule is four times as heavy as the methane molecule; nevertheless, the light molecule can exert just as much pressure, and therefore, has just as much energy as the heavy sulfur dioxide molecule. There can only be one explanation. The methane molecule must be moving faster. If this molecule is moving faster than the sulfur dioxide molecule, then it should be diffusing faster. The methane molecule does diffuse faster; in fact, it diffuses exactly twice as fast as the sulfur dioxide molecule even though it is one-fourth as heavy. Hence, the lighter a gas is, the faster it diffuses, and this relationship is an inverse proportion. As in the case of methane and sulfur dioxide, the rates of diffusion of the two gases are inversely proportional to the square roots of their densities. Since the molecular weight is proportional to the density of the gases, the molecular weight may be substituted for the density. This generalization is Graham's Law of Diffusion. The mathematical formula is:⁵⁷

$$\frac{\text{Rate of Diffusion of Gas A}}{\text{Rate of Diffusion of Gas B}} = \frac{\text{Density of Gas B}}{\text{Density of Gas A}}$$

⁵⁷Sorum, p. 44.

Problem: Compute the relative rates of diffusion of hydrogen and carbon dioxide through a fine pin-hole.⁵⁸

Solution: The molecular weights of hydrogen and carbon dioxide are 2 and 44 respectively.

$$\frac{R_{H_2}}{R_{CO_2}} = \frac{M_{CO_2}}{M_{H_2}} = \frac{44}{2} = 22 = 4.7$$

$$\text{Then } R_{H_2} = 4.7 \times R_{CO_2}$$

10. Deviations from the Gas Laws. The laws discussed above are strictly valid only for ideal gases, that is, gases which follow the gas laws perfectly. An ideal gas is non-existent, for no known gas obeys the gas laws at all possible temperatures. Since all gases can be liquified if they are compressed and cooled sufficiently, all gases become non-ideal at high pressures and low temperatures. The ideal properties are observed at low pressures and high temperatures, conditions far removed from those of the liquid state. For pressures below a few atmospheres, practically all gases are sufficiently ideal for the application of the ideal gas laws.⁵⁹

The principal reasons why real gases do not behave as ideal gases are that the molecules have mass and occupy space. The matter contained in the molecules cannot be destroyed, and the molecules can only be compressed to a limit. In other words, a gas would behave as an ideal gas only if its molecules were true mathematical points--that is, if they possessed neither weight nor dimensions. However, the molecules of real gases follow the gas laws

⁵⁹Schaum, p. 15.

so closely that any deviations from these laws are relatively insignificant. Nevertheless, it should be remembered that the gas laws are not strictly accurate and that the results are really close approximations.⁶⁰

11. Comments on Methods of Solving Gas Problems. In addition to the information previously given concerning methods under the particular type of problem, Dull states, "While the method of reasoning is preferred by most teachers and by the College Entrance Examination Board, it is often convenient to solve gas problems using the gas equations."⁶¹ In his book, Weaver adds, "The use of the gas-law-equation method depends on memory; the use of the reasoning method needs less memory and depends on understanding the principles involved."⁶² In conclusion, then, perhaps the reasoning method is the better method of solving problems involving gases.

⁶⁰Hess, p. 52.

⁶¹Dull, p. 559.

⁶²Weaver and Foster, p. 627.

CHAPTER IV

FUNDAMENTALS OF CHEMICAL EQUATIONS

1. Significance and Importance. Calculations based on chemical equations are among the most important calculations in general chemistry because of the volume of descriptive and quantitative knowledge that is condensed into these equations. Knowledge about chemical change is represented by an equation of formulas, just as each formula represents the composition of a substance in terms of the constituent atoms.⁶³

2. Definition and Components. The balanced equation is an algebraic chemical equation with the formulas and relative weights or volumes of the reacting substances on the left side and the formulas and relative weights or volumes of the products on the right side. Before an equation can be written, one must know the formulas for the reactants and products and if the reaction is possible. Through experimental evidence this information is furnished.⁶⁴ Chemical equations represent actual conditions, and the number of atoms of the reactants must equal the number of atoms of the products. Thus, every correct equation conforms in this way to the Law of Conservation of Matter which states that matter is neither created or destroyed during a chemical change.⁶⁵

⁶³Schaum, p. 40.

⁶⁴Rawlins and Struble, p. 156.

⁶⁵Jaffe, p. 115.

3. Analysis of the High School Texts. In analyzing the seven high school texts, it was found that each author included discussions of three broad types of problems relative to chemical equations. Dull, Jaffe, Hopkins, Rawlins, and Weaver presented a more thorough discussion as to theory, typical problems, and methods of solution whereas Brownlee and Lanford gave a limited treatment in these areas. The three main types of problems based on chemical equations are as follows: weight-weight problems, weight-volume problems, and volume-volume problems. In the majority of the cases, the mathematical technique used by these authors was proportion; however, Dull, Jaffe, Hopkins, and Weaver gave alternative methods of solving problems. As a rule, procedures in reasoning through the problems and arriving at a solution were given sufficient treatment.

In using the results of this analysis, the following topics will be presented: weight-weight problems, weight-volume problems, and volume-volume problems.

4. Weight-Weight Problems. All atoms and molecules have definite weights. These actual weights of atoms and molecules are proportional to their atomic and molecular weights. Hence, the balanced equation also shows the relative weights of the reactants and products. Calculations involving weight relations only, whether with solids, liquids, or gases, are designated as weight-weight calculations.⁶⁶

In weight-weight problems, the weight of one substance is given and the weight of a second substance is required. It is evident that the same weight proportions may be expressed in any unit of weight.

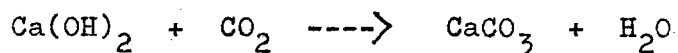
⁶⁶Schaum, p. 41

"Because the symbol of an element and the formula of a compound may represent definite weights, an equation also may be considered to represent definite weights of the substance taking part in the reaction. Thus, $2 \text{ Ag} + \text{ S} \text{ ----} \rightarrow \text{ Ag}_2\text{ S}$ may be read, 216 grams of silver plus 32 grams of sulfur yield 248 grams of silver sulfide. Note that the actual weights are based on the atomic weights."⁶⁷

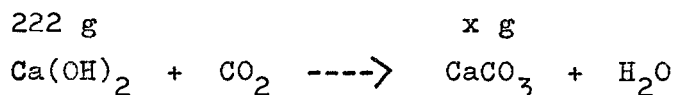
Problem: How many grams of calcium carbonate will be formed by the complete reaction between 222 grams of calcium hydroxide and carbon dioxide?

Solution:

- a. Write the balanced equation.

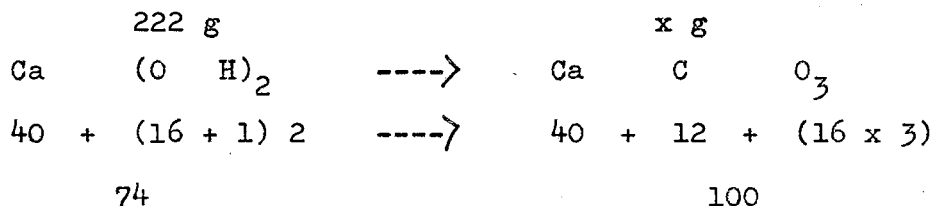


- b. Write the given weight over its formula. Write x over the formula of the substance whose weight is to be found. Cross out all other formulas in the equation, or ignore them.



- c. Since the same relationship exists between the actual weights as exists between the molecular weights of the substances involved in the equation, write the molecular weights of the substances under their respective formulas.

Do not ignore any coefficient.



- d. Write the mathematical equation represented by the known and unknown weights. Solve for x.

⁶⁷Jaffe, p. 132.

$$\frac{222 \text{ g}}{74} = \frac{x}{100} \quad 74 x = 22,200 \text{ g} \quad x = 300 \text{ g, CaCO}_3$$

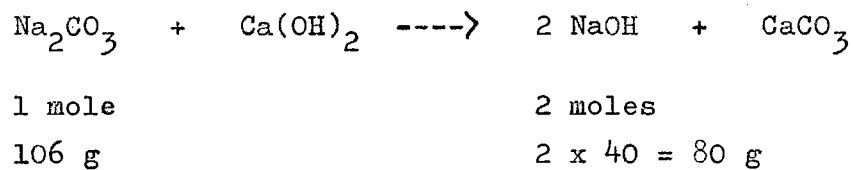
An alternate method that can be used in order to avoid the use of an equation involving x is as follows:

$$\frac{\text{Weight of reactant} \times \text{Molecular Weight of Resultant}}{\text{Molecular Weight of Reactant}} = \text{Answer}^{68}$$

A teacher or student might find another method of solving weight-weight problems easier than the preceding method. Schaum gives three methods of solving this type of problem.

Problem: Caustic soda, NaOH, is often prepared commercially by the reaction of Na_2CO_3 with slaked lime, $\text{Ca}(\text{OH})_2$. How many grams of NaOH can be obtained by treating one kilogram of Na_2CO_3 with $\text{Ca}(\text{OH})_2$?

Solution: First write the balanced equation for the reaction.



Formula weight of $\text{Na}_2\text{CO}_3 = 106$; of NaOH = 40

The equation states that 1 formula weight of Na_2CO_3 reacts with 1 formula weight of $\text{Ca}(\text{OH})_2$ to give 2 formula weights of NaOH and 1 formula weight of CaCO_3 .

First Method. The equation indicates that 1 mole Na_2CO_3 (106g) gives 2 moles NaOH (80g).

⁶⁸Jaffe, p. 133.

106 g Na_2CO_3 gives 80 g NaOH, then 1 g Na_2CO_3 gives $80/106$ g of NaOH, and 1000 g Na_2CO_3 gives $1000 \times 80/106$ g = 755 g of NaOH.

Molar Method. Number of moles of Na_2CO_3 in 1000g =

$$\frac{1000 \text{ g}}{106 \text{ g/mole}} = 9.434 \text{ moles of } \text{Na}_2\text{CO}_3$$

Since 1 mole of Na_2CO_3 yields 2 moles NaOH, 9.434 moles of Na_2CO_3 yield 2×9.434 moles = 18.87 moles of NaOH. Grams of NaOH in 18.87 moles = 18.87 moles \times 40 g/mole = 755 g of NaOH.

Proportion Method. Let x = number of grams of NaOH obtained from 1000 g of Na_2CO_3 . The problem now reads: 106 g Na_2CO_3 (1 mole of Na_2CO_3) give 80 g NaOH (2 moles NaOH); hence, 1000 g Na_2CO_3 will give x g NaOH. Then by proportion,

$$\frac{106 \text{ g } \text{Na}_2\text{CO}_3}{80 \text{ g NaOH}} = \frac{1000 \text{ g } \text{Na}_2\text{CO}_3}{x}$$

Solving,

$$x = 1000 \text{ g } \text{Na}_2\text{CO}_3 \times \frac{80 \text{ g NaOH}}{106 \text{ g } \text{Na}_2\text{CO}_3} = 755 \text{ g NaOH}^{69}$$

5. Weight-Volume Problems. Gas volume calculations involving also solids and liquids are designated as weight-volume problems, and the term volume refers to the gas volume.⁷⁰

A chemical formula may represent one molecule of a compound, one molecular weight, or mole of a compound. If a coefficient appears

⁶⁹Schaum, p. 42.

⁷⁰Ibid.

in front of a formula, it represents a definite number of molecules, molecular weights, or moles. Thus 2CO_2 stands for two molecules of the gas, two molecular weights (88), or two moles (88 grams).

In dealing with a gas or vapor, it is often necessary to know the volume that a quantity occupies. The unit of measurement of gas volumes is the volume occupied by one mole, called the gram-molecular volume. Avogadro proved that the gram-molecular volume is the same for all gases; that is, under standard conditions of temperature and pressure (0°C. , 760 mm) one mole of any gas occupied 22.4 liters. Therefore, we can use the formula of the gas to represent its gram-molecular volume. The coefficient of the formula represents the number of gram-molecular volumes. Thus, 2CO_2 stands for two volumes or 44.8 liters.⁷¹ By utilizing Avogadro's law, one can convert weight to volume, or volume to weight.

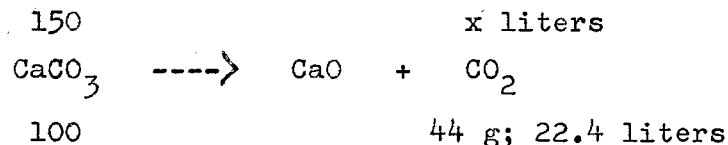
In the weight-volume problem, either the weight or volume of a substance is given, and one is asked to calculate either the volume or the weight of a second substance. One can start with a weight and calculate a volume, or, conversely, one can start with a volume and calculate a weight. The problem may ask how many grams of a chemical is required to liberate a given volume of a certain gas, measured in liters or in milliliters. On the other hand, the number of grams of the substance may be given and the question may be to find the volume of gas liberated. In solving this type of problem, it is important to keep in mind that one mole of any gas occupies a volume of 22.4 liters at standard temperature and pressure.⁷²

⁷¹Jaffe, pp. 282-283.

⁷²Dull, p. 145.

Problem: How many liters of carbon dioxide are set free by heating 150 grams of calcium carbonate?⁷³

Solution: One uses the following steps to solve this problem: write the balanced equation for the problem; write the actual weight of the CaCO_3 given above its formula; write the required volume, x liters, above the formula of CO_2 ; write the equation weights beneath the corresponding² formulas; change the one mole of CO_2 to its equivalent, which is 22.4 liters.



Set up a proportion and solve to find the value of x .

$$\frac{150}{100} = \frac{x \text{ liters}}{22.4 \text{ liters}} \qquad x = \frac{150 \times 22.4 \text{ liters}}{100}$$

$$x = 33.6 \text{ liters}$$

6. Volume-Volume Problems. "Gas volume calculations involving gases only are designated as volume-volume calculations."⁷⁴ These problems are based upon Gay-Lussac's Law and Avogadro's Hypothesis. Gay-Lussac's Law states that the ratio of the volumes of combining gases and the volume of their products may be expressed by small whole numbers. Avogadro's Hypothesis declares that equal numbers of molecules of gases under the same conditions of temperature and pressure occupy equal volumes. These principles enable one to write the volume relationship from equations representing the reaction between gaseous substances and their products.

⁷³Ibid. p. 146.

⁷⁴Lewis, p. 66.

In this type of problem, the volume of one substance is given, and one is asked to calculate the volume of another substance. In solving such problems, it is not necessary to use atomic weights at all. Since equal volumes of all gases at the same temperature and pressure have the same number of molecules, then in a correctly written molecular equation, the volumes of any two gases are proportional to the relative numbers of molecules. The coefficients in such equations are proportional to the relative volumes of the gases. Such problems are so simple that some pupils try to make them difficult.⁷⁵

Problem: What volume of ammonia must decompose to provide 60 liters of hydrogen? ⁷⁶

Solution: Write the balanced equation for the reaction. Solving a problem involving two gases, use the volume principle for both. Write the required volume, x liters, above the formula for ammonia and the 60 liters above hydrogen. Below the formulas, write the gram-molecular volume and multiply this value by the coefficient of each substance respectively.

$$\begin{array}{rcccl}
 & x & & & 60 \text{ liters} \\
 & 2 \text{ NH}_3 & \text{---->} & \text{N}_2 & + & 3\text{H}_2 \\
 2 \times 22.4 & = & 44.8 & & & 3 \times 22.4 = 67.2 \\
 \text{liters} & & & & & \text{liters} \\
 \\
 & \frac{x}{44.8 \text{ liters}} & = & \frac{60 \text{ liters}}{67.2 \text{ liters}} \\
 \\
 & x & = & \frac{60 \text{ liters} \times 44.8 \text{ liters}}{67.2 \text{ liters}} \\
 \\
 & x & = & 40 \text{ liters of NH}_3
 \end{array}$$

In the above solution, the common factor, 22.4 liters, may be canceled in order to simplify the solution.

⁷⁵Dull, p. 146.

⁷⁶Weaver and Foster, p. 226.

CHAPTER V

FUNDAMENTALS OF SOLUTIONS

1. Significance and Importance. Solutions are very significant in natural and industrial processes. In nature their application ranges from digestion and absorption of foodstuffs in solution by plants and animals to the formation of vast limestone solution caverns. In industry the application is equally wide, ranging from the refining of cane sugar and photographic processes to the separating of silver from crude zinc.⁷⁷

For several reasons, solutions are utilized in chemical work. A small amount of substance or solute may be uniformly distributed in a solution. Many chemical actions, especially reactions between ionic compounds, take place quickly in solutions. And too, the use of solutions are more convenient.⁷⁸ In laboratory work with acids, bases, and salts, it is often necessary and convenient to know their concentration. For example, a great convenience in using normal solutions is the fact that reacting normal solutions of the same normality react exactly with none of the reacting materials remaining. In other words, a liter of any normal acid solution neutralizes exactly a liter of any normal basic solution.⁷⁹ Adding to these reasons is Fr. Fred C. Hess who states, "A tremendous amount

⁷⁷Lanford, p. 146.

⁷⁸Weaver and Foster, p. 169.

⁷⁹Hopkins, p. 200.

of chemistry takes place in solution, and so it is well for us to become thoroughly familiar with both the terminology and the properties of solutions."⁸⁰

2. Definition and Components. "A solution is a substance consisting of molecules of more than one kind uniformly intermingled. More practically, however, a solution is a homogeneous substance whose composition can be expressed in terms of two or more substances which are related to the solution in such a way that a small change in the proportion of these constituents produces a corresponding change in the value of a characteristic property of the substance."⁸¹ This definition is long, but it does help us to distinguish experimentally between a solution and a mixture and between a solution and a compound. Possibly, one can more tersely state that a solution is a homogeneous substance that is not a compound. In addition, a solution consists of two components, a solvent which is the dissolving medium and a solute which is the substance dissolved.

3. Analysis of the High School Texts. Throughout the seven high school texts, the topic of solutions has been treated in a varied manner qualitatively and quantitatively. All the authors discussed the types of standard solutions, normality and molarity, the technique of titration, the meaning of pH, and the per cent strength of solutions; however, each differed in the quantitative treatment. The majority gave reasons for the importance of solutions and the knowledge of concentrations. Hopkins, Lanford, and Rawlins presented

⁸⁰Hess, p. 66.

⁸¹Cragg and Graham, p. 264.

titrations quantitatively. To a greater extent, Hopkins and Lanford emphasized the quantitative aspects of these considerations, however. A mathematical treatment of the applications of the freezing point depression principle and the boiling point increase principle in determining the molecular weight of the solute was included by the authors Hopkins, Lanford, and Rawlins. The hydrogen-ion concentration was treated qualitatively in the various high school texts, but the quantitative aspects were given only limited treatment since the calculations involve a knowledge of logarithms to a certain extent. The author Dull stars the information concerning solutions in his book and implies that it may be reserved for the better students without affecting the continuity of the book. Brownlee states, "All such calculations are an important part of the laboratory and industrial control of chemical reactions."⁸²

Using the results of this analysis, the following topics will be presented: concentration with its expression in weight-weight units as percentage composition and in weight-volume units as molarity and normality along with the techniques of titration and hydrogen-ion concentration. Since the principles of the freezing point depression and boiling point increase of solutions are used to determine the molecular weight of the solute in the solution, these particular principles have been discussed in Chapter II.

4. Concentration. The relative proportions as well as the solution constituents must be specified in identifying a solution. In general, the relative proportions of the solute and solvent

⁸²Raymond B. Brownlee et al., Elements of Chemistry (Boston, 1954), p. 146.

are best given by stating the volume or weight of each constituent in specified volume or weight of solution. Whatever the units, the quantity of solution constituent in a fixed quantity of solution is its concentration in the solution. In other words, the quantity of solute per unit of solvent is known as the concentration of the solution.⁸³ This concentration can be expressed in various manners. "The most commonly used methods are physical units as percentage of weight and volume concentrations and chemical units as molar and normal concentrations."⁸⁴ Another way of expressing concentration is weight-weight units and weight-volume units.⁸⁵ In this paper, the latter division will be utilized in the organization.

4. a. Weight-Weight Units of Concentration. This kind of concentration concerns per cent strength or percentage composition of the solution. Per cent means parts per hundred, and the per cent strength of a solution is the parts by weight of solute per 100 parts by weight of solution. From the following simple relationship, the per cent strength of the solution can be calculated:⁸⁶

$$\text{Per cent Strength of Solution} = \frac{\text{Weight of Solute}}{\text{Weight of Solution}} \times 100\%$$

Since the solution is prepared by dissolving the solute in the solvent, the weight of the solution will therefore be the sum of the weights of the solute and solvent.

⁸³Cragg and Graham, p. 269.

⁸⁴H. V. Anderson, Chemical Calculations (New York, 1955), p. 169.

⁸⁵Cragg and Graham, p. 268.

⁸⁶Sorum, p. 45.

Problem: Twelve grams of common salt were dissolved in ⁸⁸ 88 grams of water to give 100 grams of solution. Calculate the per cent strength of the solution.⁸⁷

Solution:

$$\text{Per Cent Strength of Solution} = \frac{\text{Weight of Solute}}{\text{Weight of Solution}} \times 100\%$$

$$\text{Per Cent Strength of Solution} = \frac{12 \text{ g of Salt}}{100 \text{ g of Solution}}$$

$$\text{Per Cent Strength of Solution} = 12\%$$

4. b. Weight- Volume Units of Concentration. The molarity and normality of solutions are expressed in weight-volume units of concentration and are used in volumetric experiments in which the amount of solute in a given portion of solution is related to the measured volume of solution. The normality scale is very convenient for comparing the relative volume required for two solutions to react chemically with each other. However, a limitation of the normality scale is that a given solution may have more than one normality, depending on the reaction for which it is used. On the other hand, the molarity of a solution is a fixed number because there is only one molecular weight for any substance.⁸⁸

Molarity. One mole or gram-molecular weight of dissolved substance in one liter of solution is a molar solution, represented by the letter M. A one molar solution of sulfuric acid contains 98.08 grams of sulfuric acid per liter of solution since the molecular

⁸⁷Ibid.

⁸⁸Schaum, p. 83.

weight of the acid is 98.08. A 0.5 M solution contains 0.5×98.08 grams of sulfuric acid per liter of solution. The same number of molecules is contained in a mole of any substance. Consequently, equal volumes of all molar solutions are considered as containing an equal number of molecules.⁸⁹

The mathematical relationship for the molarity of a solution is as follows:

$$\text{Molarity of a Solution} = \frac{\text{Number of Moles of Solute}}{\text{Number of Liters of Solution}}$$

Problem: Determine the molar concentration of the following solution: 18 grams of silver nitrate per liter of solution.⁹⁰

Solution: Molecular Weight of $\text{AgNO}_3 = 169.89$

$$\frac{18 \text{ g/liter}}{169.89 \text{ g/mole}} = .106 \text{ mole/liter} = .106 \text{ M}$$

Problem: How much sodium chloride per liter of solution does a .3 M solution of sodium chloride contain?⁹¹

Solution: Molecular Weight of $\text{NaCl} = 58.5 \text{ g/liter}$

$$1 \text{ M} = 58.5 \text{ g/liter}$$

$$.3 \text{ M} = 58.5 \text{ g/liter} \times .3 = 17.6 \text{ g/liter}$$

Normality: Normal solutions are prepared so that in one liter of solution there is either one gram of replaceable hydrogen or a sufficient quantity of some other substance to directly or indirectly

⁸⁹Hopkins, p. 200.

⁹⁰Schaum, p. 84

⁹¹Jaffe, p. 208.

replace one gram of hydrogen.⁹² "A normal solution is one which contains one gram-equivalent weight of the solute in one liter of solution. The gram-equivalent weight of a compound may be defined as that weight of the compound which will react with, displace, or supply one gram-equivalent weight of any other compound."⁹³

Since a normal solution may be a solution of an acid, base, or salt, it is necessary to explain normality in terms of the type of solution. Weaver gives this explanation, "Normal solutions of acids contain one gram of replaceable hydrogen ions per liter, and normal solutions of metallic hydroxides contain seventeen grams of hydroxyl ions per liter in these basic solutions. Normal solutions of salts contain an equivalent of one gram of hydrogen."⁹⁴ From a different point of reasoning, Hopkins explains that if the formula of the acid shows one replaceable hydrogen, a mole of the acid makes a liter of normal solution. If the formula of the acid has three replaceable hydrogen atoms, one-third mole per liter makes a normal solution. If the formula of the base shows one hydroxyl ion, then a mole of the base is a normal solution. In finding the normality of the salt, find the hydrogen equivalent of the salt and divide it into a mole of the anhydrous salt, using this weight of solute to form a liter of solution. For example, in $Al_2(SO_4)_3$, two aluminum atoms are equivalent to six hydrogen atoms (valence of three of Al x 2 atoms of Al). In this case, one would divide

⁹²Dull, p. 209.

⁹³Joseph A. Babor and Chester B. Kremer, How to Solve Problems in General Chemistry (New York, 1941), p. 53.

⁹⁴Weaver and Foster, p. 629.

a mole of aluminum sulfate by six to find the weight of the solute. In conclusion, one liter of a normal solution contains one gram of hydrogen ion or its equivalent.⁹⁵

According to Schaum, the mathematical relationship for the normality of a solution is as follows:

$$\text{Normality of Solution} = \frac{\text{Number of Gram-Equivalents of Solute}}{\text{Number of Liters of Solution}}$$

Problem: Calculate the normality of 7.88 grams of nitric acid per liter of solution.⁹⁶

Solution: Equivalent Weight of HNO_3 = Molecular Weight
Then 1 N HNO_3 contains 63.02 grams HNO_3 per liter of solution.

$$\text{Normality} = \frac{7.88 \text{ g/l}}{63.02 \text{ g/g-eq}} = 0.125 \text{ gram-equivalent/liter}$$

$$\text{Normality} = 0.125 \text{ N}$$

Problem: What volume of .5 N sodium sulfate can be prepared from 40 grams of sodium sulfate?⁹⁷

Solution: Molecular weight of Na_2SO_4 = 142 g/mole
Equivalent weight of Na_2SO_4 = .5 x 142 g = 71 g
One-half of an equivalent weight of Na_2SO_4 = .5 x 71 g = 35.5 g.
This weight is present in 1 liter of .5N Na_2SO_4 . If 1 liter of .5N Na_2SO_4 requires 35.5 g of solute, 40 g of the salt will produce as many liters as 35.5 is contained in 40, or $\frac{40}{35.5}$ liters = 1.12 liters.

⁹⁵Hopkins, pp. 200-201.

⁹⁶Schaum, p. 79.

⁹⁷Babor and Kremer, p. 54.

Titration. "Titration is the process of determining the concentration, or normality, of an unknown solution by means of a standard solution which contains a known quantity of reagent in a definite volume of solution."⁹⁸

During a chemical change, equal volumes of acid and basic solution of the same normality neutralize each other exactly. In substituting a 0.1 N solution for a 1 N solution, ten times the volume of the weaker solution is needed for the same effect. For a given reaction then, less volume is required the more concentrated the solution. In more general terms, volume and normality are inversely proportional, and the following equation holds for the volume relation of normal solutions:

$$\frac{V_1}{V_2} = \frac{N_2}{N_1} \quad \text{or} \quad V_1 \times N_1 = V_2 \times N_2$$

where V_1 is the volume of the solution with normality N_1 , and V_2 is the volume of the solution with normality N_2 .

Problem: What weight of hydrogen nitrate is present in three liters of nitric acid that just neutralizes 234 milliliters of 4N sodium hydroxide solution?⁹⁹

Solution:

$$3 \text{ liters} \times N_1 = .234 \text{ liters} \times 4N$$

$$N_1 = \frac{.234 \text{ liter} \times 4N}{3 \text{ liters}} = .312 N$$

1 N HNO_3 contains 63 g of hydrogen nitrate per liter. Three liters of .312 N HNO_3 contains: $63 \times .312 \times 3 = 58.97 \text{ g.}$

⁹⁸Schaum, p. 80.

⁹⁹Weaver and Foster, p. 630.

Hydrogen Ion Concentration. Frequently, the small differences in the acidity or alkalinity of solutions, especially those that are near the neutral point, are of great importance in biological, electrolytic, and fermentation processes, and in farming, baking, and manufacturing many products. The most widely used method of expressing hydrogen ion concentration is commonly called the pH system. To make this clear, suppose you dilute a normal acid solution with nine volumes of pure water. The solution will then be one-tenth normal and will contain .1 gram of hydrogen ion per liter. Expressed with a negative exponent, the concentration is 10^{-1} gram of hydrogen ion. Then the pH is 1. In like manner, if a volume of this solution is again diluted with nine volumes of pure water, you obtain a solution which is one-hundredth normal and contains 10^{-2} gram of hydrogen ions per liter. Therefore, this solution has a pH value of 2. Very careful measurements of the conductivity of pure water show that its hydrogen ion concentration is 10^{-7} grams per liter. This is a pH of 7 and is the neutral point. In addition, acids have a pH value less than 7 while bases have a pH value greater than 7.¹⁰⁰

Chemists have found it convenient to express hydronium ion concentrations logarithmically, or as powers of 10. In order to avoid negative values so far as possible, the pH of a solution is defined as the negative logarithm, base ten, of the hydronium ion concentration. In other words, the pH is the logarithm of the reciprocal of the hydronium ion concentration.

¹⁰⁰Hopkins, p. 202.

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = \log_{10} \left[\frac{1}{[\text{H}_3\text{O}^+]} \right]$$

The $[\text{H}_3\text{O}^+]$ represents the hydronium ion concentration in moles per liter.

Problem: What is the pH corresponding to a hydronium ion concentration of .0049 moles/liter? 101

Solution:

$$\begin{aligned} \text{pH} &= -\log (.0049) = -\log (4.9 \times 10^{-3}) \\ &= -.69 - (-3) = 2.31 \end{aligned}$$

Problem: What hydronium ion concentration corresponds to a pH of 11.68?

Solution:

$$\begin{aligned} -\log [\text{H}_3\text{O}^+] &= \text{pH} = 11.68 \\ \log [\text{H}_3\text{O}^+] &= -11.68 = -12.00 + .32 = \underline{12.32} \\ \text{Taking antilogs, } [\text{H}_3\text{O}^+] &= 2.1 \times 10^{-12} \end{aligned}$$

To provide more background concerning this topic, it is necessary to include a limited discussion of the ionization of water and equilibrium. Pure water has a definite, though small electrical conductivity which is due to the hydrogen and hydroxyl ions formed by the reversible reaction, $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. The hydrogen ion concentration at room temperature of pure water is 10^{-7} moles per liter; therefore, the pH is 7. A higher concentration of hydrogen ions, as in an acid solution, will give a lower

¹⁰¹Cragg and Graham, p. 445.

pH. On the contrary, a basic solution will have a higher pH because the concentration of hydrogen ions is correspondingly decreased as the concentration of hydroxide ions is raised. From the equilibrium constant, it can be seen that water is so slightly ionized that its own concentration may be taken as constant. Thus, with only negligible error, we may write:



At room temperature, the K_i , or ionization constant for water, is 1.0×10^{-14} . If H^+ is raised, as by adding an acid, then for K to remain equal to 10^{-14} it is essential for OH^- to diminish correspondingly, and vice-versa.¹⁰²

It follows that $\text{pH} + \text{pOH} = 14$. Thus, when either the pH or pOH is known, it is possible to determine the other.¹⁰³

¹⁰²Selwood, p. 210.

¹⁰³Cragg and Graham, p. 445.

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