QUALITATIVE
CHEMICAL ANALYSIS

(THEORETICAL AND PRACTICAL)

QUALITATIVE
CHEMICAL ANALYSIS

A LABORATORY GUIDE

BY

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PREFACE

This little work has been primarily prepared for the use of Chinese students, but I believe that my friend and former pupil Mr. Z. Z. Zee has evolved a text-book which will be hailed with delight by science teachers not only throughout China but also in the schools and colleges of Western lands.

For many years I have felt the need of such a book for my own students, and although much has been written about "test-tubing," yet I feel that there is no better introduction to the study of chemistry, whether for educational or professional purposes, than a course of qualitative analysis, and a student who has gone through such a course will have acquired both dexterity in the use of apparatus and knowledge that will be of incalculable value to him in his after-career.

The theoretical aspect of the science has also been kept in view throughout the course and the student is encouraged, or rather compelled, to think for himself and finally to become so interested in his study that a spirit of inquiry and research is fostered.

There are two ways in which a text-book may be prepared, it may either be simply an examination "cram" book or it may aim at supplying the materials for a *bona-fide* course of study. A careful examination will show that this book has the latter aim and the teachings on such subjects as Ionization, Mass Action and Solution Pressure are thoughtful, lucid and up-to-date.

To those about to use the book may I give the following advice: —

(1) Be sure you understand the theoretical explanation as well as the practical part of your work.

(2) Make your notes as you proceed with your work. Do not leave them to be written up or rather "faked up" out of the laboratory.

(3) Learn to work neatly and you will obtain exact views of the science. Prof. Roscoe says, "Those who work in a mess not infrequently get their minds in a muddle."

(4) Look at the label of a bottle when you take it from the shelf and give a second confirmatory look when you replace it.

(5) In adding reagents, a drop or two will, except in a few special cases, be enough to indicate a precipitate.

(6) Enter your results clearly and simply. In many cases a three column arrangement is enough, thus,

Experiment | Result | Inference.

I hope this work will receive from critics and teachers a favourable recognition and that all will acknowledge that Mr. Zee has kept before him the main object of teaching experimental science, viz: "to train students to solve simple problems by experiment, to work accurately and with a clearly defined purpose, and to reason from observation."

F. CLEMENT COOPER.

St. John's University,
January, 1912.

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AUTHOR'S PREFACE

In preparing this little volume for the use of schools where science is generally taught in English, the author has two reasons in mind: First, to combine the theoretical side with the practical; and secondly, to eliminate some of the features found in other text-books which are often burdensome to the beginner without being practical for elementary work.

With the first object in view, the introductory chapters are written on some of the general principles of chemistry which have more or less to do with the subject. These chapters, the author believes, will lead the student to deductive reasoning, and should be thoroughly acquainted with before procedure of any work, though constant reference to them is equally important as the work progresses. Special attention is called to the notes and questions at the end of each table in Part III, which will serve as a sort of supplement to Part I. Other points of interest that may suggest themselves from time to time should be discussed thoroughly in the class. Never let anything go by half-understood.

In order to carry out the second object, Parts II and III have been arranged in such a way as to contain only the most essential requisites for an elementary course. As it is impossible as well as useless to remember the descriptions of different ions alone, the two parts should be studied side by side. For this reason, the order of arrangements have been made to coincide with one other. No leaps must be made in any of the ions thus arranged.

Many criticisms have been made upon the tabular system of teaching analysis as being too mechanical. Some American colleges have actually given it up, making the students form their own scheme according to the directions of the book. While this is in some respects superior to the old method, its success must not be overrated; for lazy students will invariably copy the schemes from others, often giving rise to inaccuracy and absurdity. To

compromise the two methods, the tabular form is used in this book with exercises at the back. Students are required to follow the tables intelligently and not blindly. They are supposed to dispense with them entirely after once or twice working on them. As a further safe-guard against machine-work, no result may be considered conclusive until confirmed by some independent tests selected by the student himself from the descriptive part.

Finally, it may be added that the table on the analysis of organic acids is given in this book only to show that such separations are sometimes possible. Organic analysis is such a broad subject itself that it is impossible for this book to cover any field of it. Unless the student has extra time to spare and special books at hand, he should not be encouraged to work the organic part.

Among other books consulted may be mentioned the works of Fresenius, Wells, Scott, Brush and Penfield. The chapter on the Reactions of Metals (Part II) is a revision and rearrangement of the one by Briggs and Stewart.

The author is under obligation to many teachers and friends at Yale for valuable suggestions, especially to Prof. P. T. Walden, under whose instruction most of the notes were compiled.

Above all, special gratitude is due to another teacher of his, Prof. F. C. Cooper of St. John's University, who has critically read the entire manuscripts and has made many important alterations.

Shanghai, China,
    January, 1912.

Qualitative Chemical Analysis

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CHAPTER I

INTRODUCTION

Chemical Analysis is a branch of chemistry which aims at the breaking up of compounds and the discovery of their constituents. It is generally divided into two parts; *Qualitative*, if the nature of the constituents alone is concerned; and *Quantitative*, if the amount of the several constituents present in a substance is to be ascertained.

While both processes are equally important from the analytical point of view, Qualitative is more so to scientific men in general. Students in engineering, medicine, biology, etc., to whom the question of percentage may not be of frequent occurrence, will find it absolutely indispensable to possess at least a knowledge of the composition of certain substances. Moreover, in order to carry on any quantitative work satisfactorily and systematically, it must be preceded by qualitative. It is to this part only that this book is devoted.

Contrary to superficial views, qualitative analysis is neither guess work nor machine work. It is a systematic summary of the ingenious methods devised by former chemists through careful experimentation. These methods, by which best results can be obtained in the shortest period of time, are based upon the principles of general chemistry more or less, and should be studied in an intelligent manner. One who thoughtlessly rushes through the analytical tables, or blindly follows the instructor's directions without pausing at each step and asking himself *why ?*, is nothing more than the piston pushed by steam. To guard against such useless effort, a thorough grasp of some of the fundamental principles is necessary, although a full discussion of theories belongs to the part of general and physical chemistry. In analysis, it is the brain that does the large part of the work, and not the hand.

CHAPTER II

IONIZATION AND IONS

When one element enters into union with other elements, a multitude of combinations may be formed. It would be an enormous task if we were to devise a separate method of detection for each particular compound. To simplify this, we have a way of regarding many substances as if they were binary compounds, that is, each compound consists of two *units* only, irrespective of the number of atoms it may contain. These units we call "radicals." A radical may be only one element as in H|Cl (hydrogen chloride); or may be a combination of elements, as in $NH_4|C_2H_3O_2$ (ammonium acetate). Each radical behaves independently of the other. An H radical, for example, will invariably turn blue litmus paper red, whether it combines with Cl, Br, I, or SO_4; while any substance containing a $C_2H_3O_2$ radical, whether it be a potassium or an ammonium salt, will emit an odor of vinegar when treated with HCl or H_2SO_4. We are thus enabled to group such compounds as HCl, HBr, HI, etc., under one head (called acids) and those like $NH_4C_2H_3O_2$, $KC_2H_3O_2$, $Pb(C_2H_3O_2)_2$ under another head (called acetates). Such a method of grouping is based on what is known as the Theory of Ionization which briefly stated is as follows:—*All acids, bases and salts, when dissolved in water, are capable of being dissociated into two or more parts called ions.*

While it is impossible to treat the Ionization Theory in full, a few of the important facts may be enumerated here:—

(1) In every dissociable substance there are two kinds of ions, each carrying with it an electric charge. Those charged positively are called *cations*; those charged negatively, *anions*. The former go to form the *positive* or *basic radical*, and the latter, the *negative* or *acid radical*. In AgCl, for instance, silver is the cation represented by Ag^+ or Ag·, while chlorine is the anion represented by Cl^-, or Cl'.

(2) Ions differ from atoms in being able to exist in a free state. Unlike molecules, their existence is possible in solutions only. The properties possessed by ions are likewise different from

those of atoms or molecules. Metallic copper, for example, is red; but all solutions of copper salts are blue in color, which is a property characteristic of copper ions only.

(3) No ions can exist without being counterbalanced by an equivalent amount of oppositely charged ions. The number of charges carried by each ion determines the valence of the corresponding radical. One bivalent positive radical, for instance, is equivalent to two univalent negative radicals; two trivalent positive radicals are equivalent to three bivalent negative radicals; and so on. A list of common radicals with their names and valences will be given at the end of the book.

(4) The fact that all similar ions possess common properties greatly simplifies the work of chemical analysis. One general method is sufficient to detect all substances containing some particular ion in common. Thus, any silver salt in solution, whether a nitrate or sulphate, gives a white precipitate with HCl, soluble in ammonia.

(5) The existence of *complex ions* explains the reason why elements of the same kind sometimes act differently under different circumstances. Ammonium sulphocyanide, when added to a ferric salt, instantly produces a blood-red coloration, but it has no effect on potassium ferrocyanide, although both salts contain iron in common. This can only be explained by assuming that in the latter case, iron has entered into combination with cyanogen to form the complex anion $Fe(CN)_6''''$ whose behavior is entirely different from the simple cation Fe''.

(6) The mobility of ions in solution enables compounds to exchange radicals under certain conditions. The reaction

$$CaCl_2 + (NH_4)_2CO_3 = \underline{CaCO_3} + 2NH_4Cl,$$
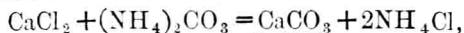
would be impossible unless the Ca ions are free to move towards the CO_3 ions and vice versa. This principle forms the corner-stone of practical chemistry and will be treated more fully in the chapter on Mass Action.

(7) Finally, the degree of dissociation determines the strength of acids and bases. HCl is said to be a stronger acid than $HC_2H_3O_2$ because in solution it gives out its ions more readily than acetic acid. The method by which the degree of dissociation can be determined is too long to be given here.

CHAPTER III

LAW OF MASS ACTION

In analytical, as well as in general and physical chemistry, we often come across such equations as will work both ways. For instance, if we pass carbon dioxide gas into a solution of calcium chloride, we get a precipitate known as calcium carbonate, as represented by the equation

$$CaCl_2 + H_2O + CO_2 = \underline{CaCO_3} + 2HCl.$$
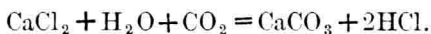
If, however, we add HCl to the precipitate, it dissolves with evolution of carbon dioxide, and we have another equation

$$\underline{CaCO_3} + 2HCl = CaCl_2 + H_2O + \overline{CO_2}.$$
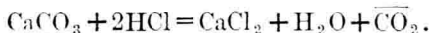
By comparing these two equations, it will be seen that the factors are exactly the same, except that they are in reverse order. The question then arises: Why should two such phenomena, apparently contradicting each other, co-exist? To answer such a question a mere equation is inadequate, because it does not tell us under what conditions the reaction takes place.

A chemical reaction capable of reacting in either direction is called a **reversible reaction**. *Theoretically*, every chemical reaction is reversible. The main factor that determines the direction of a reversible reaction is the **molecular concentration**, that is, the concentration of the *active* molecules in the substances participating in the reaction. Suppose we start with the materials on the left side of the equation of a reversible reaction. At first, the molecules of these materials encounter one another very frequently and in course of their collision, a number of new molecules (on the right side) are formed at the expense of their own. These new molecules increase in number rapidly and begin to act in the reverse direction. So the process goes on continually until finally a stage is reached when the forward speed of the acting molecules is exactly counterbalanced by the backward speed of the reacting molecules. Such a stage is called the *chemical equilibrium*, and is generally represented

by double arrows, equally thick, pointing in opposite directions. Thus

$$A + B \rightleftharpoons C + D.$$
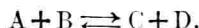
A saturated solution of a salt is a simple illustration of such a phenomenon. At a given time, there are just as many molecules *returning from* the solution as those *going into* it. The reaction then apparently comes to a halt, and the addition of more salt simply deposits it at the bottom.

In the equation

$$A + B \rightleftharpoons C + D,$$
$$c_1 \quad c_2 \qquad c_3 \quad c_4 \tag{1}$$

in which c_1, c_2, c_3 and c_4 are the respective molecular concentrations, let us suppose F_1 to be the tendency of A and B to combine, and F_2 that of C and D to combine. Then the speeds of the forward and reverse actions will be respectively

$$S_1 = F_1 c_1 c_2 \text{ and } S_2 = F_2 c_3 c_4.$$
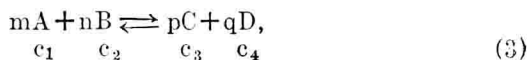
As soon as equilibrium is established,

$$S_1 = S_2;$$

$$\therefore \quad F_1 c_1 c_2 = F_2 c_3 c_4, \text{ or}$$

$$\frac{c_3 c_4}{c_1 c_2} = \frac{F_1}{F_2}.$$

But $\frac{F_1}{F_2} = k$ (being a ratio of two constants); therefore, $\frac{c_3 c_4}{c_1 c_2} = k.$ (2)

If we put (1) into the generalized form

$$mA + nB \rightleftharpoons pC + qD,$$
$$c_1 \quad c_2 \qquad c_3 \quad c_4 \tag{3}$$

where m, n, etc., may represent any numerical co-efficient, equation (2) becomes

$$\frac{c_3{}^p c_4{}^q}{c_1{}^m c_2{}^n} = k. \tag{4}$$

That is, *in a reversible chemical reaction, when the state of equilibrium has been reached, the product of all the active masses of the substances on one side of the equation, divided by that on the other side of the equation,*

is equal to constant (*equilibrium constant*), which is the **Law of Mass Action.**

From equation (2) and (4), it is clear that the left-hand expression may be made greater or less than k by changing one of the values either in the numerator or in the denominator. In other words, equilibrium will be disturbed by the alteration of concentration. If, therefore, we keep increasing or diminishing one substance involved in the equation, we are able to push the reaction *completely* either to the right or to the left as we please. This is exactly what takes place when a solution of sodium chloride is evaporated with sulphuric acid. At the time of equilibrium,

$$NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + HCl,$$
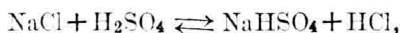
$$\text{and} \quad \frac{C_{NaHSO_4} \times C_{HCl}}{C_{NaCl} \times C_{H_2SO_4}} = k.$$

But HCl, being more volatile than H_2SO_4, is removed as soon as formed. C_{HCl} is thus kept infinitely small, and the ratio $\frac{C_{NaHSO_4} \times C_{HCl}}{C_{NaCl} \times C_{H_2SO_4}}$ is always $< k$. In order to restore equilibrium, the reaction is forced to go to the right until completion. Thus,

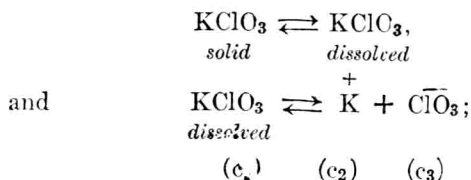$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + \overline{HCl}.$$
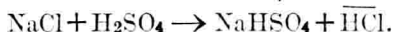
Conversely, if we add concentrated HCl to a saturated solution of $NaHSO_4$, complete reaction takes place in the opposite direction. Here HCl is kept in excess and C_{NaCl} is made very small through crystallization of solid NaCl. Thus,

$$\underline{NaCl} + H_2SO_4 \leftarrow NaHSO_4 + \overline{HCl}.$$

The Law of Mass Action finds a very important application in the study of analytical chemistry. It is the basis of all chemical separations, of which precipitation is the commonest method. All insoluble substances are thrown out from the solution until one of the acting substances is exhausted.

In the chapter on Ionization, we have discussed the formation of ions when a substance is dissociated in water. To take a

concrete example, let us dissolve, say, some $KClO_3$ crystals. Equilibrium is maintained in the system:—

$$KClO_3 \rightleftarrows KClO_3,$$
solid   dissolved

and $KClO_3 \rightleftarrows \overset{+}{K} + \overline{ClO_3};$
dissolved

$$(c_1) \quad (c_2) \quad (c_3)$$

whence $\dfrac{c_2 c_3}{c_1} = k.$

In a saturated solution, the value of c_1 becomes itself a constant, since no more $KClO_3$ will dissolve. Therefore $c_2 c_3 = k$. This value k is known as the *solubility constant*. At this stage, a slight change in concentration will immediately disturb the equilibrium. The addition of KCl (introducing more K ions) or of $NaClO_3$ (introducing more ClO_3 ions) will throw down $KClO_3$ in form of crystals which redissolve on adding water.

In general, then, we have three conditions ; viz.,

     1.   Solution,   when $c_2 c_3 < k$
     2.   Saturation,   ,, $c_2 c_3 = k$
     3.   Precipitation,   ,, $c_2 c_3 > k$.

In the case of silver chloride, the solubility constant is exceedingly small. The water soon becomes saturated when a little silver chloride is formed. Therefore all silver can be precipitated as chloride. On adding ammonia, a new compound $Ag(NH_3)_2Cl$ is formed. The introduction of the complex ion $\overset{+}{Ag}(NH_3)_2$ tends to diminish the $\overset{+}{Ag}$ ions. Hence solution results.

A still more striking example may be seen in the sulphur precipitations of metals. The sulphides of manganese, cadmium, and copper are all insoluble in water, but their solubility constants are all different, (CuS being the most insoluble, and MnS, the least so.) Supposing that at the state of equilibrium,

$$\underset{Mn}{C_+} \times \underset{S}{C_-} = k' \text{ (solubility constant of } MnS),$$

$$\underset{Cd}{C_+} \times \underset{S}{C_-} = k'' (\quad ,, \quad\quad ,, \quad\quad ,, \; CdS),$$

$$\underset{Cu}{C_+} \times \underset{S}{C_-} = k''' (\quad ,, \quad\quad ,, \quad\quad ,, \; CuS):$$

then, in the order of their solubility,

$$k' > k'' > k'''$$

The addition of $(NH_4)_2S$ precipitates all of them, because $(NH_4)_2S$, being a salt, is highly dissociated, and furnishes enough $\overline{S}$ ions to combine with any of the three metals, so that

$$\underset{Mn}{C_+} \times \underset{s}{C_-} > k'$$

$$\underset{Cd}{C_+} \times \underset{s}{C_-} > k''$$

$$\underset{Cu}{C_+} \times \underset{s}{C_-} > k'''$$

If, instead of $(NH_4)_2S$, we use the weak acid H_2S, the $\overline{S}$ ions given out will then be only sufficient to precipitate the last two but not the first one ; for here

$$\underset{Mn}{C_+} \times \underset{s}{C_-} < k'$$

$$\underset{Cd}{C_+} \times \underset{s}{C_-} > k''$$

$$\underset{Cu}{C_+} \times \underset{s}{C_-} > k'''$$

If again we add concentrated HCl so as to make H_2S still less dissociated, only the most insoluble substance (CuS) will be precipitated; for here we have

$$\underset{Mn}{C_+} \times \underset{s}{C_-} < k'$$

$$\underset{Cd}{C_+} \times \underset{s}{C_-} < k''$$

$$\underset{Cu}{C_+} \times \underset{s}{C_-} > k'''$$

Molecular concentration has been defined as the concentration of the *active* molecules present in the substances taken. The *activity* of molecules is determined by the speed of their motion. The faster they move, the greater work they are able to perform. Solid NaCl and solid $AgNO_3$ may be kept mixed for a long time without forming AgCl and $NaNO_3$, because in a solid state the particles are not so free to move as in a liquid state. To hasten a

chemical reaction, therefore, it is not merely a question of putting in more molecules; anything that tends to increase or diminish the molecular activity must also be taken into account. We have a number of cases where *temperature* plays an important rôle in a chemical analysis. Aluminium hydroxide, for example, precipitates better in boiling ammonia, while lead chloride, precipitated from cold, readily dissolves in hot water. The question of *pressure*, which is another great factor in a reversible reaction, is not so frequently met with in ordinary analytical work. In organic distillations, where too high temperature is liable to decompose the substance, reduced pressure is often used with advantage. As these belong to the part of physical chemistry, a detailed discussion of the theory of phases and their relation to temperature and pressure will not be attempted here.