

C. H. SORUM

INTRODUCTION TO
SEMIMICRO
QUALITATIVE ANALYSIS

THIRD EDITION

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Qualitative Analysis

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INTRODUCTION TO Semimicro
Qualitative Analysis

Preface to the Third Edition

There have been no major changes in procedures in this edition. A new alternative test for antimony has been added and details of many procedures have been modified but the basic methods are the same as in the second edition. The modifications will in every case help insure better analytical results.

The section of the book dealing with the analysis of salts and salt mixtures has been rearranged somewhat for greater clarity.

Parts of Chapter II, which deals with the theory of qualitative analysis, have been rewritten. The section devoted to complex ions has been extended. The following topics have been added: pH; Hydrolysis; Indicators; Oxidation Potentials; Balancing Oxidation-Reduction Equations.

The problems in Chapter II have been replaced by a new set. The questions at the end of the other chapters have been enlarged and rearranged.

The author wishes to express his deep appreciation for the suggestions, comments and criticisms which he has received from users of the previous edition. In particular he is indebted to his colleagues on the freshman chemistry staff at the University of Wisconsin.

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Note to Instructors

A group of questions will be found at the end of each chapter. These can be used as the basis for an oral review of each chapter's content or they can be assigned as homework. A few problems, with answers, are given at the end of Chapter 2. If a more complete coverage of problems is desired, the author's *How to Solve General Chemistry Problems* Second Edition (Prentice-Hall, Inc., 1958), or some comparable problem book may be used as a companion text.

A list of the required equipment is given on page 228. The student is introduced to each piece of equipment, and any special technique involved in the use of the equipment, at the time it is first used in the plan of analysis. If H_2S gas is used as a precipitating reagent the student will need to prepare two or three hydrogen sulfide bubbling tubes from 6 mm. glass tubing in the manner described on page 90. If each student is to prepare his own H_2S by heating a mixture of sulfur, paraffin, and asbestos in the fashion described in Note 2 on page 90, simple generators of the type illustrated in the figure on that page must be set up. Five-inch stirring rods will need to be cut from $\frac{1}{8}$ -inch glass rod and firepolished. Otherwise, the items are standard semimicro pieces of the type available at most supply houses.

A list of all reagents used, with directions for preparing all solutions, is given on pages 223 to 228. Tables of ionization constants, instability constants, oxidation potentials and solubility products are given along with the appropriate text material in Chapter 2.

The experimental procedures and specific tests have been checked and rechecked; if the directions are followed with reasonable care, good results will be obtained.

All equations for reactions in solution are presented in net ionic form. This is in conformity with the principle that the equation should indicate the species that predominate in a reacting system. No effort is made to present the detailed mechanisms of the more complex reactions; all that is attempted is a simplified equation that will give a picture of the major species which are involved.

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The practice of qualitative analysis

THE FIRST semester's laboratory work in general chemistry was concerned, to a considerable extent, with the preparation and properties of certain elements and their compounds. In the course of this laboratory work, the student was frequently called upon to *test* for a substance or to prove the *identity* of a substance. Oxygen was *identified* by the fact that it caused a glowing splint to burst into flame. Carbon dioxide produced a white precipitate of calcium carbonate when passed into limewater, whereas solutions containing sulfate ions gave a white precipitate when treated with a solution of barium ions. Further examples might be cited, all pointing to the fact that a student who has had an introductory laboratory course in general chemistry has learned to *identify* various substances.

In the laboratory work with which this book is concerned, *identification* of substances will be of primary interest. The study of qualitative analysis is a study of the ways and means by which substances can be identified. Specifically, inorganic qualitative analysis is concerned with finding out which metallic ions (cations) and acid radicals (anions) are present in substances and mixtures of substances.

A complete system of qualitative inorganic analysis would include methods for detecting all cations (metallic ions) and all anions (acid

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radicals) as well as all the elements. Not only would procedures be given for the detection of cations of such common metals as copper, tin, iron, aluminum, and zinc and such anions as sulfate, phosphate, and carbonate, but the detection of the less common metals such as rhenium, niobium, platinum, and cerium and such anions as tellurate, molybdate, ferrocyanide, and vanadate would also be included. Such a complete course would be quite involved.

An understanding of the *methods* of qualitative analysis and a knowledge of the *principles* which underlie it can be obtained by a study of the identification of a few common and representative cations and anions. Those considered in this course are the following:

Cations (metallic ions): Ag^+ , Pb^{++} , Hg_2^{++} , Hg^{++} , Bi^{+++} , Cu^{++} , Cd^{++} , Sn^{++} , Sn^{++++} , Sb^{+++} , As^{+++} , Fe^{++} , Fe^{+++} , Al^{+++} , Cr^{+++} , Mn^{++} , Zn^{++} , Ni^{++} , Co^{++} , Ba^{++} , Ca^{++} , Mg^{++} , Na^+ , K^+ , NH_4^+ .

Anions (acid radicals): SO_4^{--} , SO_3^{--} , CO_3^{--} , BO_3^{---} , CrO_4^{--} , PO_4^{---} , AsO_4^{---} , S^{--} , Cl^- , Br^- , I^- , NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$.

In order to show how qualitative analysis works out in actual practice, let us take a solution containing all the cations listed above and examine the method by which the presence of each cation is proved.

A first thought might be to add some superreagent that would give a different and very characteristic precipitate with each cation in the mixture. Obviously, however, such a procedure would be no good because the mixture of cations, each giving a different and characteristic precipitate, would give a completely confusing mixture of precipitates.

The answer to this objection would be to find a specific reagent for each cation, a reagent that would give a precipitate or colored solution with one, and only one, cation. If there were such a complete set of specific reagents, qualitative analysis would be very simple. Unfortunately, such an ideal collection of reagents does not exist. With three or four exceptions, a reagent that gives a characteristic reaction with one ion either gives a characteristic reaction with other ions as well, or else its characteristic reaction with one ion is interfered with by other ions. In other words, *in order to identify a certain cation it must generally be alone, free from other cations.*

The answer to the question of how to proceed with the detection of the cations in the above solution is thus quite obvious. The cations

must first be *separated*; then they can be *identified*. The whole plan of qualitative analysis is a series of *separations* and *identifications*.

The next question is how to go about separating all the cations listed when they are found together in the same solution. It is possible that a system could be worked out whereby the cations could be separated and identified one at a time. The more practical method, employed in all systems of qualitative analysis, is to separate the cations a handful at a time. The procedure, in brief, is as follows: A small handful of cations, three to be specific, is first taken out. This handful of three is then separated into three parts by taking out one and leaving two, and then separating these two from each other. The separated cations are then easily identified by means of characteristic reactions.

Having taken out and separated the first handful, we next take out a second handful, then a third, leaving a fourth and last handful. The original mixture of cations is separated into four handfuls. Each of these handfuls is separated in turn and the separated cations are identified. If the handful is a small one, consisting of only three cations, it is separated by taking out one, leaving two and then separating these two. If the handful is a large one, as is actually the case with the second, third, and fourth handfuls, the large handful is first separated into two small handfuls; then the separation proceeds by taking out first one and then another until each cation has been isolated.

The next question is, How do we go about picking out these handfuls? The handfuls, more correctly referred to as *groups*, are taken out by the addition of a specific reagent, called a *group reagent*. This reagent forms insoluble compounds with the cations in that particular group but permits all other cations to remain in solution. The group is thereby taken out as a mixture of insoluble substances.

Outline 1, page 5, shows the content of each group and the group reagent that is added to precipitate out each group. This outline should be examined carefully, since it gives the whole plan of group separation of cations.

Hydrochloric acid is the group reagent for the first group, called the *silver group*. Separation of the cations of the silver group from all other cations depends on the experimental fact that the chlorides of silver, lead, and mercury(I) are insoluble in dilute HCl, whereas the chlorides of all other metals are soluble.

The group reagent for the second group, the *copper-arsenic group*, is H_2S . Separation of the cations of the copper-arsenic group from

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the remaining cations depends on the fact that the sulfides of the former are insoluble in HCl, whereas the sulfides of the latter are soluble.

The group reagents for the third group, the *aluminum-nickel group*, are NH_4OH and $(\text{NH}_4)_2\text{S}$. The sulfides and hydroxides of the cations of the aluminum-nickel group are insoluble in alkaline solution, whereas the sulfides and hydroxides of the cations of the last group, the *barium-magnesium group*, are soluble.

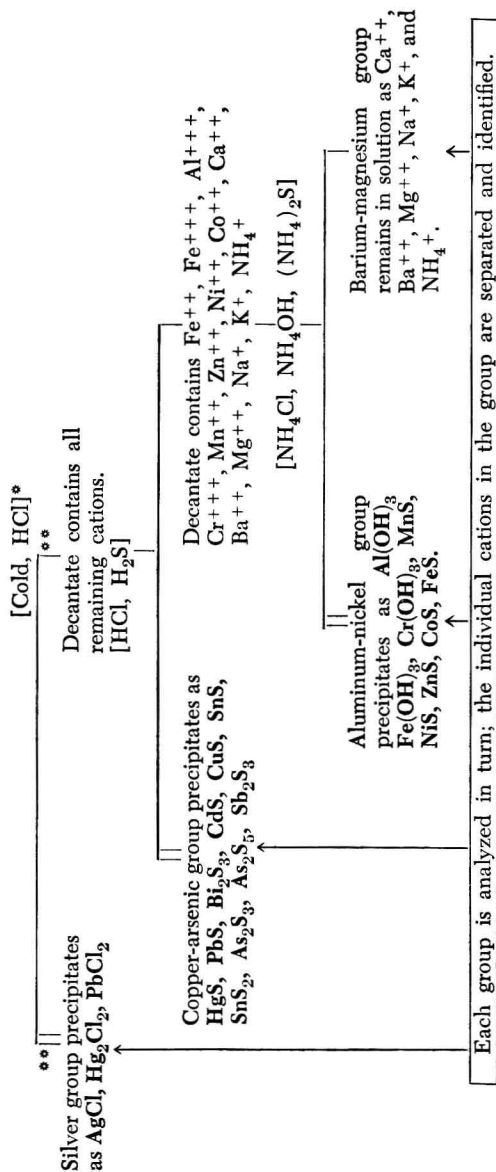
The last question is, How do we go about separating and identifying the cations in each handful? The detailed answers to that question will be left to Chapters 3, 4, 5, and 6. At this point it will be sufficient to call attention to Outlines 2, 3, 4, and 5, on pages 74, 87, 125, and 153, respectively. These outlines show, schematically, how the separation and identification of the cations in each group are carried out.

It is obvious, from what has been said, that the separation and identification of the cations follow an orderly plan. It is also obvious, from an examination of Outlines 2, 3, 4 and 5, that the execution of this orderly plan of separation and identification is going to call for careful and extensive laboratory work, and the understanding of the plan is going to require knowledge of a great many principles and facts. So that the student may have a better chance to learn these principles and facts, so that he may acquire the techniques required for the various procedures, and may learn to recognize the colors and other characteristics of the solutions and precipitates that make identification of the various cations possible, the following program will be followed. A practice solution ("known" solution) containing all the cations of a particular group will first be analyzed. This known solution will then be followed by the unknown solution (or solid) for that group, in which the student goes through the same steps that he has taken with the known. The series of group knowns and unknowns for the four groups will be followed by an unknown that contains combinations of all four cation groups in the form of an alloy.

Thus, bit by bit, separation and identification of the metallic ions will be studied. The student will then be ready to extend his efforts to a study of the identification of anions. This he will do by analyzing salts and salt mixtures.

In keeping with this objective of studying the qualitative procedures of the separate groups before undertaking a complete analysis, the following substances will be analyzed and in the following order.

Solution contains Ag^+ , Hg_2^{++} , Pb^{++} , Hg^{++} , Bi^{+++} , Cu^{++} , Cd^{++} , Sn^{++} , Sn^{++++} , As^{+++} , H_2AsO_3^- , AsO_4^{---} , Sb^{+++} , Fe^{++} , Fe^{+++} , Al^{+++} , Cr^{+++} , Mn^{++} , Zn^{++} , Ni^{++} , Co^{++} , Ca^{++} , Ba^{++} , Mg^{++} , Na^+ , K^+ and NH_4^+ .



* A bracketed formula [cold HCl] means that the substance (HCl in this case) is added as a reagent.

•• The notation || means separation by centrifuging and decanting. The double vertical parallel lines at the left refer to the precipitate and the one vertical line at the right refers to the decantate.

OUTLINE 1: THE SEPARATION OF CATIONS INTO GROUPS

Schedule of Laboratory Work

1. *One silver group known.* This solution contains all the cations of the silver group. It will not contain cations of other groups. Obtain it and all subsequent knowns from the instructor. Follow the directions given in Procedures 1 to 4, inclusive.

2. *One or two silver group unknowns.* These solutions contain cations of the silver group. They will not contain cations of other groups. Obtain these and all subsequent unknowns from the instructor. Follow the directions given in Procedures 1 to 4, inclusive.

3. *One copper-arsenic group known.* This solution contains all the cations of the copper-arsenic group. It will not contain cations of other groups. Follow the directions given in Procedures 5 to 14, inclusive.

4. *One or two copper-arsenic group unknowns.* These solutions contain cations of the copper-arsenic group. They will not contain cations of other groups. Follow the directions given in Procedures 5 to 14, inclusive.

5. *One aluminum-nickel group known.* This solution contains all the cations of the aluminum-nickel group and will not contain cations of other groups. Follow the directions given in Procedures 15 to 21, inclusive.

6. *One or two aluminum-nickel group unknowns.* These solutions contain cations of the aluminum-nickel group. They will not contain cations of other groups. Analyze according to the directions given in Procedures 15 to 21, inclusive.

NOTE

In the presence of phosphates or borates, a modified plan of analysis must be used for the aluminum-nickel group. Unknowns ordinarily issued in the course will not contain phosphates or borates that necessitate using the modified procedure.

7. *One barium-magnesium group known.* This solution contains all the cations of the barium-magnesium group. It will not contain cations of other groups. Follow the directions given in Procedures 22 to 27, inclusive.

8. *One or two barium-magnesium group unknowns.* These solutions contain cations of the barium-magnesium group. They will not

contain cations of other groups. Analyze according to the directions given in Procedures 22 to 27, inclusive.

9. *One alloy.* This solid may contain any or all of the 21 metals. Follow the directions given in Procedure 28.

10. *Preliminary tests and specific tests for anions.* Follow the directions given in Experiments 1, 2, 3, and 4, pages 175, 177, 178, and 179.

11. *Complete analysis of solids for both cations (metallic ions) and anions (acid radicals).* The remainder of the laboratory work will consist of the complete analysis of solid unknowns for cations and anions. Follow the directions given in Chapter 8.

Record of Laboratory Work and Laboratory Reports

A record of all laboratory work is to be kept on the blank pages at the end of each chapter in this manual in accordance with the following directions.

1. As each group known or unknown is being analyzed the outline for that group must be developed in the manual. This outline is similar to those printed in this manual. The object of making such an outline is to enable the student to visualize the steps of the analysis and record his own findings. Each step in the outline must be recorded concurrently with the actual laboratory performance of that step.

2. All confirmatory tests obtained in the analysis of a group known must be approved by the instructor. Confirmatory tests obtained in the analysis of an unknown need not be thus approved.

3. The group known must be finished and the completed outline for this group known must be approved by the instructor before an unknown will be issued. The student must demonstrate to the instructor that he is familiar with the analysis of the group before he is permitted to start the analysis of the unknown.

4. When a group unknown is reported to the instructor, the manual should contain:

(a) The approved outline of the group known.

(b) All equations for the reactions that took place in the analysis of the group known.

(c) The outline for the unknown.

5. The alloy will not be issued until the student is able to demon-

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strate to his instructor a proper understanding of the analysis of the alloy.

6. When the alloy is reported the manual should contain:

(a) A composite outline showing how it was analyzed.

(b) Equations for dissolving the metals proved to be present in the alloy.

7. Salts and salt mixtures will be reported in accordance with the instructions given in Chapter 9.

8. The first salt will not be issued until the student can demonstrate a satisfactory understanding of its plan of analysis. Experiments 1, 2, 3, and 4, pages 175, 177, 178, and 179, must be performed before the first salt mixture is analyzed.

9. Special solids will be reported in the same manner as salts.

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The theory of qualitative analysis

FROM WHAT has been stated in Chapter 1, it is evident that the whole plan of qualitative analysis is based on the relative solubilities of the compounds formed by the various ions. Separation and identification of cations and anions involve a series of processes of solution and precipitation in which the ion in question eventually appears as a precipitate or as a solution of distinctive color. The study of qualitative analysis is thus largely concerned with solutions, solubility, and formation of precipitates. It is concerned with the best conditions for the formation of precipitates, the best conditions for dissolving certain precipitates, and the best methods for separating one ion from another. It is interested in the best techniques, the best laboratory practices, and the most effective equipment for accomplishing the desired separations and identifications. It wants to know why one substance forms a precipitate while another does not, why one substance dissolves in a specific reagent while another does not, why one ion reacts in one way while another ion reacts in a different manner. It is interested in knowing exactly the manner in which different ions react, exactly what happens when a precipitate forms, and exactly what takes place when a solid dissolves in a specific reagent. It is concerned with representing correctly, in the form of balanced equations, the reactions that take place.

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Before the specific aspects of qualitative analysis just mentioned are discussed in detail, it is desirable that a number of fundamental concepts be reviewed.

Molarity and Per Cent Strength of Solutions

Since the separation and detection of the ions are dependent upon selective precipitation it is obvious that, if good results are to be obtained, solutions of precise *concentrations* must be used. The concentration of a solution represents the *quantity of solute* which is present in a *definite quantity of solution* or in a *definite quantity of solvent*. Concentrations of solutions used in the present plan of analysis will generally be expressed in terms of *molarity*. In a few instances, solutions of specific *per cent strength* will be used. *The molarity of a solution represents the number of moles of solute per liter of solution*. A molar solution, referred to by the notation 1 M, contains one mole of solute in a liter of solution. A one-tenth molar solution (0.1 M) contains one-tenth mole of solute per liter of solution. A molar solution of H_2SO_4 contains 98 g. of H_2SO_4 per liter of solution. A liter of 0.1 M H_2SO_4 will contain 9.8 g. of H_2SO_4 . (See problems 1 to 6, page 71.)

“Per cent” means “parts per one hundred parts.” Therefore *the per cent strength of a solution represents the number of parts by weight of solute per 100 parts by weight of solution*. If 10 g. of salt were dissolved in 90 g. of water to give 100 g. of solution, the per cent strength of the solution would be 10%. That is

$$\frac{10 \text{ g. of salt}}{100 \text{ g. of solution}} = 0.10.$$

Note that this gives a decimal per cent. This decimal per cent is commonly converted to parts per 100 by multiplying by 100. The standard formula for expressing per cent is, accordingly,

$$\text{per cent strength} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 100\%.$$

(See problems 7 to 12, page 71.)

Rate of Reaction

When two substances that can react with each other are brought together a definite time interval is necessary for the reaction to take